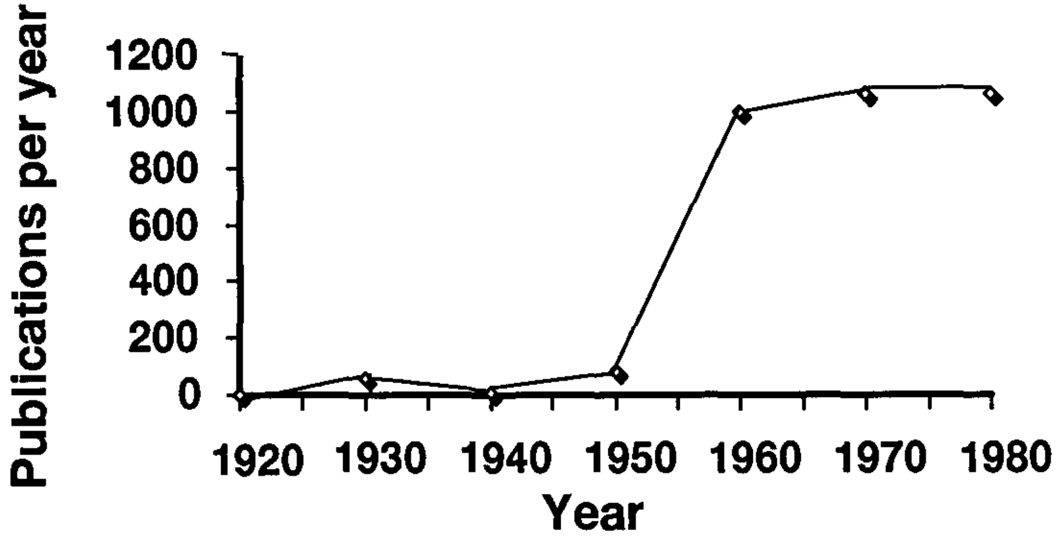
Radiation Processing

Basic Aspects

Radiation Chemistry: Developments

- Discovery of X-rays, Röentgen 1895
- Discovery of Radioactivity, Becquerel 1896
- Since the fifties, our understanding of radiation physics, chemistry and biology has increased tremendously



Swallow (1960) and Helman and Ross (1980)

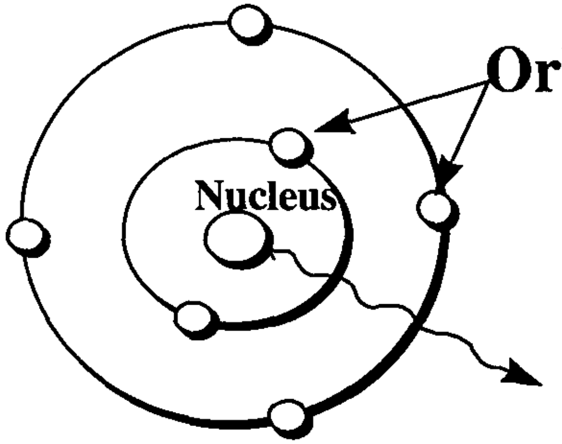
Radioactivity

- Consists of α, β and γ – emissions with energies characteristic of the emitting nucleus

α– particles: Helium nucleus, He^{2+} ion, emitted from the nucleus

β– particles: Fast electrons emitted from the nucleus

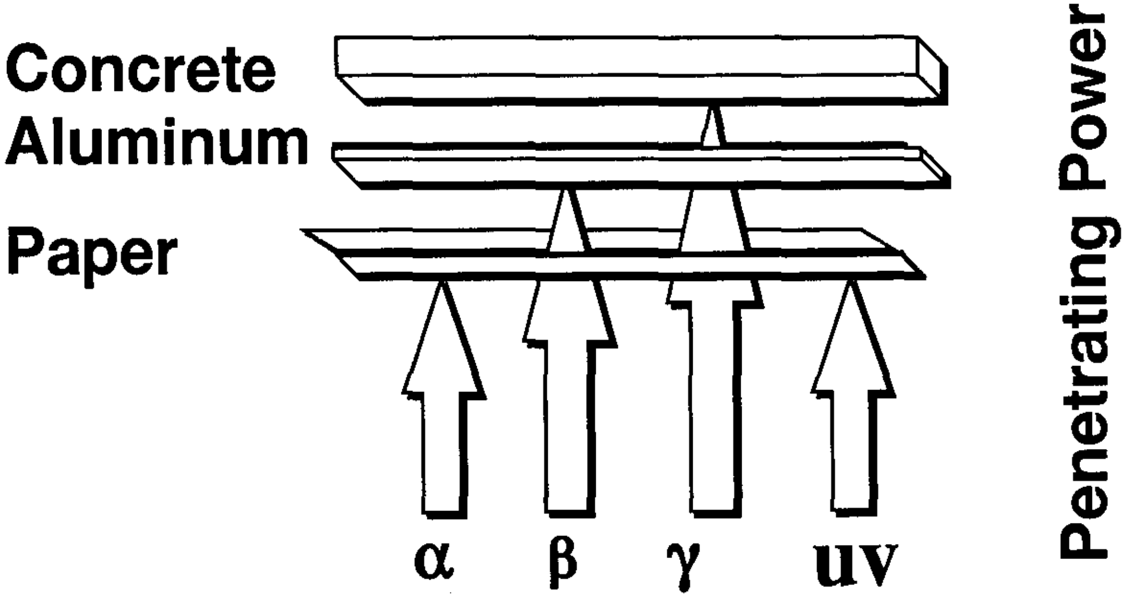
γ– rays: Uncharged electromagnetic radiation emitted from the nucleus, usually along with β-particle



An Atom

Radioactive Decay: $C_t = C_o e^{-\lambda t}$

Different Penetration of Vacuum UV, α, β and γ



- The difference in penetration is a result of different probabilities of interaction of α, β, γ and vac-uv radiation with orbital electrons of a molecule

Induced Radioactivity

- Induced radioactivity produced by nuclear reactions of H^+, D^+, He^{2+}, neutrons and γ- rays

$$^{27}Al + {}^{4}He^{2+}\ (\alpha) \longrightarrow {}^{30}P + n$$

$$^{30}P \longrightarrow e^+ + {}^{30}Si$$

- Neutrons are the most important initiators of induced radioactivity

Neutron-Induced Radioactivity

$n + {}^{2}H \longrightarrow ({}^{3}H) \longrightarrow {}^{3}He + e^{-}$ $(t_{1/2} \sim 12.4y)$

$n + {}^{27}Al \rightarrow ({}^{28}Al) \longrightarrow {}^{28}Si + e^{-}$ $(t_{1/2} \sim 2.3min)$

$n + {}^{113}Cd \longrightarrow ({}^{114}Cd) \longrightarrow {}^{114}Cd + \gamma$
$(t_{1/2} \sim 43d)$

Some Threshold Values for Nuclear Activation

$^{2}H + \gamma\ (2.23\ MeV) \longrightarrow\ ^{1}H + n$

$^{181}Ta + \gamma\ (7.64\ MeV) \longrightarrow\ ^{180}Ta + n$

$^{197}Au + \gamma\ (8.07\ MeV) \longrightarrow\ ^{196}Au + n$

$^{204}Pb + \gamma\ (8.38\ MeV) \longrightarrow\ ^{203}Pb + n$

$^{70}Zn + \gamma\ (9.29\ MeV) \longrightarrow\ ^{69}Zn + n$

$^{65}Cu + \gamma\ (9.91MeV) \longrightarrow\ ^{64}Cu + n$

(IAEA Technical Report No. 188, 1979)

Induced Radioactivity

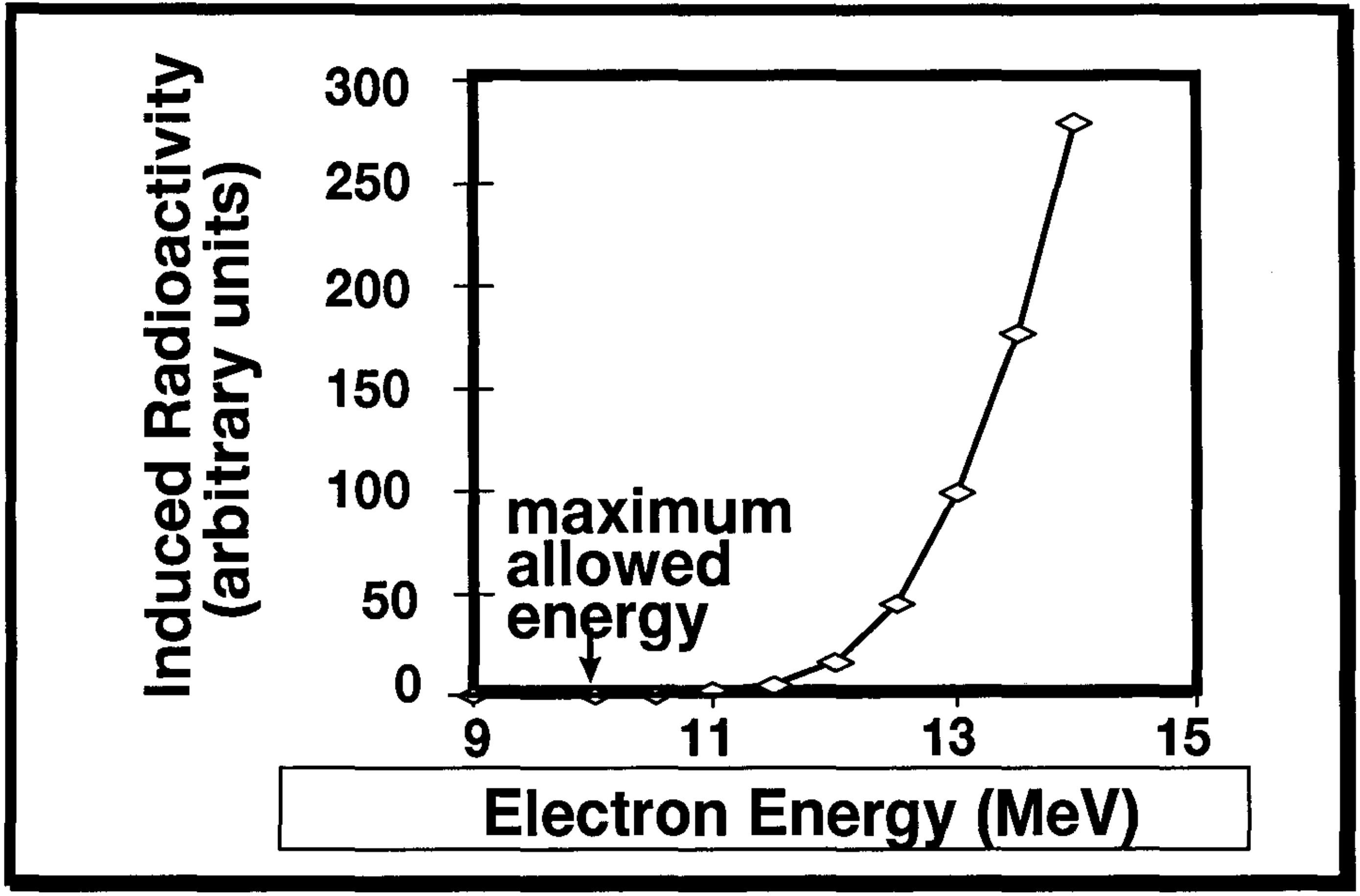
- The energy levels permitted for use in food irradiation are specifically selected to avoid any conditions which could induce significant levels of radioactivity in the treated commodities

- The permitted energy levels are:

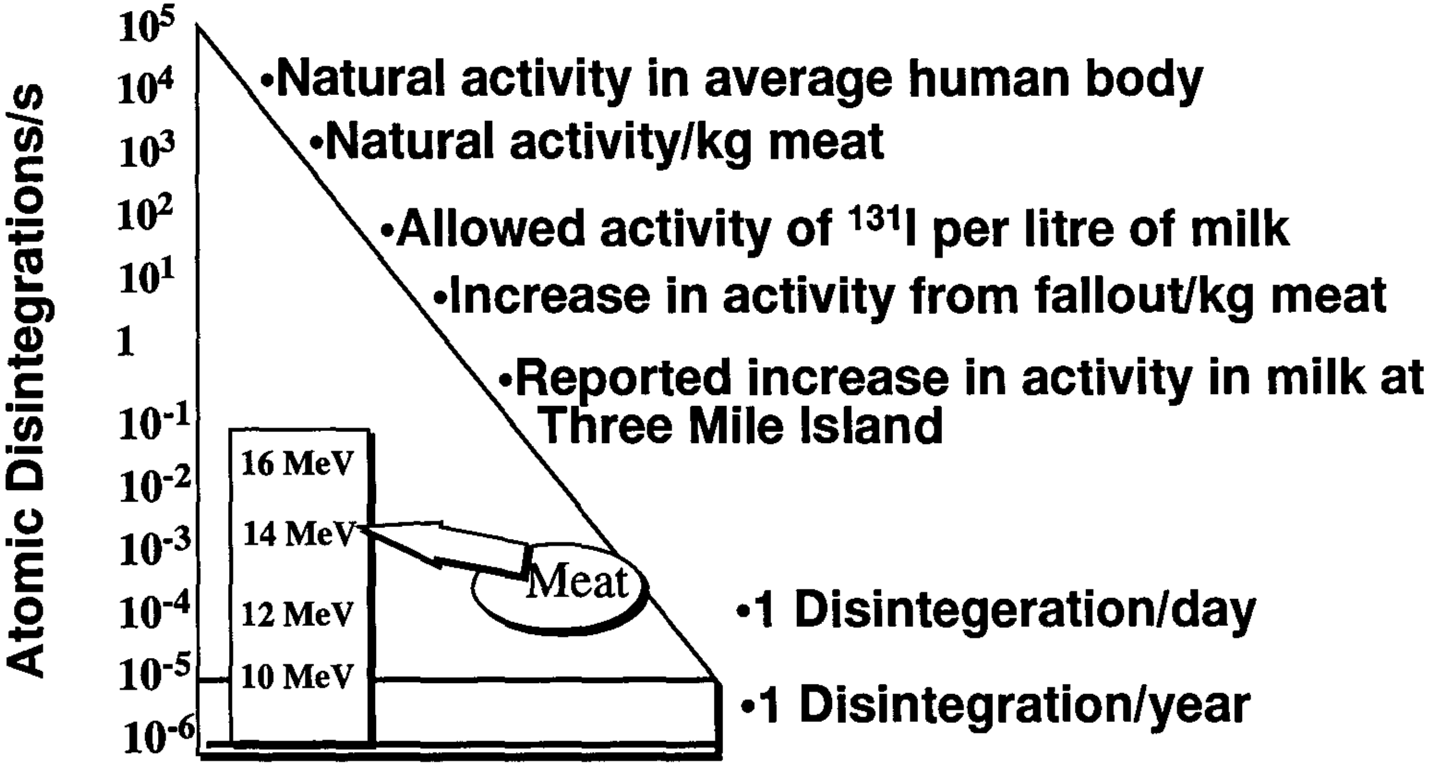
X-rays (or γ-rays)	$\leq$ 5 MeV
Electrons	$\leq$ 10 MeV

- For radiation processing of items other than food, electrons or X-rays up to 10 MeV can be used as needed, without concerns about induced radioactivity

Induced Radioactivity vs Electron Energy



Natural and Induced Radioactivity from Various Sources (Becker, 1979)



- Natural activity in average human body
- Natural activity/kg meat
- Allowed activity of ^{131}I per litre of milk
- Increase in activity from fallout/kg meat
- Reported increase in activity in milk at Three Mile Island
- 1 Disintegeration/day
- 1 Disintegration/year

- In “pure” organic polymers, induced radioactivity should be lower than in foods; in metals it would be higher

Sources for Radiation Processing

- Natural radioactive isotopes are not suitable for radiation processing
- Radiation processing feasible with artificially produced radioactive isotopes

$^{60}\text{Co}\ (\gamma),\ \ ^{137}\text{Cs}\ (\gamma)$

- Radiation processing helped by the development of electron accelerators to produce

Electron (e^-) beams, X-rays

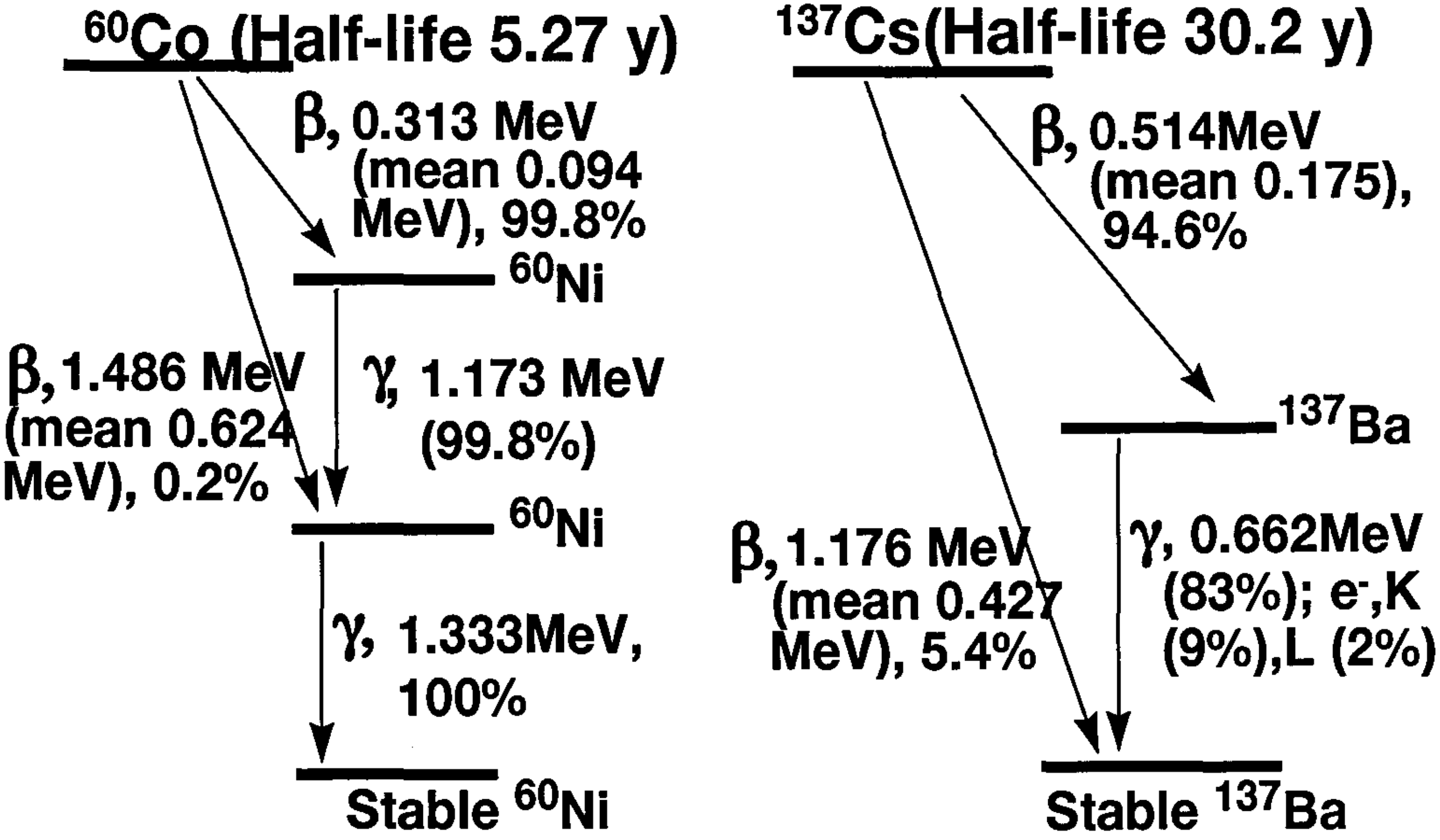
$$e^-\ (\leq 10\,\text{MeV}) \xrightarrow{\text{Metal}} \text{X-rays}$$

- In electron accelerators one can choose the electron energy, as required for a given application
- The mode of action of γ- and X-rays is exactly the same
- The mode of action of e^- from accelerators and β- particles from radioactive isotopes, is also the same

Decay Characteristics of Some of the Natural and Artificial Radioactive Isotopes

Isotope	Half-Life	Type and Energy (in MeV) Principal Radiation Emitted
Natural Isotopes		
^{226}Ra	1620 y	α, 4.777 (94.3%) α, 4.589 (5.7%)
^{222}Rn	3.83 d	α, 5.49
Artificial Isotopes		
^{137}Cs	30.2 y	β, 1.18 (max) (8%) β, 0.52 (max) (92%) } 0.24 (av) γ, 0.6616 (82%)
^{60}Co	5.27 y	β, 0.314 (max) 0.093 (av) γ, 1.332 γ, 1.173
^{3}H (tritium)	12.26 y	β, 0.018 (max)
^{32}P	14.22 d	β, 1.710 (max)

Radioactive Decay of the Gamma-Emitting Isotopes



^{60}Co (Half-life 5.27 y)

β, 0.313 MeV (mean 0.094 MeV), 99.8%

^{60}Ni

β, 1.486 MeV (mean 0.624 MeV), 0.2%

γ, 1.173 MeV (99.8%)

^{60}Ni

γ, 1.333MeV, 100%

Stable ^{60}Ni

^{137}Cs(Half-life 30.2 y)

β, 0.514MeV (mean 0.175), 94.6%

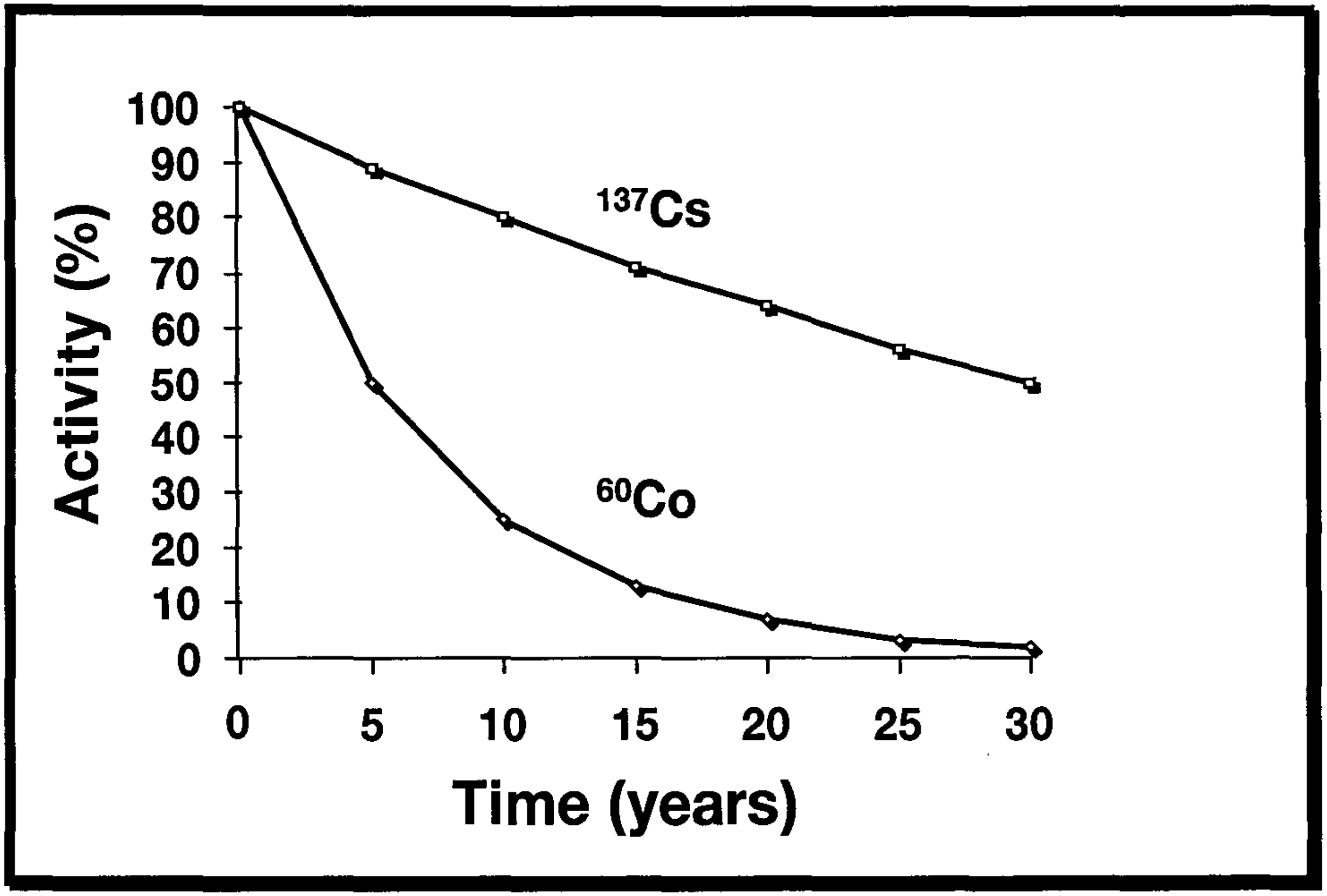
^{137}Ba

β, 1.176 MeV (mean 0.427 MeV), 5.4%

γ, 0.662MeV (83%); e^-,K (9%),L (2%)

Stable ^{137}Ba

Radioactive Decay of ^{137}Cs and ^{60}Co

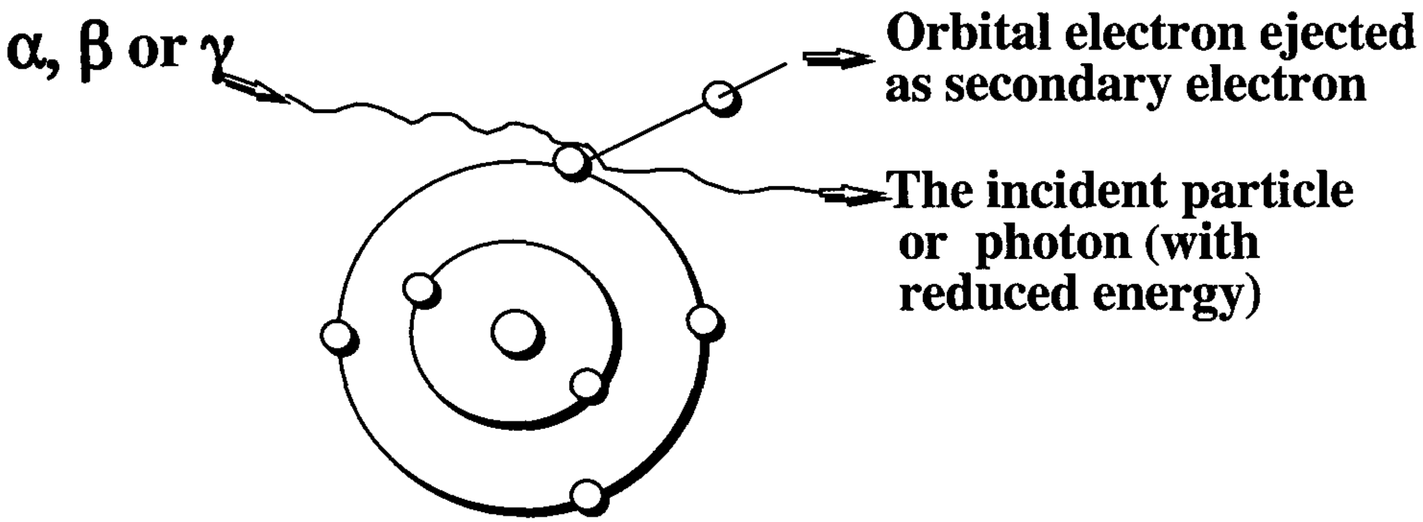


Interaction of Ionizing Radiation with Matter

A Simplified Picture

- The energy transfer mechanism involves interactions between the incident particles or photons and orbital electrons of the atomic/molecular constituents of a substrate

Interaction of Ionizing Radiation With Matter



α, β or γ

Orbital electron ejected as secondary electron

The incident particle or photon (with reduced energy)

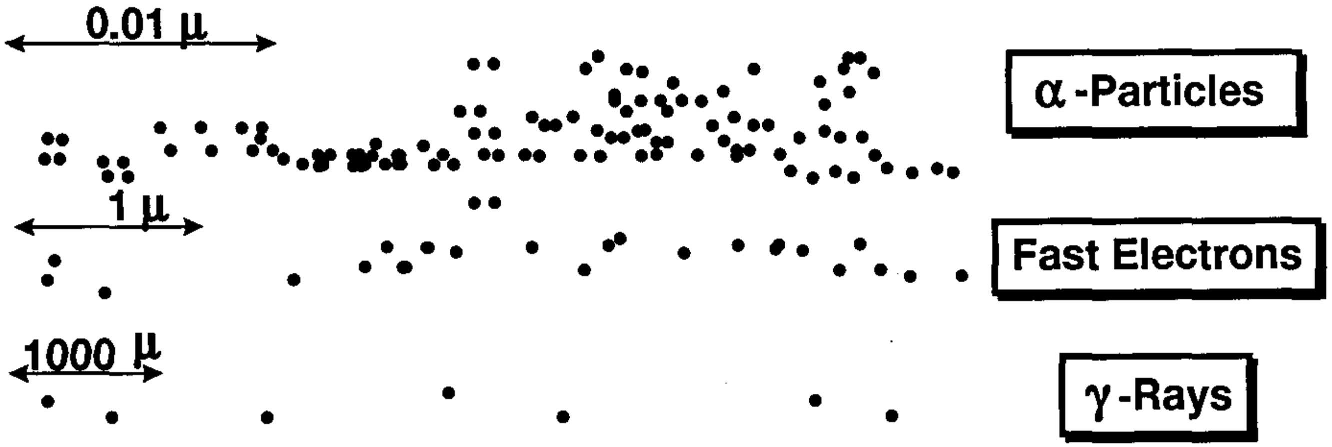
Energy Deposition Event

(for details see Klots in Ausloos, 1968)

- The probability of interaction follows the order, $\alpha > \beta > \gamma$ and hence the order of their penetration in matter
- Energy loss per event, mainly 20-100 eV
- Radiolysis similar to vacuum UV photolysis

Energy Deposition

- When α and e^-(β) beams or γ -rays interact with matter, the energy is distributed heterogeneously

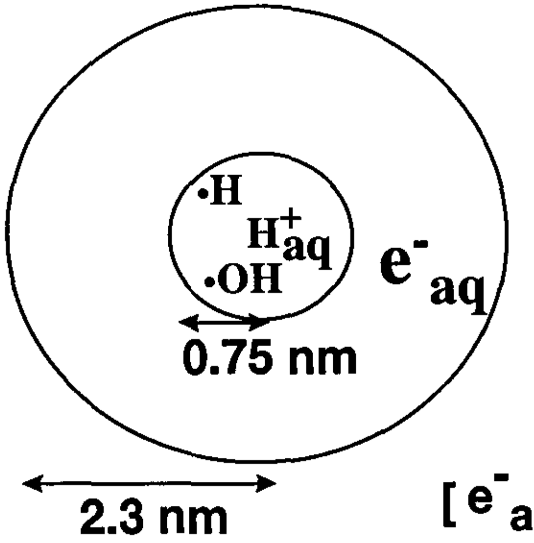


- Clusters of ionization and excitation (spurs) produced in liquids by irradiation
- Each dot represents a spur (~100 eV), a small region where energy is absorbed producing excited and ionized species

$$H_2O \rightsquigarrow H_2O^* + H_2O^+ + e^-$$

$$RH \rightsquigarrow RH^* + RH^+ + e^-$$

A Typical Spur in Water

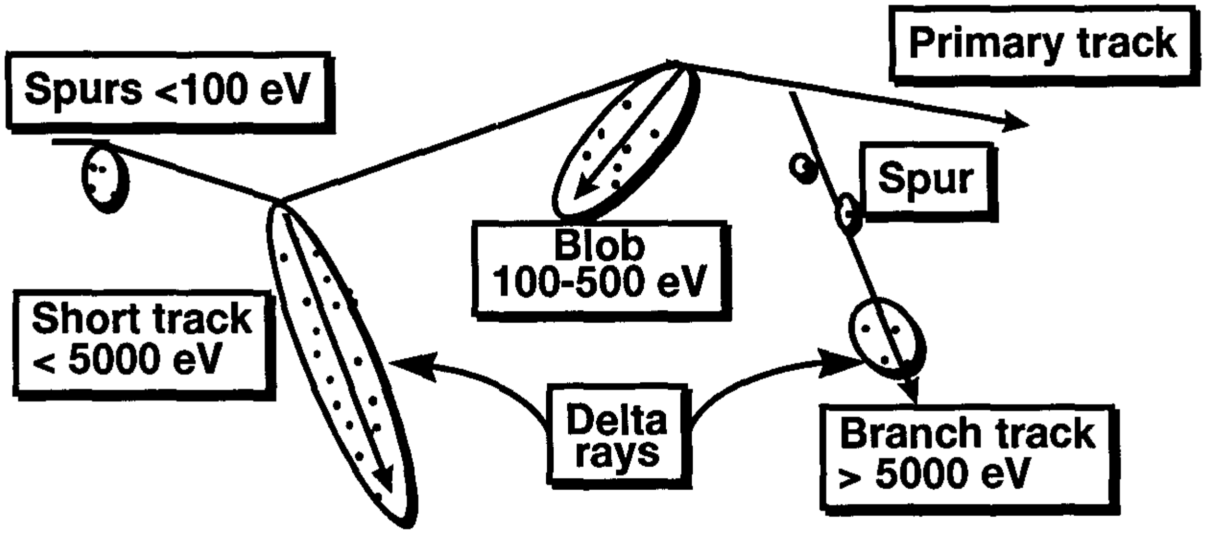


$G(e^-_{aq}) \sim 5$
$G(\bullet OH) \sim 6$

$[e^-_{aq}] \approx [\bullet OH] \approx 0.1\ mol.dm^{-3}$ (Av)[a]
$[\bullet OH] \approx 2\ mol.dm^{-3}$ (Spur Core)[b]

Adapted from Singh and Singh, 1982. Initial concentration, (a) averaged over total spur volume (diameter 4.6 nm); (b) within the spur core (diameter 1.5 nm)

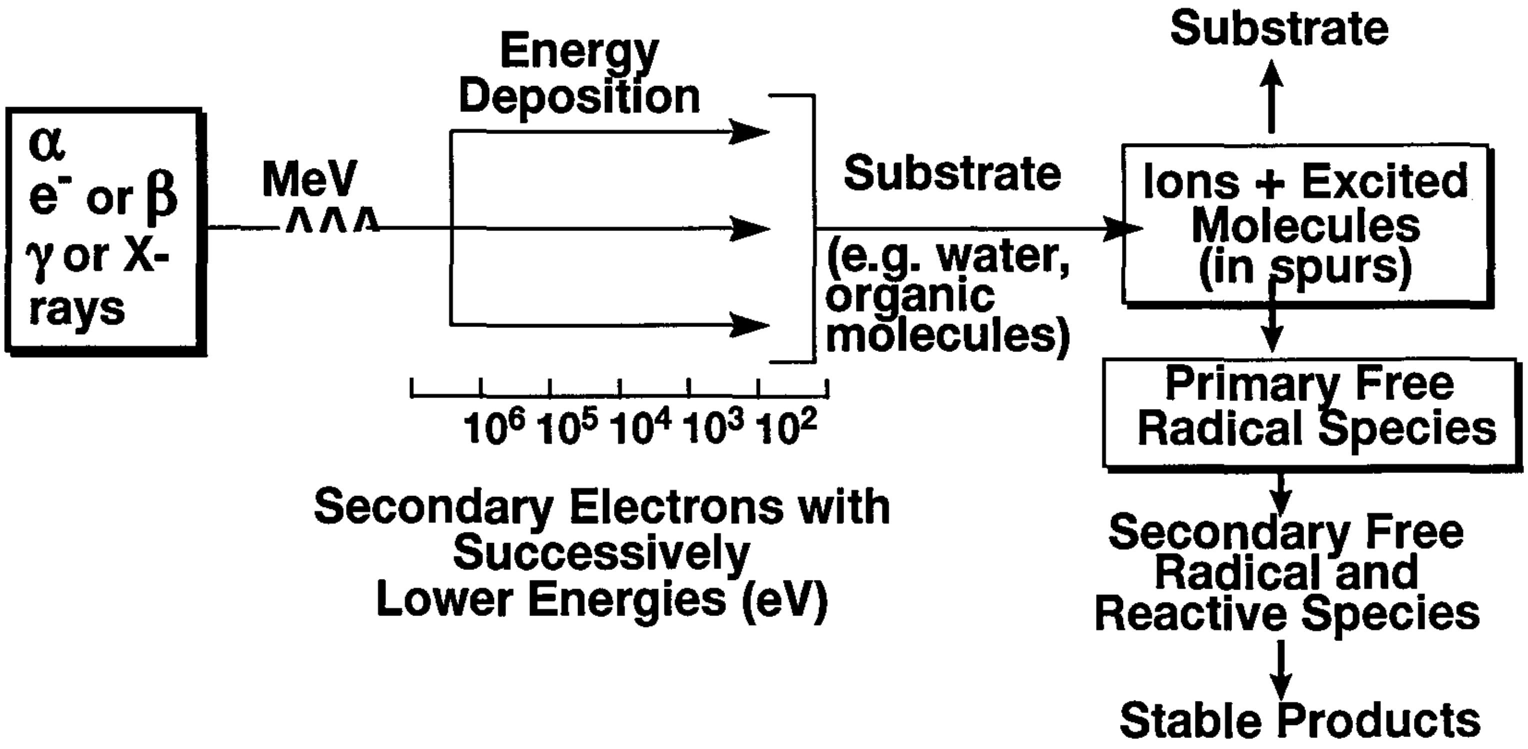
Distribution of Ions and Excited Molecules in the Track of a Fast Electron



- The quantity of energy deposited determines whether an individual event will give rise to a spur or a larger group of ions and excited molecules
- Blobs (100-500 eV) and short tracks (< 5000 eV) can be considered as groups of overlapping spurs
- Delta rays are secondary electrons of energy less than 10,000 eV
- For 10 MeV e^- : 75% spurs, 17% short and branched tracks, 8% blobs

(Spinks and Woods, 1990)

Basic Similarity of Radiolytic Effects by Different High Energy Radiations



α
e^- or β
γ or X-rays

MeV

Energy Deposition

10^6 10^5 10^4 10^3 10^2

Secondary Electrons with Successively Lower Energies (eV)

Substrate
(e.g. water, organic molecules)

Substrate

Ions + Excited Molecules (in spurs)

Primary Free Radical Species

Secondary Free Radical and Reactive Species

Stable Products

- Steps in Energy Deposition (Cascade Effect) Leading to Radiation-induced Product Formation

Basic Similarity of Radiolytic Effects by Different High Energy Radiation (contd)

- So, despite different types of high-energy radiation (charged particles or γ-rays or x-rays), the actual chemical effects are brought about by low energy electrons (10-100 eV). That is the reason for the similarity of the radiolytic effects
- However, the dose rate for the different radiations is different. This leads to different concentrations of spurs and reactive species affecting the product yields

Energy Absorption in Mixtures

- Components of a mixture absorb energy in proportion to their respective electron densities

Electron density = number of orbital electrons
per unit weight

- For gamma and electron irradiation of organic aqueous systems, a reasonable approximation is that the components of a mixture absorb energy in proportion to their weight

Biological System, 75% water and 25% organic
Energy absorbed, ~75% by water and
~25% by organic

LET

- Linear Energy Transfer (LET) is the rate of energy transfer from charged particles or photons to matter
- Its value increases with the mass of the particle
- However, this concept is of no direct interest for food irradiation, though it is of interest in other radiation processing applications and in radiotherapy

LET (contd)

Some Typical Values for Accelerated Particles

Particle	Energy (MeV)	Range in Air[a] (mm)	Range in Aluminum (mm)	Range in Water (mm)	Average LET in Water (keV µm^{-1})
Electron (e^-)	1	4,050	1.5	4.1	0.24
	3	14,000	5.5	15	0.20
	10	42,000	19.5	52	0.19
Proton (H^+)	1	23	0.013	0.023	43
	3	140	0.072	0.14	21
	10	1,150	0.64	1.2	8.3
Helium nucleus (He^{2+})	1	5.7	0.0029	0.0053	190
	3	17	0.0077	0.017	180
	10	105	0.057	0.11	92

[a] at 15°C, 100 kPa

Check

Radiation Processing

Physical Effects

Widely Used in

- Welding
- Industrial Radiography
- Ion Implantation
- Gemstone Irradiation

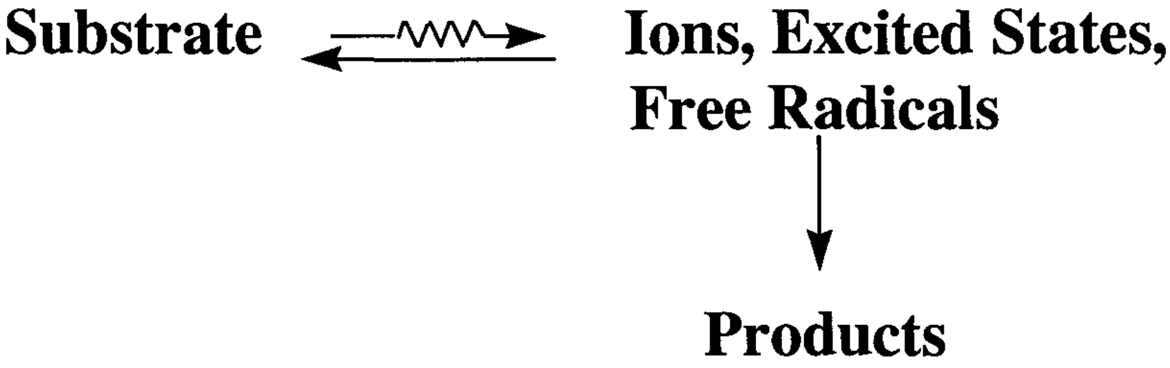
See Woods and Pikaev (1994), for details and references

Radiation Processing

Chemical Effects

1. Background
2. Basic Aspects
3. Formation and Reactions of Short-Lived Reactive Species
4. Products From Typical Organic Compounds

Irradiation, Overall Effect



Substrate

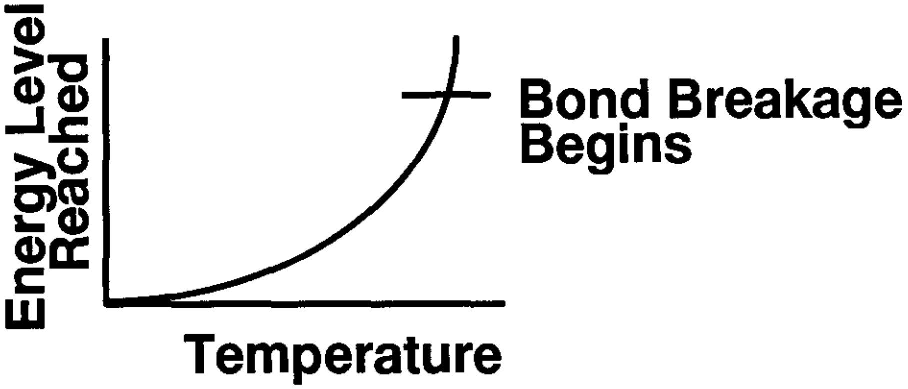
Ions, Excited States,
Free Radicals

Products

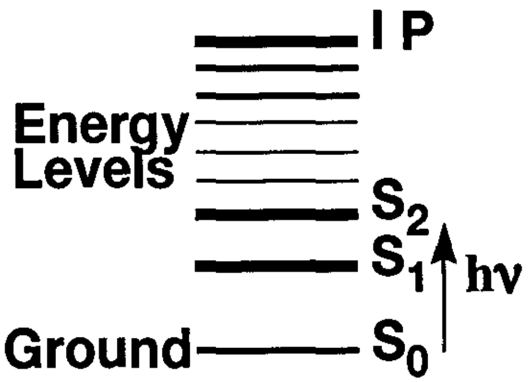
- Generally, higher the yields of excited states, the lower the overall decomposition, e.g., aromatic compounds degrade less than aliphatic compounds

Forms of Energy Supply

(1) Heat
(Pyrolysis)



(2) Light
(Photolysis)

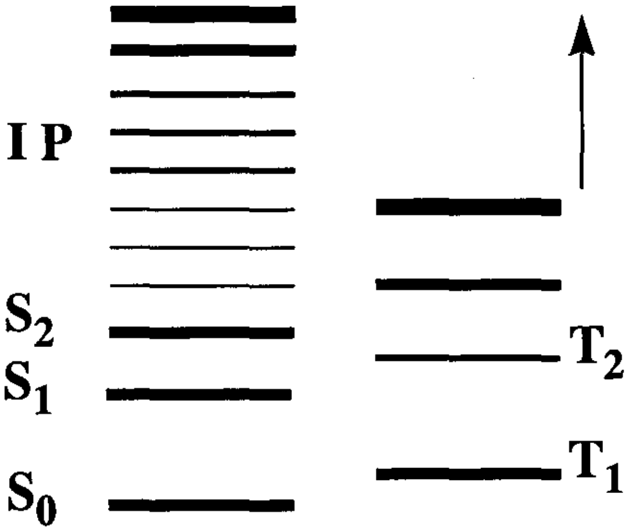


Excitation level dependent on the energy of the quanta

Temperature of the system generally unchanged

- Bond breakage generally from S_1 or higher levels (dependent on energy of quanta and bond dissociation energies)

High Energy Radiation
(Radiolysis)



- Ionization and excitation
- Singlet and triplet states
- Variety of bonds broken

- Bond dissociation energy still important

- Ionic reactions also important

Comparison: Pyrolysis (Heat Treatment) Photolysis and Radiolysis (Irradiation)

Factor	Pyrolysis	Photolysis	Radiolysis
Temperature	High	Room Temp	Room Temp
Energy Distribution in Liquids/Solids	Homogeneous	Homogeneous	Heterogeneous
Free Radicals	Yes	Yes	Yes
Ions	No	Rarely	Yes
Excited States	Rarely	Yes	Yes

Energy Required for Ionization: W and IP

- W-value is the energy required for one ionization event (one ion pair, e.g., $H_2O^+ + e^-$)
- Ionization potential (IP) is the minimum energy required to produce one ion pair

Comparison of W-values and IP[1]

Gas	W-value (eV)	IP (eV)
H_2O	29.6	12.6
CH_4	27.3	13.0
C_2H_6	25.0	11.7

[1] From Swallow (1960)

Energy Required for Ionization
W and IP

- Comparison of the W-value and the IP data suggests that excited molecules are formed in addition to the ionized species, since W > IP

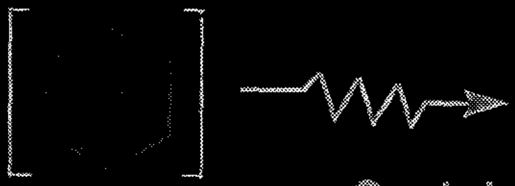
- The difference between W and IP is the energy going into excitation

W - IP = Excitation Energy

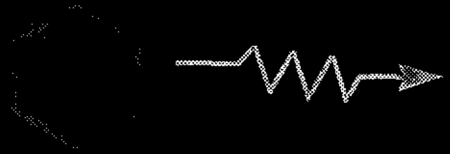
- Evidence for the formation of both ionized species and excited species is available in literature

Charge Transfer

In general, a cation (positive charge) will transfer its charge to a molecule whose ionization potential (IP) is lower. For example

Cyclohexane 

Cyclohexane$^{+\cdot}$ (IP = 9.9 eV)

Cyclohexane$^{+\cdot}$ + Benzene 

Cyclohexane + Benzene$^{+\cdot}$ (IP = 9.2 eV)

- IP Cyclohexane > IP Benzene

Molecular Energy Transfer

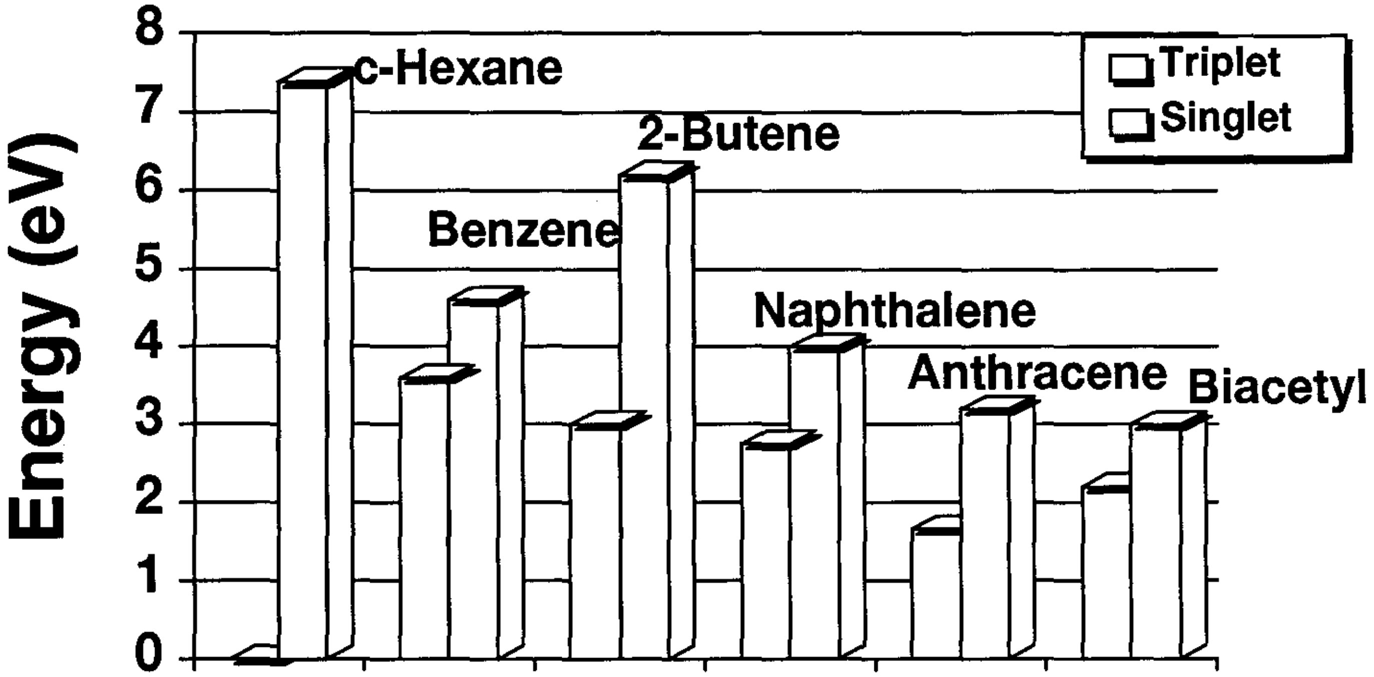
- Excited state formation can lead to the formation of the lowest excited singlet and triplet states of organic molecules

- Again, energy transfer can take place from excited molecules. For example

$$\text{Benzene} \rightsquigarrow \text{Benzene}^{*} + \text{Benzene}^{+\cdot} + e^{-}, \text{etc.}$$
$$\text{Benzene}^{*} + \text{Naphthalene} \rightarrow \text{Benzene} + \text{Naphthalene}^{*}$$

- The excited singlet and the excited triplet levels of naphthalene are lower than the corresponding ones in benzene

Singlet and Triplet Energy Levels of Donors and Acceptors



- The singlet energy levels of c-hexane and 2-butene are estimates (Auslöös, 1968)
- Singlet state transfers energy to lower singlet state and triplet state only to lower triplet state

Bond Breakage and Formation and Bond Energies

Chemical reactions are accompanied by bond formation or breakage

Bond breakage

$$\text{Energy} + H_3C - CH_3 \rightarrow H_3\dot{C} + \dot{C}H_3$$

Bond formation

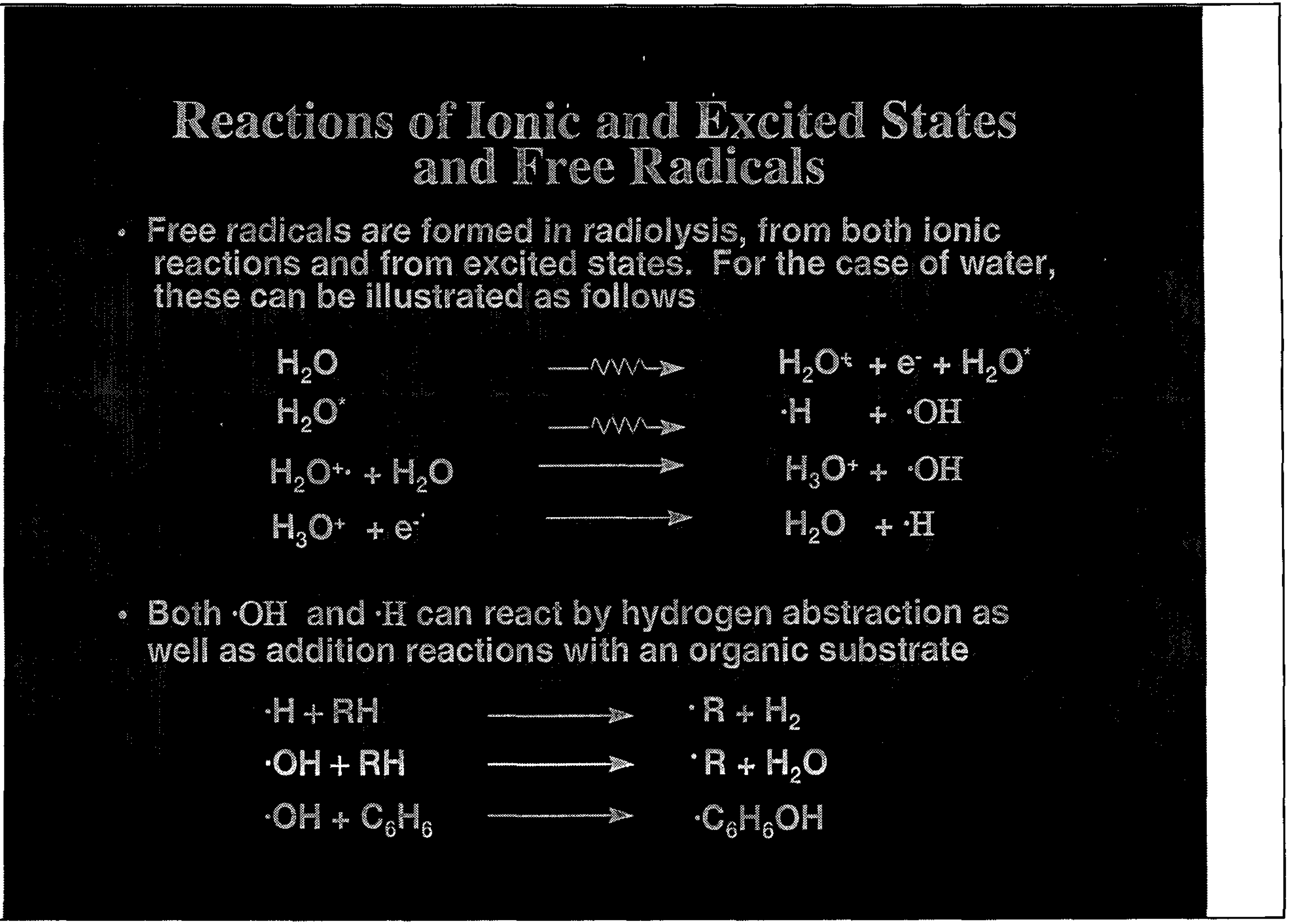
$$H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C - CH_3 + \text{energy (heat)}$$

Generally, bond breakage requires energy and bond formation results in energy release

Typical Bond Dissociation Energies

Bond Broken	ΔH, kcal/mole	Bond Broken	ΔH, kcal/mole
$H_3C - H$	102	$H_3C - CH_3$	84
$H_5C_2 - H$	99	$F_3C - CF_3$	70
$H_9C_4 - H$ (tertiary)	91		
$H_5C_6 - H$	103	$H_3CS - H$	88
		$H_3C - SH$	73
$H_3C - I$	53	$H - OH$	119
$H_3C - F$	110	$HO_2 - H$	90
		$HO - OH$	51

1 cal = 4.2 J



Reactions of Ionic and Excited States and Free Radicals

- Free radicals are formed in radiolysis, from both ionic reactions and from excited states. For the case of water, these can be illustrated as follows

$$H_2O \rightsquigarrow H_2O^{+\cdot} + e^- + H_2O^*$$

$$H_2O^* \rightsquigarrow \cdot H + \cdot OH$$

$$H_2O^{+\cdot} + H_2O \longrightarrow H_3O^+ + \cdot OH$$

$$H_3O^+ + e^- \longrightarrow H_2O + \cdot H$$

- Both ·OH and ·H can react by hydrogen abstraction as well as addition reactions with an organic substrate

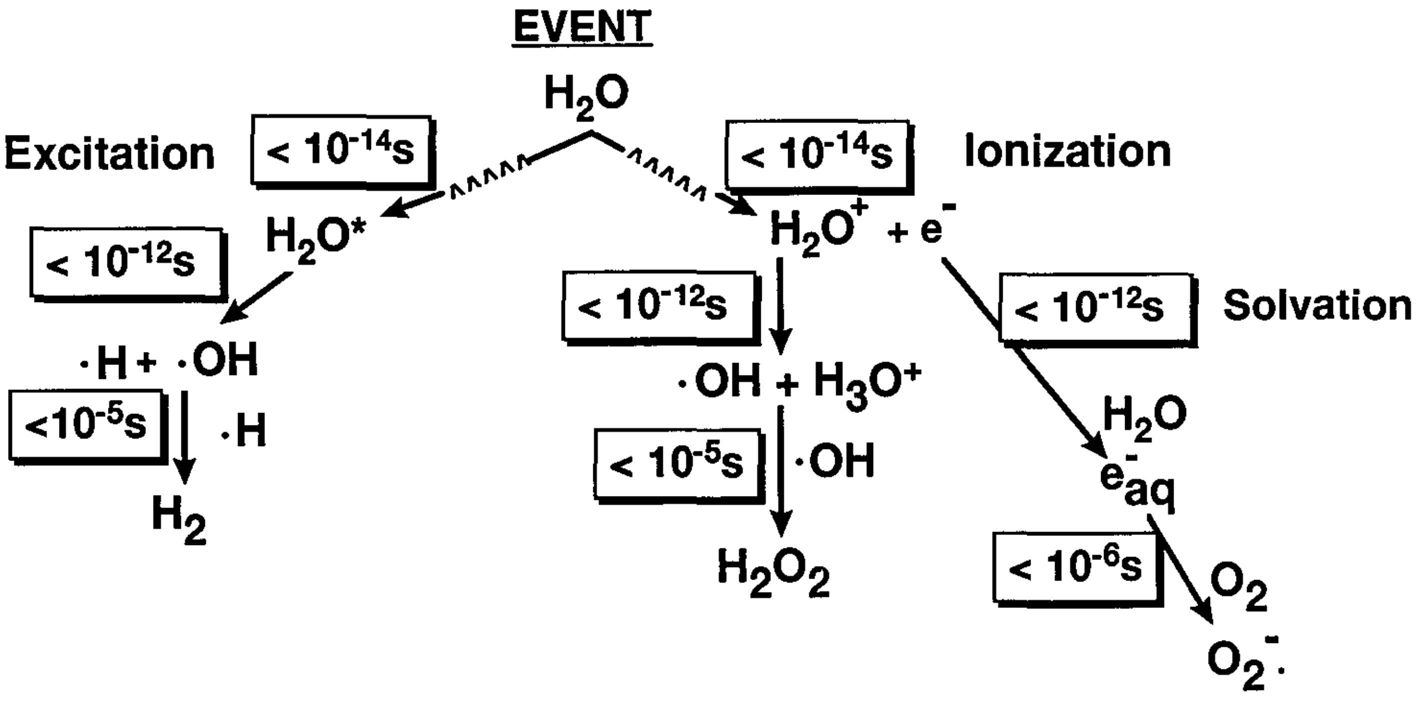
$$\cdot H + RH \longrightarrow \cdot R + H_2$$

$$\cdot OH + RH \longrightarrow \cdot R + H_2O$$

$$\cdot OH + C_6H_6 \longrightarrow \cdot C_6H_6OH$$

- Water is the most studied liquid in radiation chemistry

Radiolysis of Water



EVENT

H_2O

Excitation $< 10^{-14}$s

H_2O^*

$< 10^{-12}$s

$\cdot H + \cdot OH$

$< 10^{-5}$s $\cdot H$

H_2

$< 10^{-14}$s Ionization

$H_2O^+ + e^-$

$< 10^{-12}$s

$\cdot OH + H_3O^+$

$< 10^{-5}$s $\cdot OH$

H_2O_2

$< 10^{-12}$s Solvation

H_2O

e^-_{aq}

$< 10^{-6}$s O_2

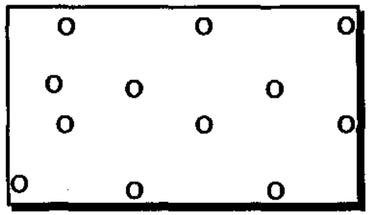
$O_2^{-}\cdot$

- The species present at 10^{-7}s :

  e^-_{aq} , $\cdot H$, $\cdot OH$, H_2O_2, H_3O^+ ,$O_2^{-}\cdot$

Transition From Inhomogeneous to Homogeneous Distribution of Free Radicals in Liquid Water

(i) γ- Irrad $\sim 10^{-12}$s



[Spur] -Low number

$[e^-_{aq}] \approx [\cdot OH] \approx 0.1$ mol.dm^{-3}(Av)^a

$[\cdot OH] \approx 2$ mol.dm^{-3} (Spur Core)^b

(ii) G (e^-_{aq}) ~ 2.7

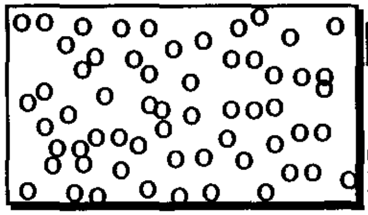
G ($\cdot$OH) ~ 2.7

Homogeneous Distribution ($\cdot$OH, e^-_{aq}, $\cdot$H)

$[e^-_{aq}] \approx [\cdot OH] \approx 10^{-9}$ mol.dm^{-3}(γ)^c

$\approx 10^{-3}$ to10^{-6} mol .dm^{-3} (e^-)^d

(iii) e^- Irrad $\sim 10^{-12}$ s



[Spur] -Very high number

$[e^-_{aq}] \approx [\cdot OH] \approx 0.1$ mol.dm^{-3}(Av)^a

$[\cdot OH] \approx 2$ mol.dm^{-3} (Spur Core)^b

a. Averaged over total spur volume; b. Initial Concentration within the spur core; c. γ - Irradiation; d. e^-- Irradiation

Transition From Inhomogeneous to Homogeneous Distribution of Free Radicals in Liquid Water

(i) Represents spur formation on energy absorption from a single gamma photon in 10^{-12} s or less

(ii) Shows homogeneous distribution of reactive species on diffusion of spurs in about 10^{-7} s

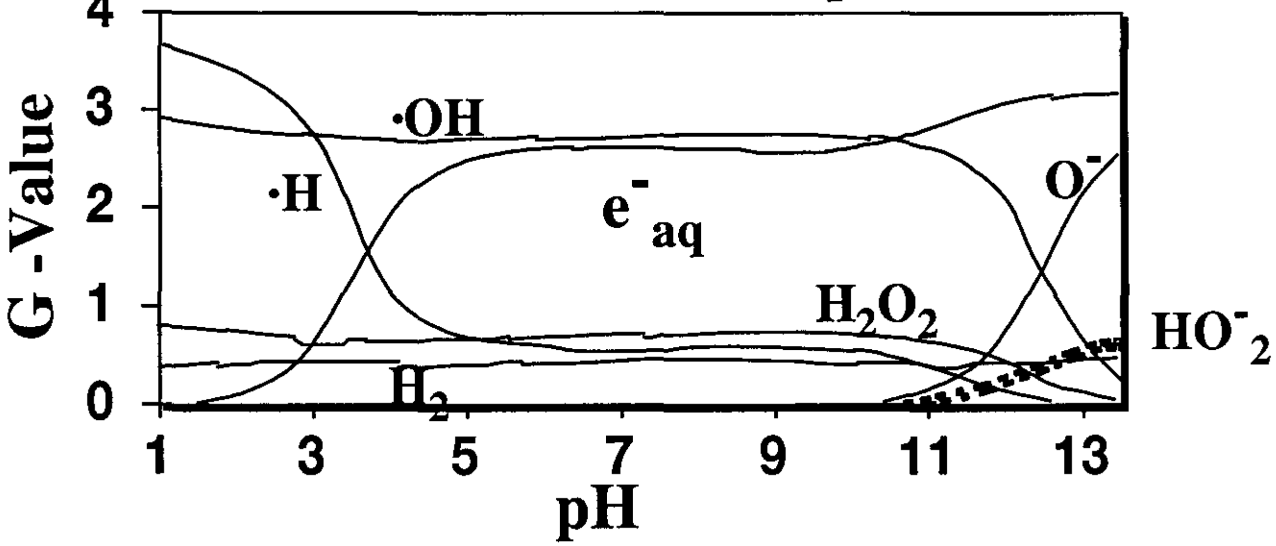
(iii) Represents spur formation on energy absorption from a single electron in 10^{-12} s or less. The higher spur concentration [spur] on electron irradiation is not drawn to scale

Singh (1991)

pH Dependence of Yields on Radiolysis of Water

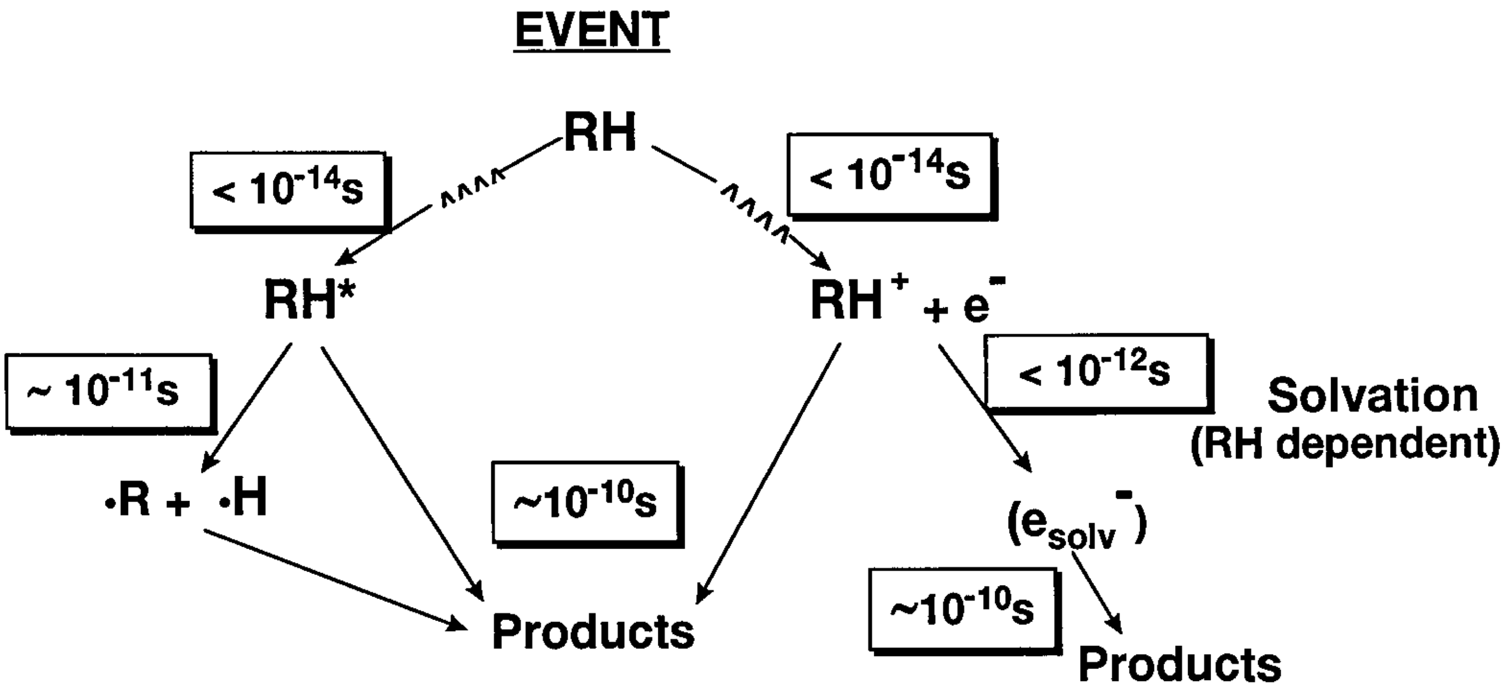
$$e^-_{aq} + H^+ \rightarrow \cdot H$$

$$\cdot H + OH^- \rightarrow e^-_{aq}$$



- The pH range of most foods lies between 2 and 8

Radiolysis of Organic Liquids



EVENT

RH

$< 10^{-14}$s

$< 10^{-14}$s

RH^*

$RH^+ + e^-$

$\sim 10^{-11}$s

$< 10^{-12}$s

Solvation
(RH dependent)

$\cdot R + \cdot H$

$\sim 10^{-10}$s

(e_{solv}^-)

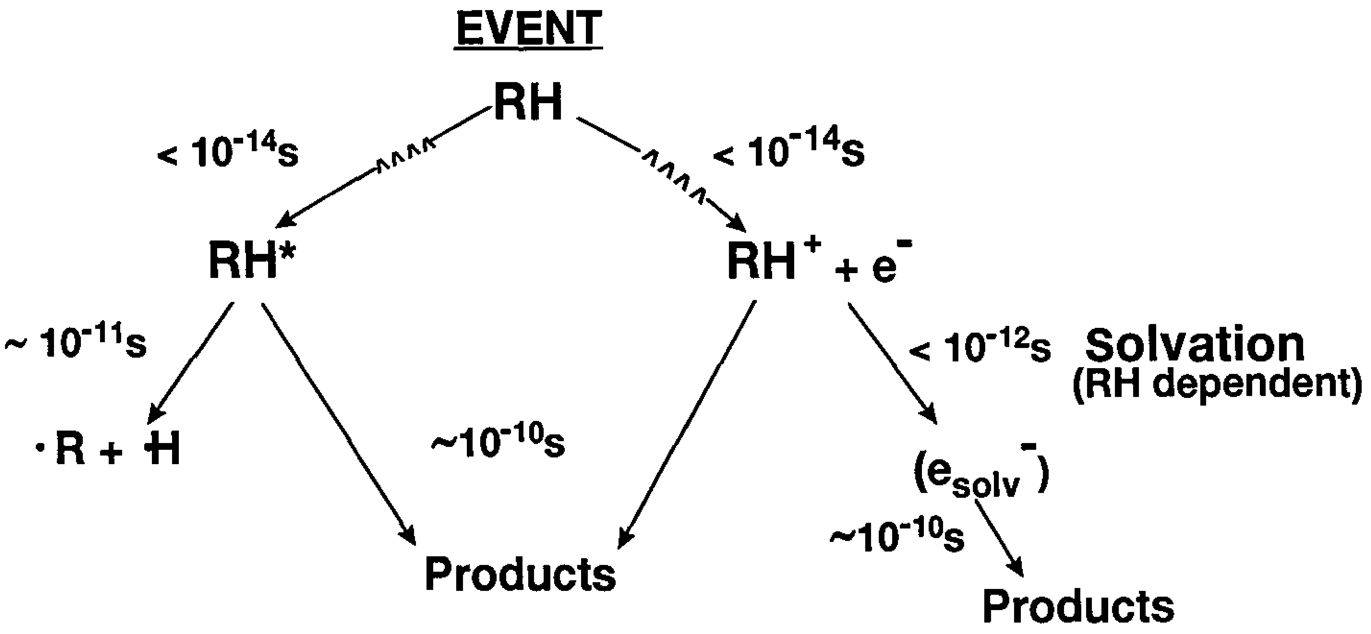
$\sim 10^{-10}$s

Products

Products

- Excitation longer lived and more important in organic systems, than in water
- Ionic species formed but much shorter lived than in water
- In the presence of air/O_2, peroxy radicals and $O_2^{-\cdot}$ formed

RADIOLYSIS OF ORGANIC LIQUIDS

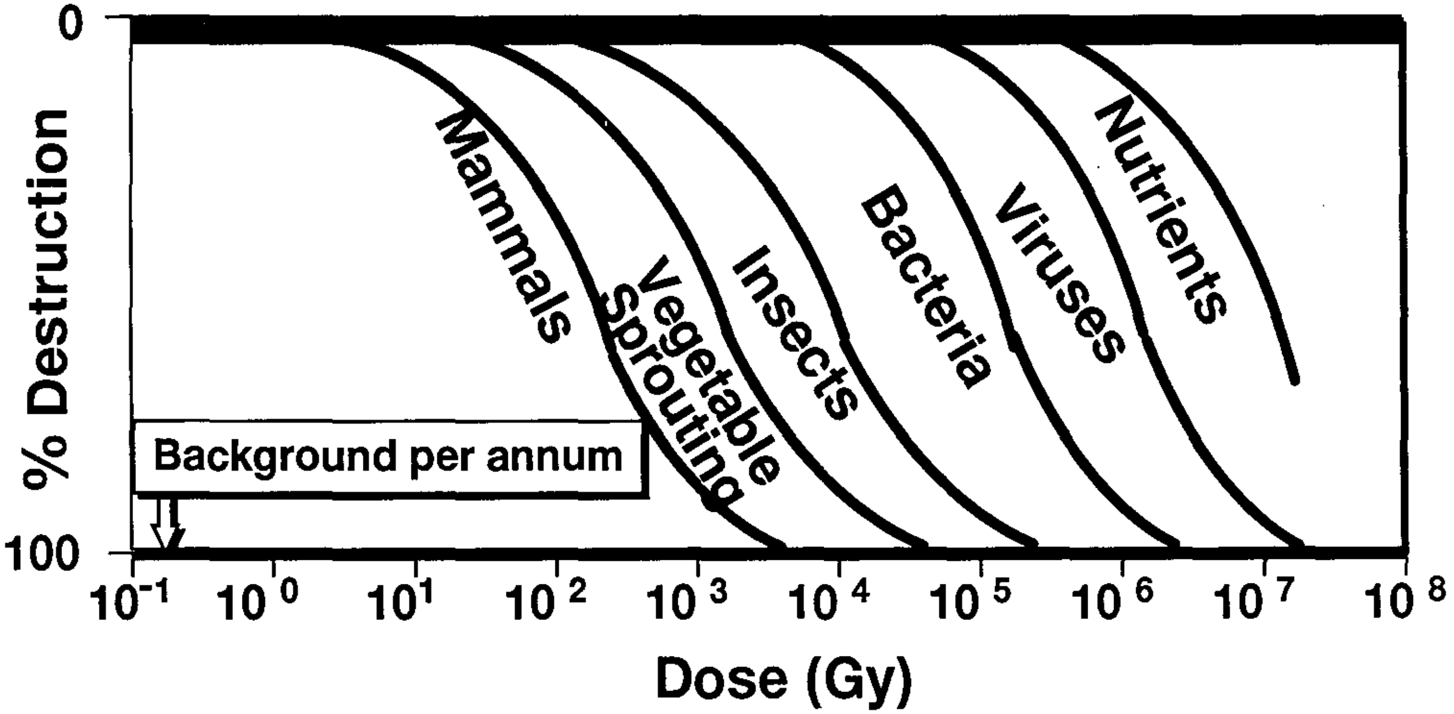


- Excitation longer lived and more important in organic systems, than in water
- Ionic species formed but much shorter lived than in water
- In the presence of air/O_2, peroxy radicals and O_2^- formed

Biological Effects

- Biological Effects Studied soon after Röntgen Discovered X-rays in 1895
- Irradiation of human skull led to loss of hair (1896)

Basis for Beneficial Effect of Irradiation



- These differential senstivities of different functional entities to inactivation are the basis of beneficial effects of irradiation

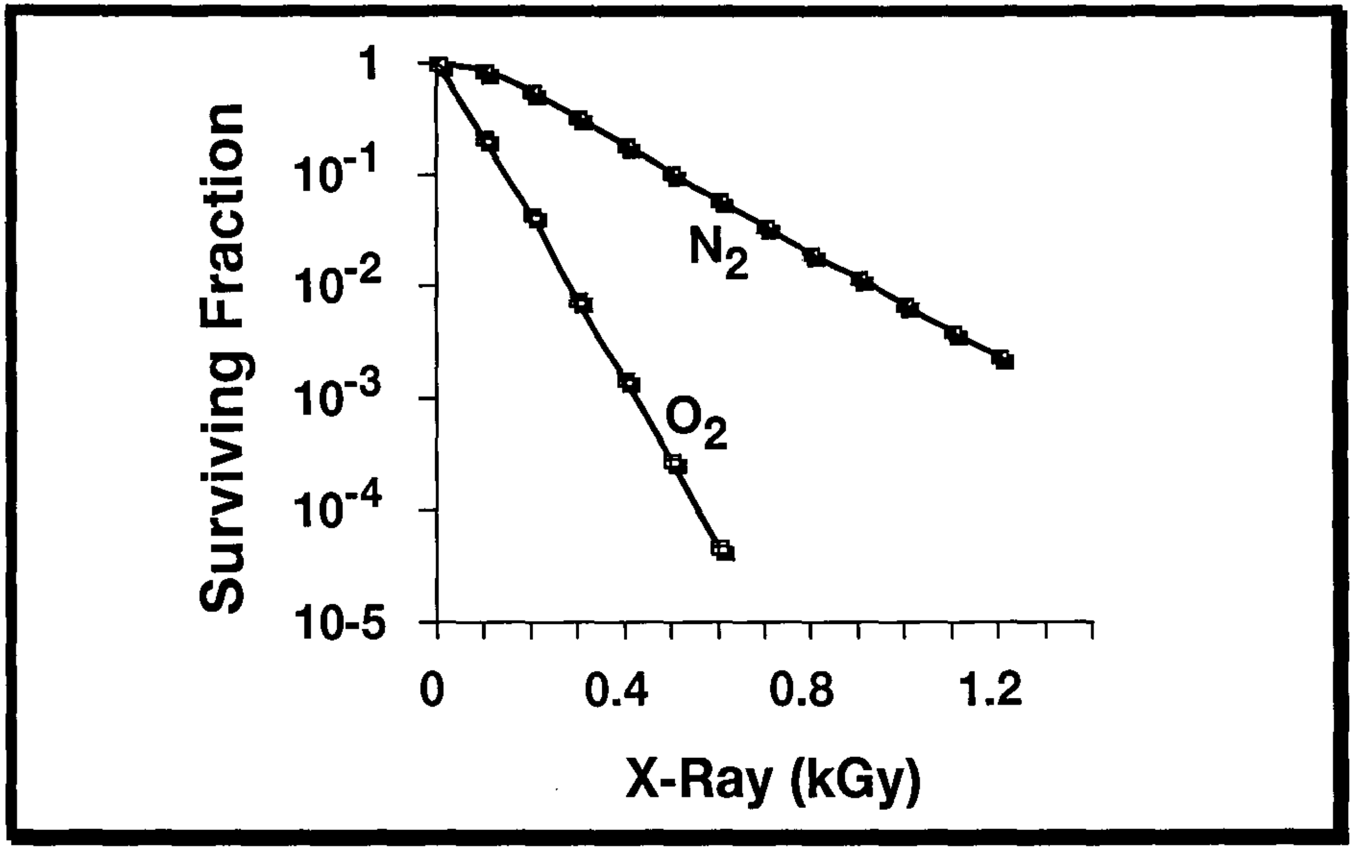
Irradiation

Microorganism Inactivation

- Irradiation used to control microorganism levels (food, sewage, medical devices)

- Irradiation harmful to humans; so, exposure of humans kept within safe limits

Radiation-Inactivation of *E. coli*



E.coli cultured aerobically in broth and irradiated in O_2-saturated or N_2-saturated buffer (Casarett,1968)

Concluding Remarks

- Physicists, chemists and biologists have contributed to the high level of understanding of the basic aspects of radiation science, which forms the foundation of radiation processing

- One of the biggest industrial applications of radiation processing, crosslinking of polyethylene and the heat-shrink phenomenon, were discovered by Prof. Arthur Charlesby in 1957 when he was investigating the effects of high energy radiation on polymers