



Free-Radicals: Chemistry and Biology

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<http://iscamap.chem.polimi.it/citterio/education/free-radical-chemistry/>



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Radiation Chemistry

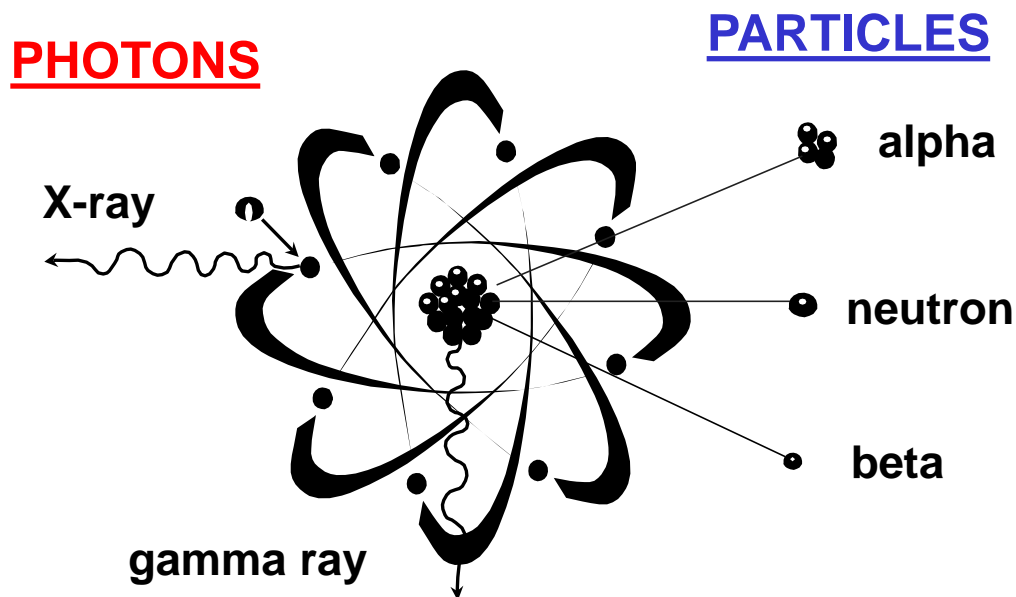
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Ionizing Radiation

Two general categories of ionizing radiation:



Radioactivity units:

Radioactivity is measured in the number of disintegrations radioactive material undergoes in a certain period of time.

- dpm; dps (Becquerel)
- Curie (Ci)

One curie =: 37 billion dps = 3.7×10^{10} dps; Historically – 1 gram of Ra-226



Ionizing Radiations

Ionizing Radiations :

Electromagnetic ($m = 0$, $E = h\nu$) → X e γ ray

Particles ($m > 0$, $E = \frac{1}{2} mv^2$) → particles α , β^\pm , p, n,...

- Charged Particles: α , β^\pm , p

 - direct ionization of media atoms

- Neutral Particles: n, X, γ

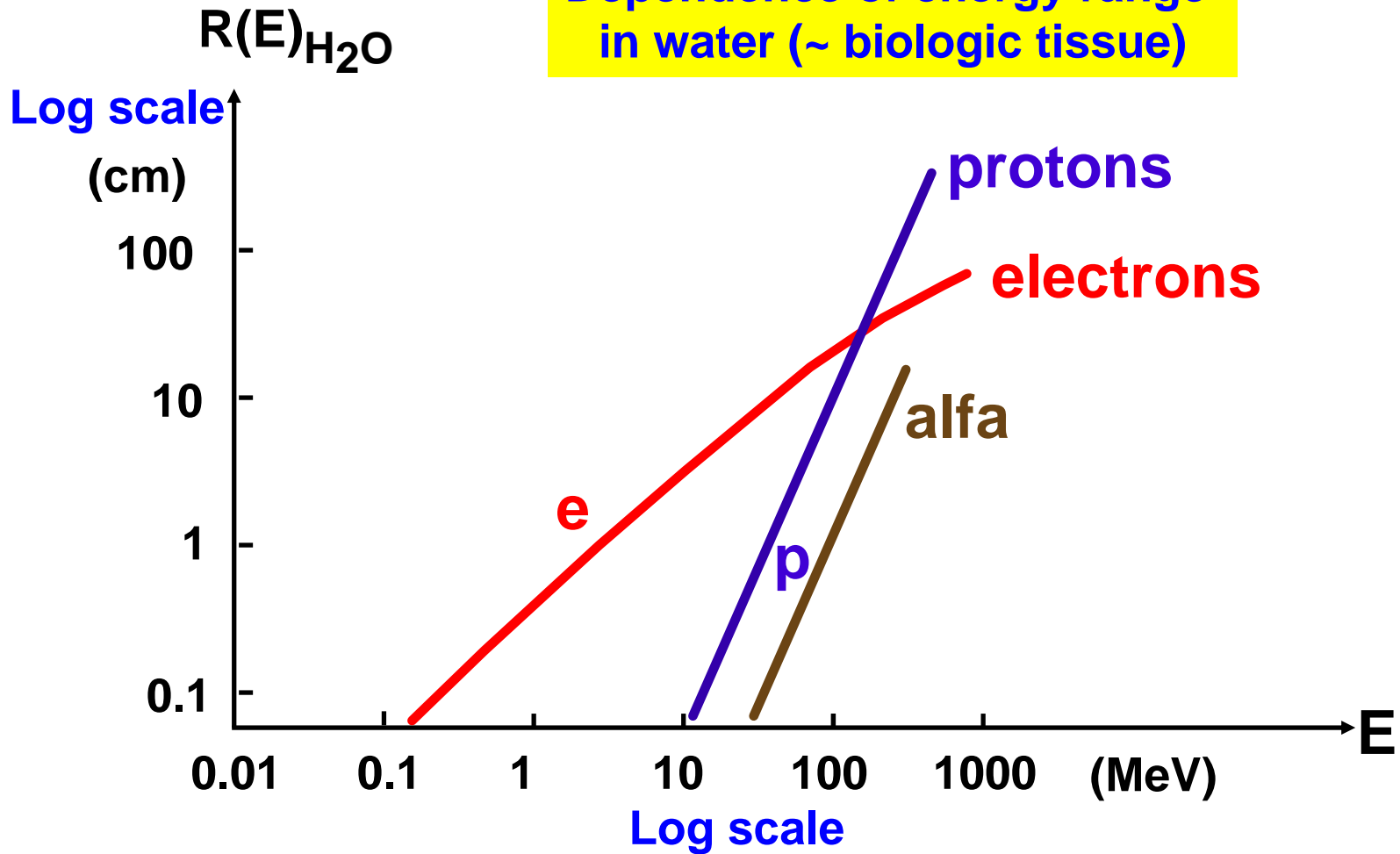
 - indirect ionization - production of secondary charged particles

- When radiation interacts with target atoms, energy is deposited, resulting in **ionization** or **excitation**.
- The absorption of sufficient energy from ionizing radiation ($E \geq 100$ eV) produces damage to molecules by direct and indirect actions (fragmentation, bond breaking, polymerization,...).
- For **direct action**, damage occurs as a result of **ionization** of atoms on key molecules in the biologic system. This causes inactivation or functional alteration of the molecule.
- **Indirect action** involves the production of reactive **free radicals** whose toxic damage on the key molecule results in a biologic effect.



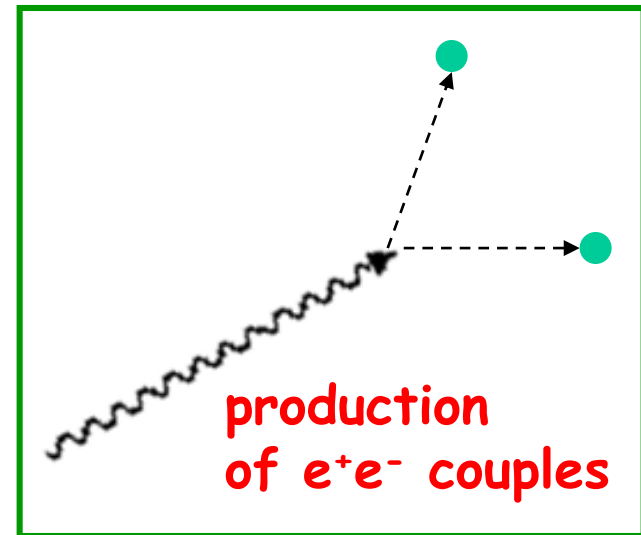
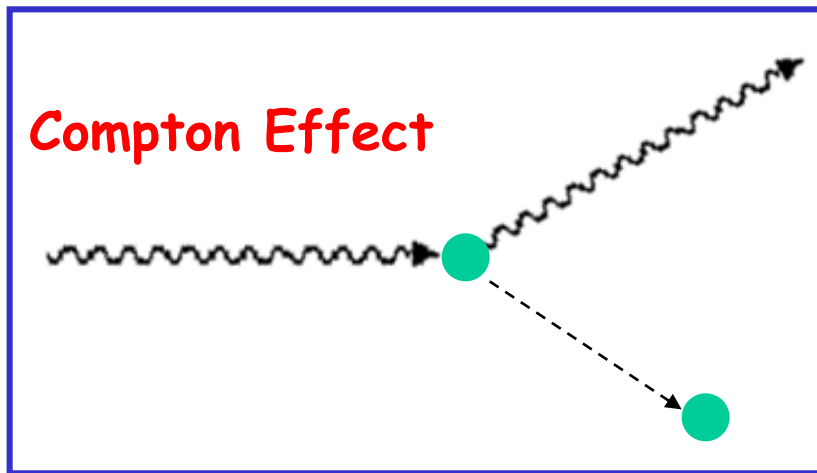
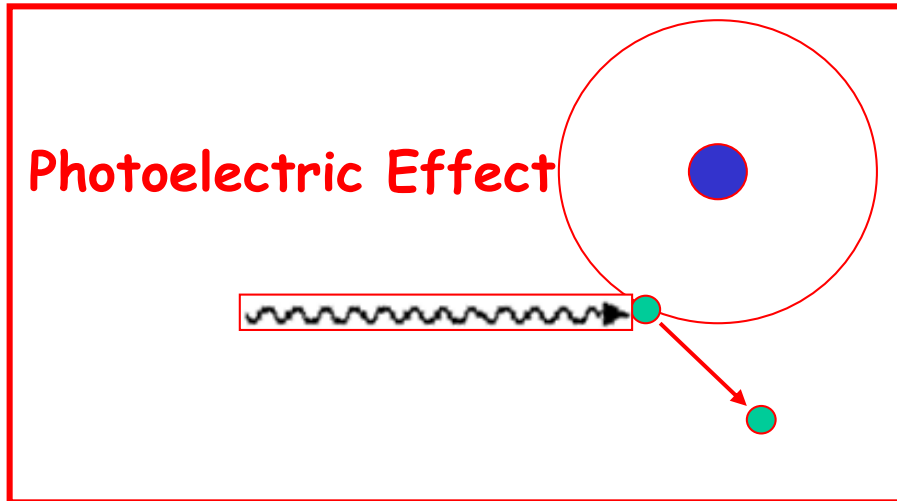
Range and Energy of Different Particles

Dependence of energy range in water (~ biologic tissue)





X and γ Ray (Photons) - Matter Interaction





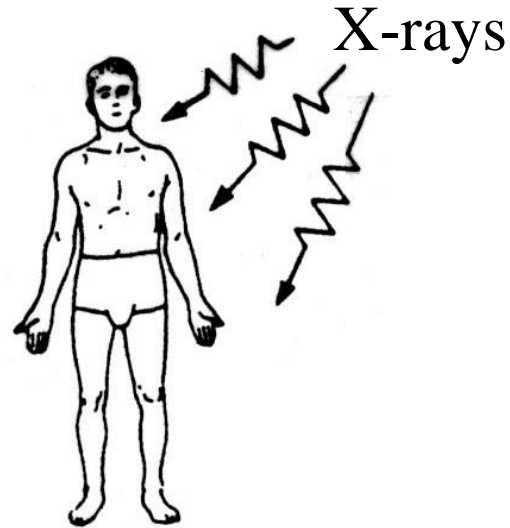
Energy Equivalent of Lethal Radiation Dose

Total body irradiation

Mass = 70 kg

LD50 dose = 4 Gy

4 Gy = 67 calories



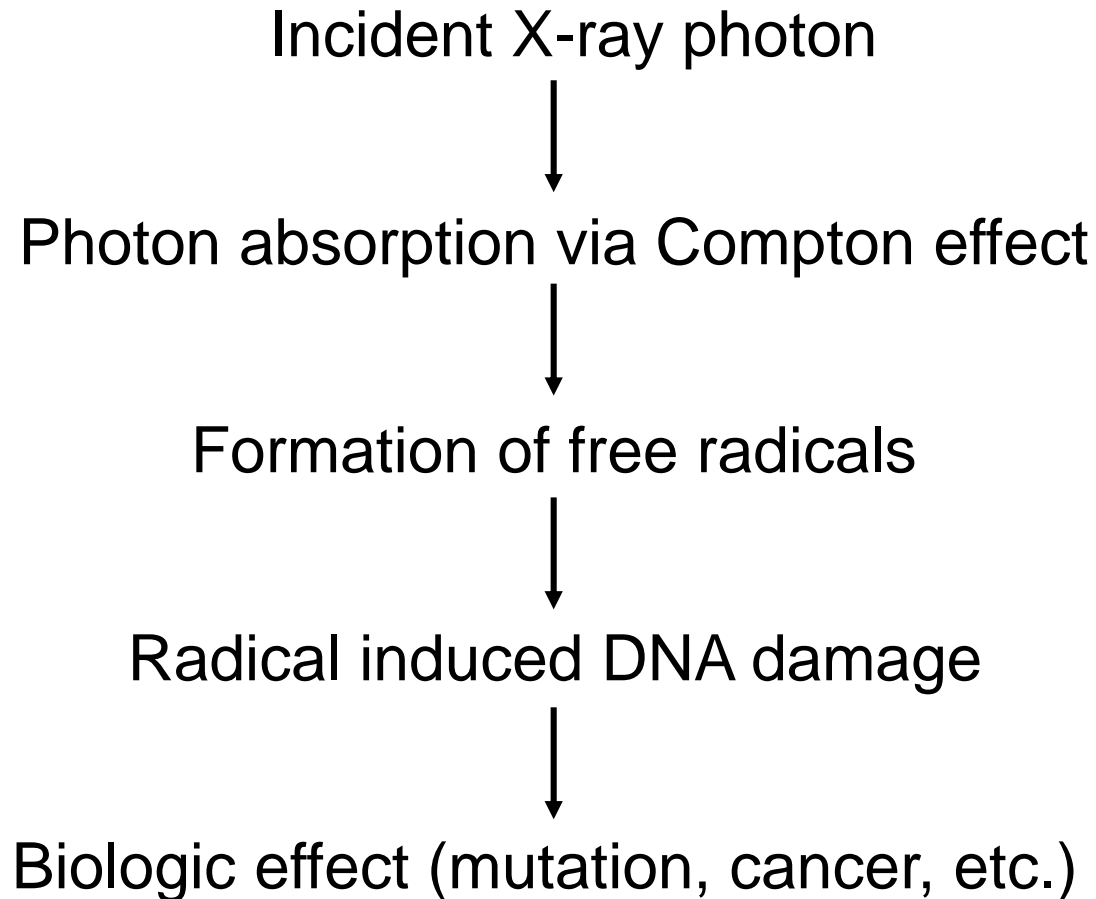
67 calories
equivalent to
energy in one sip
(3 ml) of hot coffee



*Lethal dose is
relatively modest
amount of energy*



Sequence of Radiation Effects

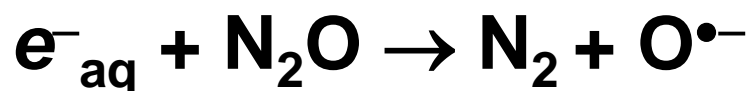




Radiation Chemistry Useful to Study Radicals

- **Selectively Oxidize/Reduce**

- Although both oxidizing and reducing radicals are produced in solvents by ionizing radiation, one or the other can usually be selectively scavenged.



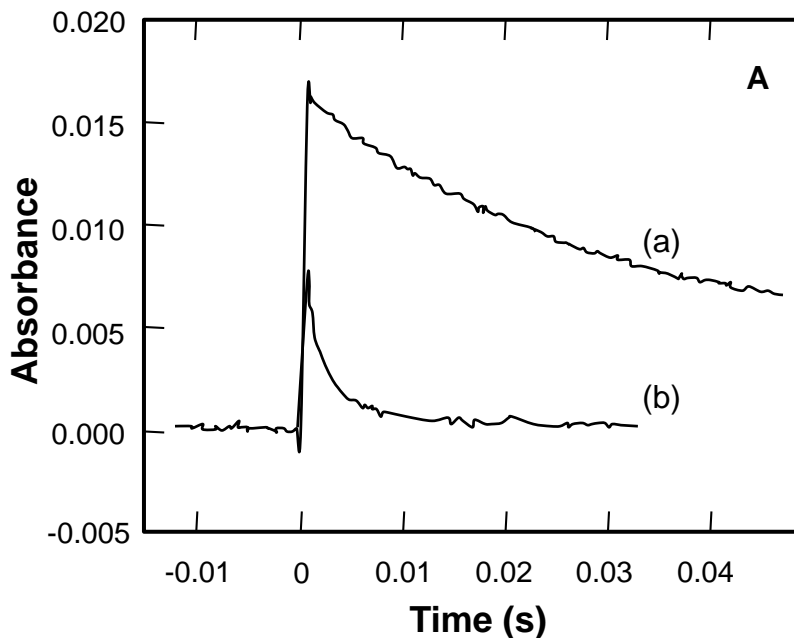
- Scavenger (N_2O) converts reducing species (e^-_{aq}) into an oxidizing one ($O^{\bullet-}$).

- **Generate Uniform Concentrations of Transients**

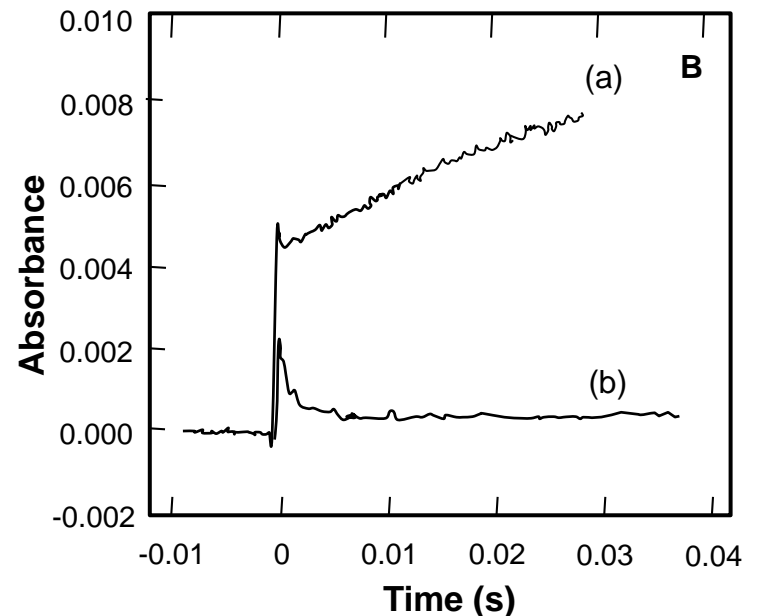
- Ionizing radiation generates a constant concentration of transients if the energies are sufficient to penetrate the sample.
- For certain solvents, in particular water, radiation chemists have carefully measured yields of primary radicals coming from the solvent.

Radiation Chemistry Provides Selectivity Through Redox Potentials

- An example is to use $\text{Br}_2^{\bullet-}$ to selectively oxidize tryptophan and tyrosine residues in proteins.
- Tryptophan and tyrosine are easily oxidized amino acid residues.
- However, $\text{Br}_2^{\bullet-}$ cannot oxidize most amino acids, whereas $\bullet\text{OH}$ can.



Decay of Trp• radical at 520 nm after radiolysis of a 70 mM lysozyme solution in pH 6.2 phosphate buffer (10 mM) containing 0.1 M KBr. Radiolytic dose 20 Gya) N_2O saturated and (b) O_2 saturated solution.



Time dependence of the transient absorbance measured at 410 nm under the above indicated conditions (a) N_2O saturated solution and (b) O_2 saturated solution.

Radiolytic Yields of Radicals are Well-Characterized

- Radiation chemists have also characterized scavenging efficiencies for secondary radical formation.
- The Schuler formula can be used to determine the yield of radicals in water

Radiation Chemical Yields

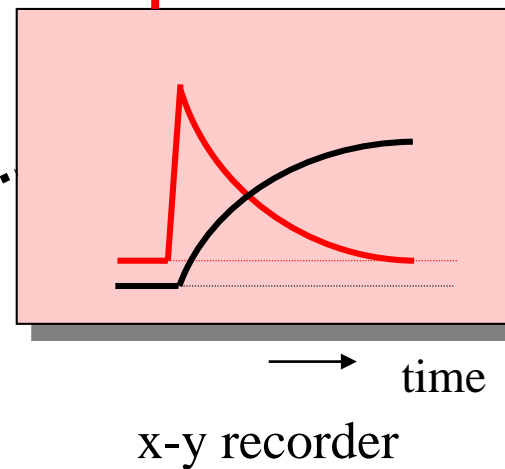
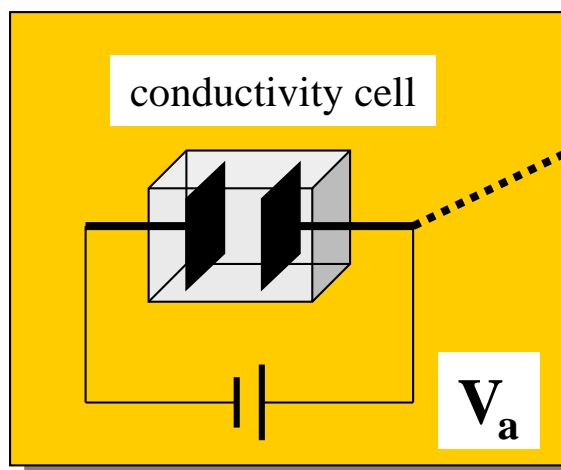
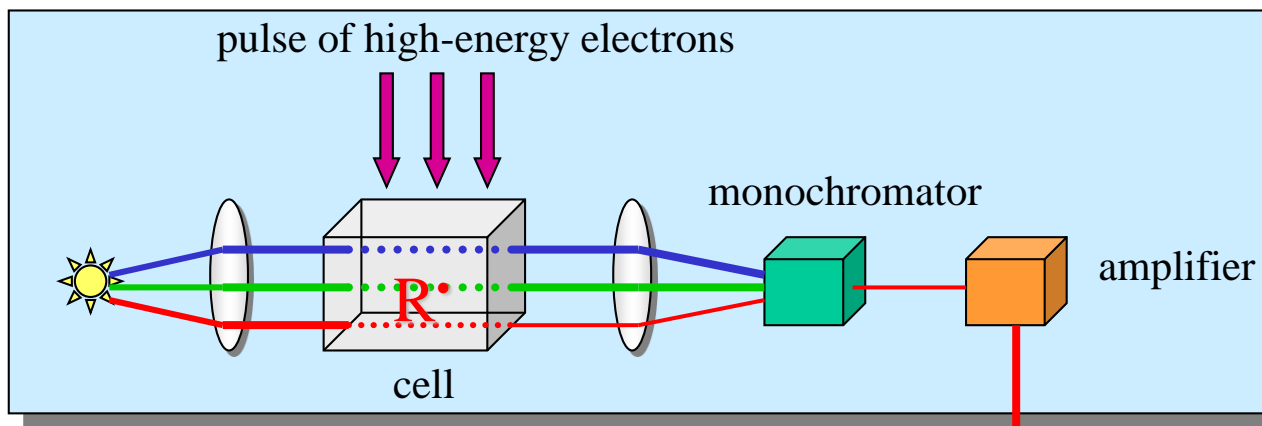
G is number of free radicals formed
from 100 eV of energy absorbed

- The Schuler formula gives the yield of secondary radicals formed from the reaction of hydroxyl radicals and the scavenger S at concentration [S]: $\bullet\text{OH} + \text{S} \xrightarrow{k_s} \text{secondary radical}$

$$G^{\text{N}_2\text{O}}(\bullet\text{OH}) = 5.2 + 3.0 \frac{\left(\frac{k_s[S]}{4.7 \times 10^8} \right)^{1/2}}{1 + \left(\frac{k_s[S]}{4.7 \times 10^8} \right)^{1/2}}$$



Use of Ionizing Radiations for Radical Studies: Time Resolved Conductivity





Radiation Chemistry:

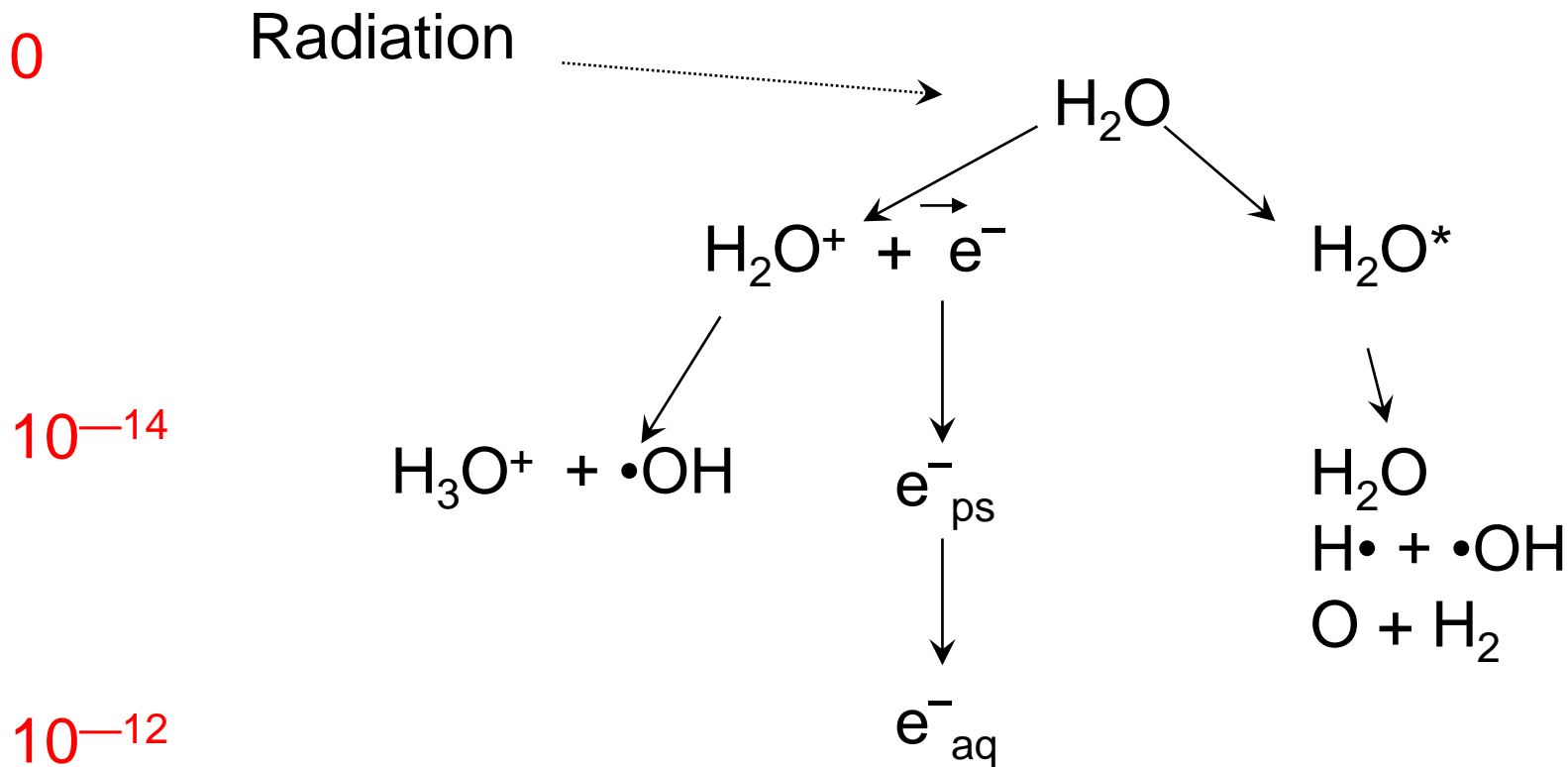
Species: $e^-_{(aq)}$, $H\cdot$, $HO\cdot$, H_2O_2 , H_2 , $O_2^{\cdot-}$

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Global Scheme of the First Stages





Physical Stage

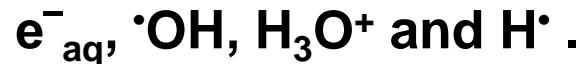
- The first act in the radiolysis of water:
 - ✓ Ionization: $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{e}^-$ having an excess kinetic energy
 - ✓ Excitation: $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^*$. Process is minor than ionization
- These two entities H_2O^+ and H_2O^* are very unstable and disappear in $\sim 10^{-14}$ s :
 - ✓ $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_3\text{O}^+$ (acid-base reaction)
 - ✓ H_2O^* de-excites or cleaves:
 - ✓ $\text{H}_2\text{O}^* \rightarrow \cdot\text{OH} + \cdot\text{H}$ is the most probable cleavage, but there are other possible cleavage paths ($\text{O} + \text{H}_2$)
- e^- slows and then thermalizes with the solvent in ~ 2 stages.



Physical-chemical Stage

- During the first 10^{-12} s, the molecules do not have time to move significantly.
- The environment therefore consists principally of heterogeneous regions (spurs) notably at the end of the ionization track of the secondary electrons.

- **These spurs contain the surviving species**



- **Yield**

- 1 ps after the primary radiolytic act, the quantification of the destruction of water is, per 100 eV absorbed, :



- These data are the yields in molecules/100 eV:

$$1 \text{ mol}\cdot\text{J}^{-1} = 1.036 \times 10^{-7} \text{ moles}/100 \text{ eV}$$

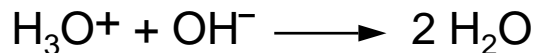
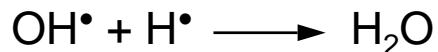
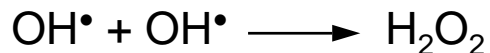
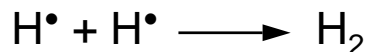
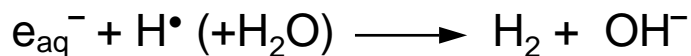
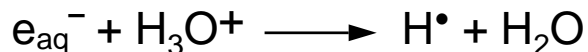
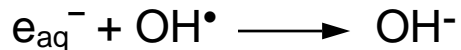
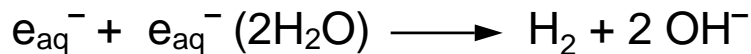
- Problem: origin of H_2 at this stage.



Recombination Reactions

- Recombination reactions are favored by the large local concentrations.
- They are in competition with diffusion (producing an homogenation of the media)

$$\frac{\partial [i]}{\partial t} = D_i \nabla^2 [i] - \sum_j k_{i,j} [i][j]$$



There is formation of
molecular species:
H₂ and H₂O₂.



Chemical Stage

- The homogenization of the media is complete after about 10 ns.
- At this time, the media has become a homogeneous solution of free radicals and molecular products:



- At this stage, the yields are (γ from ^{60}Co , accelerated electrons) :

$$g(\text{OH}) = G_{\text{OH}} = 0.29 \mu\text{mol}\cdot\text{J}^{-1}$$

$$g(\text{H}) = G_{\text{H}} = 0.057 \mu\text{mol}\cdot\text{J}^{-1}$$

$$g(\text{e}^-_{\text{aq}}) = G_{\text{e}} = 0.28 \mu\text{mol}\cdot\text{J}^{-1}$$

$$g(\text{H}_2) = G_{\text{H}_2} = 0.046 \mu\text{mol}\cdot\text{J}^{-1}$$

$$g(\text{H}_2\text{O}_2) = G_{\text{H}_2\text{O}_2} = 0.072 \mu\text{mol}\cdot\text{J}^{-1}$$



Chemical Balance in Water Radiolysis

- Destruction of water:

$$\begin{aligned}G(-\text{H}_2\text{O}) &= 2 g(\text{H}_2) + g(\text{H}) + g(e^-_{\text{aq}}) \\ &= 2 g(\text{H}_2\text{O}_2) + g(\text{OH})\end{aligned}$$

1. Conservation of O : $G(-\text{H}_2\text{O}) = 2 g(\text{H}_2\text{O}_2) + g(\text{OH})$

2. Conservation of H :

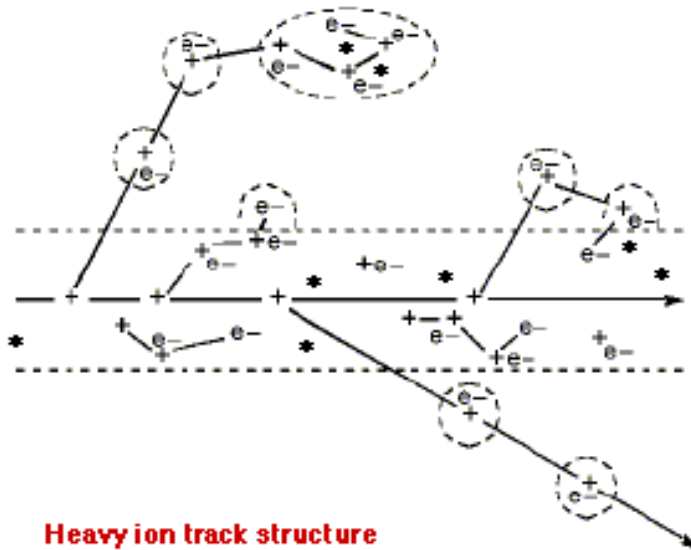
$$\begin{aligned}G(-\text{H}_2\text{O}) &= g(\text{H}_2) + 1/2 g(\text{H}) + 1/2 g(e^-_{\text{aq}}) + \\ &\quad g(\text{H}_2\text{O}_2) + 1/2 g(\text{OH}) \\ \Rightarrow 2 g(\text{H}_2\text{O}_2) + g(\text{OH}) &= g(\text{H}_2) + 1/2 g(\text{H}) + 1/2 g(e^-_{\text{aq}})\end{aligned}$$

The yields are not significantly modified by temperature (0-200°C).



Effect of Linear Energy Transfer (LET)

- The distribution of energy deposits vary: the probability of short tracks increases with LET depending on the placement of the clusters of radicals (spurs).
- The recombination in the heterogeneous zones are much more probable as the LET is elevated because the concentration of free radicals is very high.
- **As a consequence, the yields of radicals decrease as the yield of molecular products increase with LET**



from
J.A. LaVerne's
NDRL Web Site



Yields

LET (keV μm^{-1})*	e^-_{aq}	OH	H	H ₂	H ₂ O ₂	HO ₂
0.2	0.26	0.27	0.055	0.045	0.068	0
61	0.072	0.091	0.042	0.096	1.00	0.005

*Yields ($\mu\text{mol}\cdot\text{J}^{-1}$) in water at pH 7

When the LET increases, reactions having low probability under low LET radiation become feasible: for example, the reaction



is produced in the heterogenous zone.

In summary, the balance of water radiolysis is modified:



Irradiation with high LET radiation produces the appearance of $\text{O}_2^{\cdot-}$ and/or the hydroperoxyl radical $\text{HO}_2\cdot$. In the absence of solutes, dismutation produces oxygen:





Effect of pH

- Experimentally: the yields are constant between pH 3 and 10.
- Nevertheless, there are acid-base equilibria:

Acid-base pairs	pK _a
HO ₂ /O ₂ ⁻	4.8
H/e ⁻ _{aq}	9.6
OH/O ⁻	11.9
H ₂ O ₂ /HO ₂ ⁻	11.6

- **But the equilibria are not always established**



Reactions of e^-_{aq}

- In acidic media: these reactions are in competition



- In summary, $g(e^-_{aq}) \searrow 0$ and $g(H) \nearrow$ for $pH < 3$: and under $pH \sim 2$, $g(e^-_{aq}) = 0$.
 - The more, reaction (1) occurs in the heterogeneous regions: $g(H) \nearrow$
- In basic media:
 - Competitions for e^-_{aq} :
 - $H + O^- \rightarrow e^-_{aq} + H_2O \quad 2.3 \times 10^7 M^{-1} \cdot s^{-1}$
 - $H + H \rightarrow H_2 \text{ etc. ...}$
 - Conclusion : It remains the same in basic media.
 - OH gives birth to its basic form O^- .



Yields

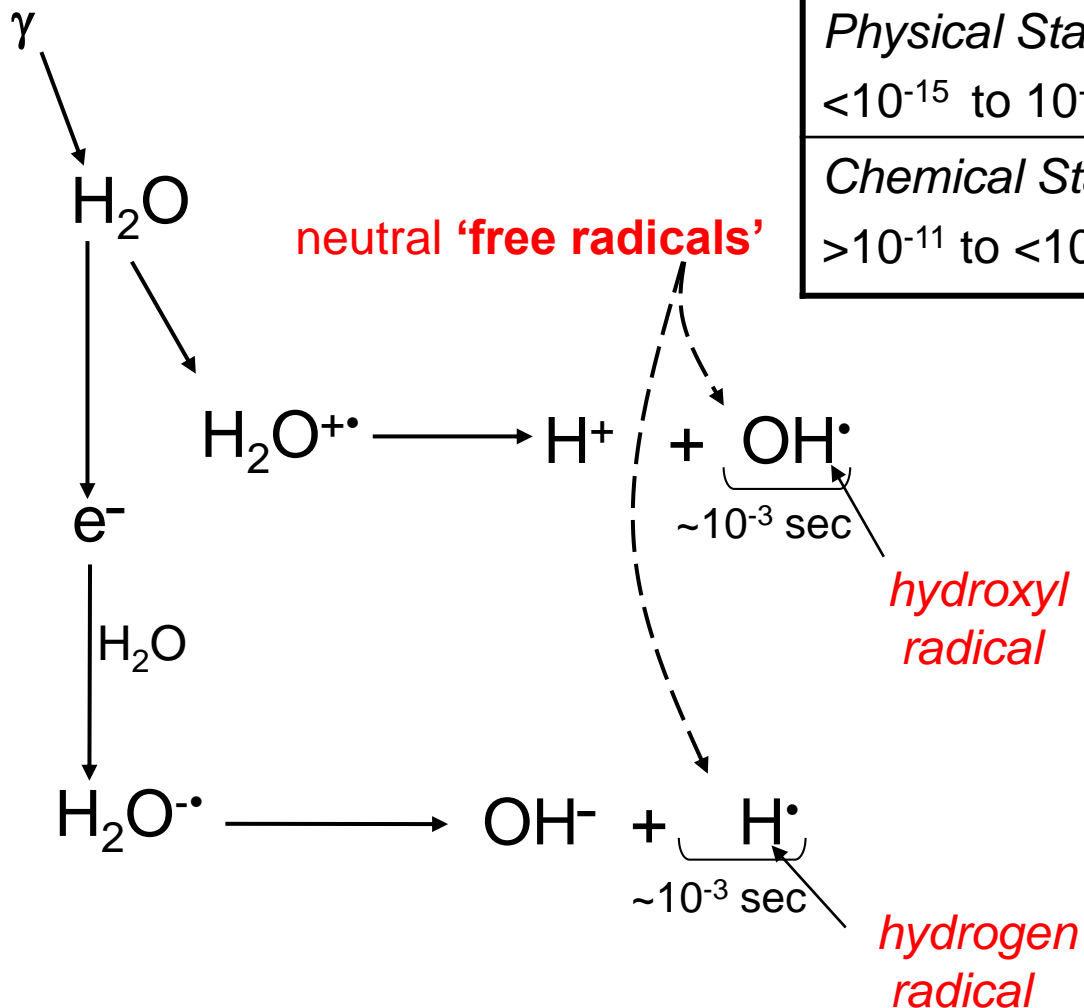
pH	H ₂	H ₂ O ₂	e ⁻ _{aq}	H [•]	OH [•]	O ⁻
0.46	0.041	0.081	0	0.378	0.301	0
3-11	0.047	0.073	0.28	0.062	0.28	0
13	0.041	0.062	0.29	0.062	0.03	0.28

Radiolytic yields ($\mu\text{mol}\cdot\text{J}^{-1}$) for water irradiated with γ rays or with electrons having energies between 1-20 MeV.



Radiation interaction with water

Initial reaction with cells

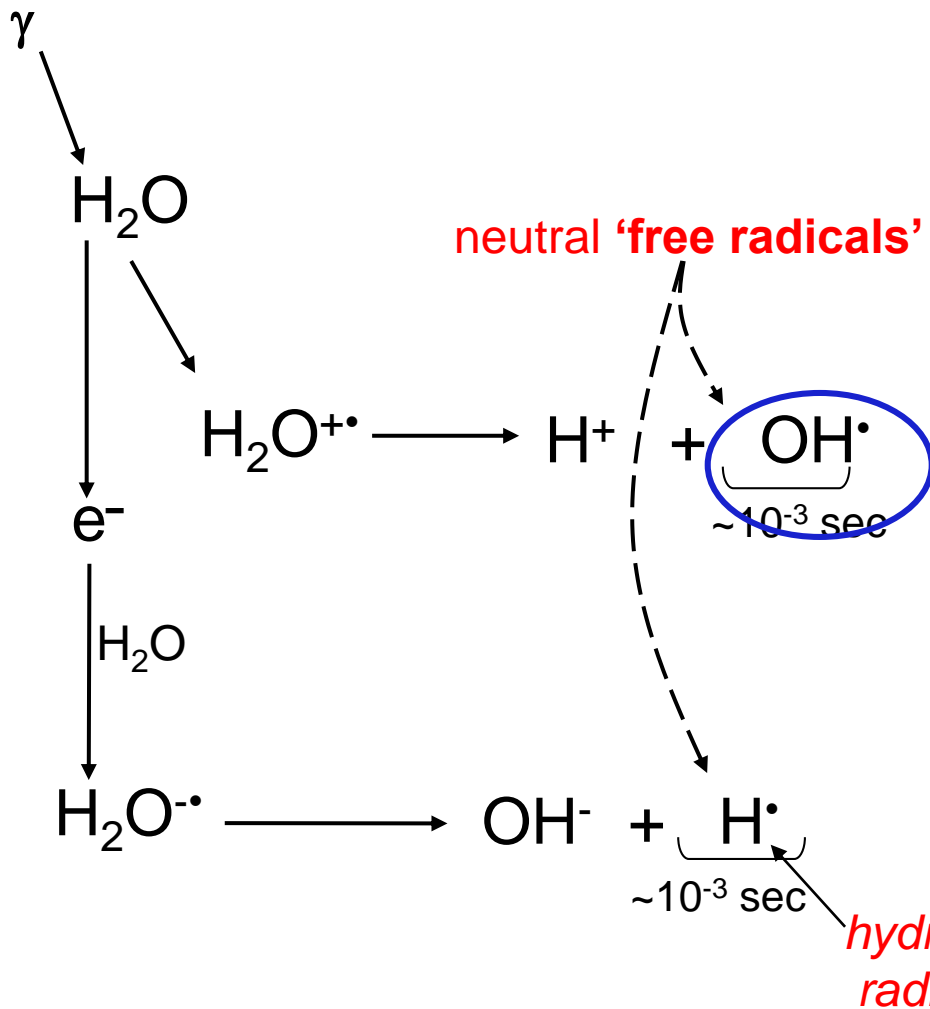


Times	Events
<i>Physical Stage</i> $<10^{-15}$ to 10^{-11} s	Formation of ions and free radicals
<i>Chemical Stage</i> $>10^{-11}$ to $<10^{-6}$ s	Indirect action of ions and free radicals



Radiation interaction with water

Subsequent reaction with cells

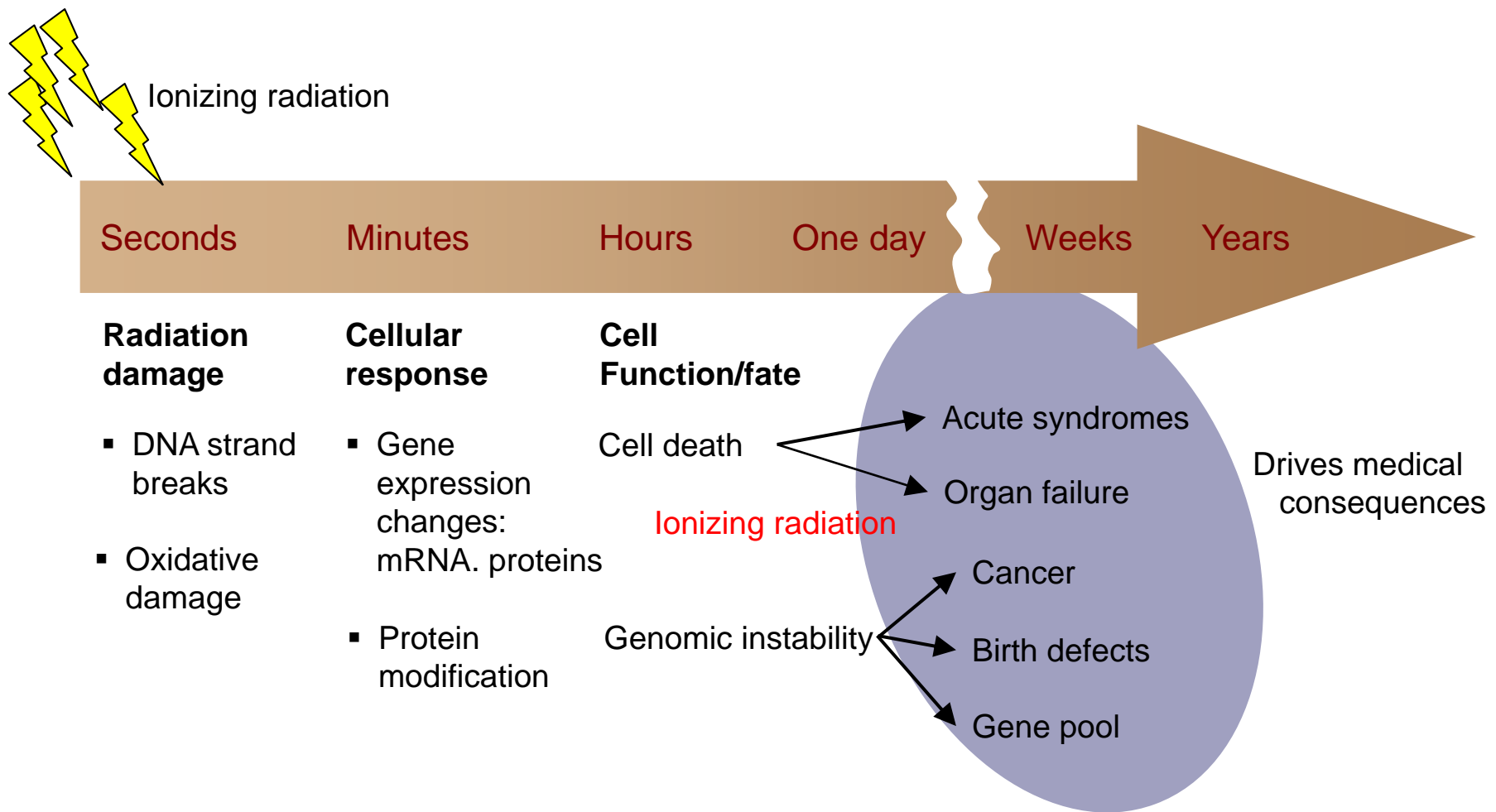


The highly reactive hydroxyl radical is particularly damaging to DNA

The presence of oxygen amplifies the effects of hydroxyl radical

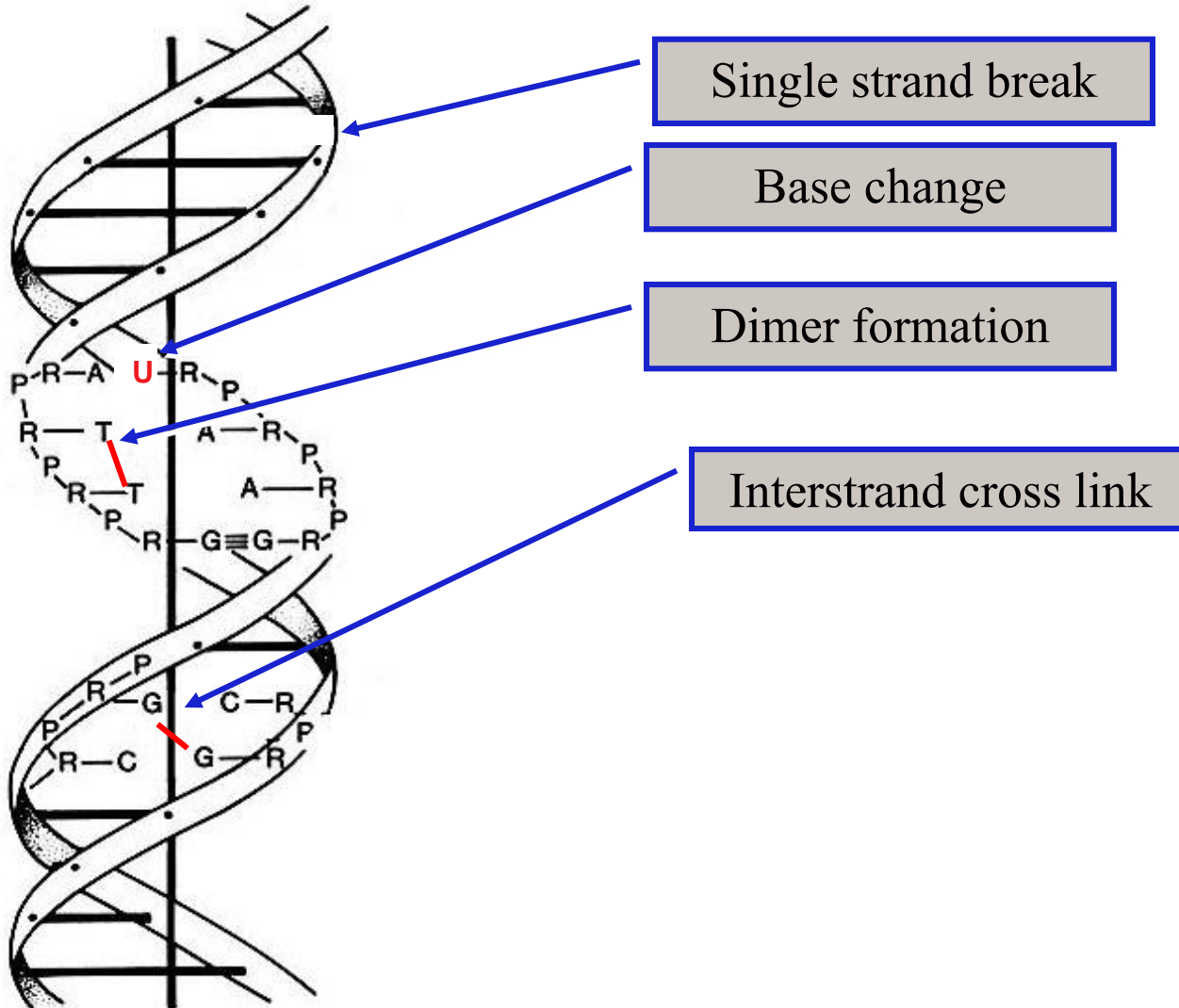


Time Response of Living Systems to Ionizing Radiation



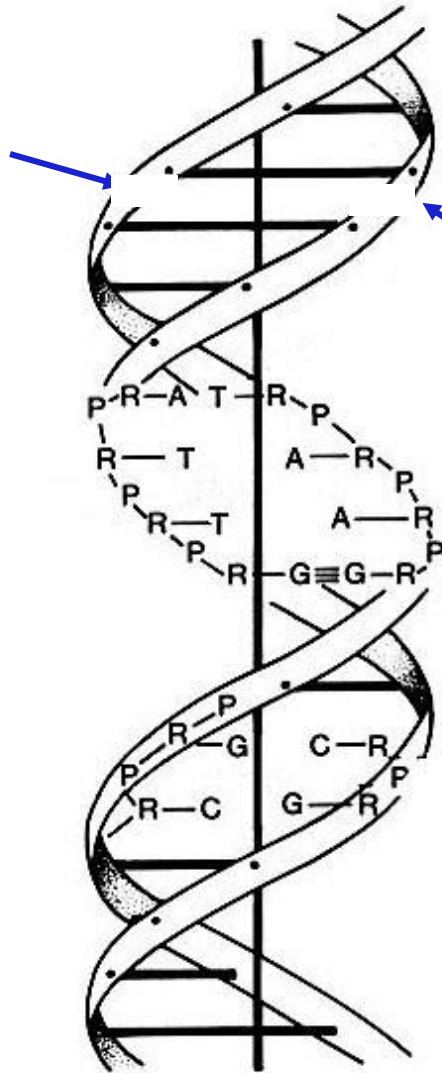


Examples of DNA lesions induced by Radiation





Examples of DNA lesions induced by Radiation

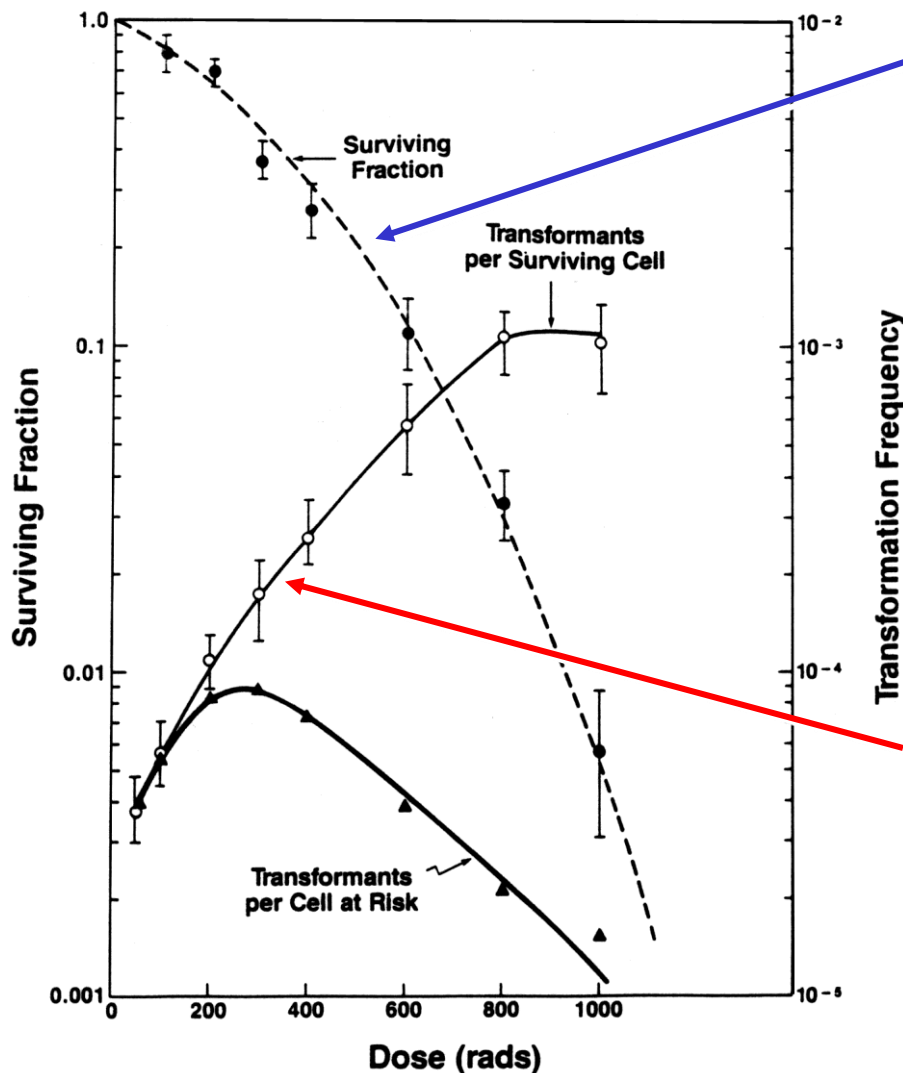


Double strand break

*Most severe
type of damage*



Radiation induced DNA lesions cause cell death & transformation



Decreased cell survival

Surviving cells transformed and become cancer cells



How much Radiation is Received?

(U.S. annual values)

Source Exposure (mrem/yr)

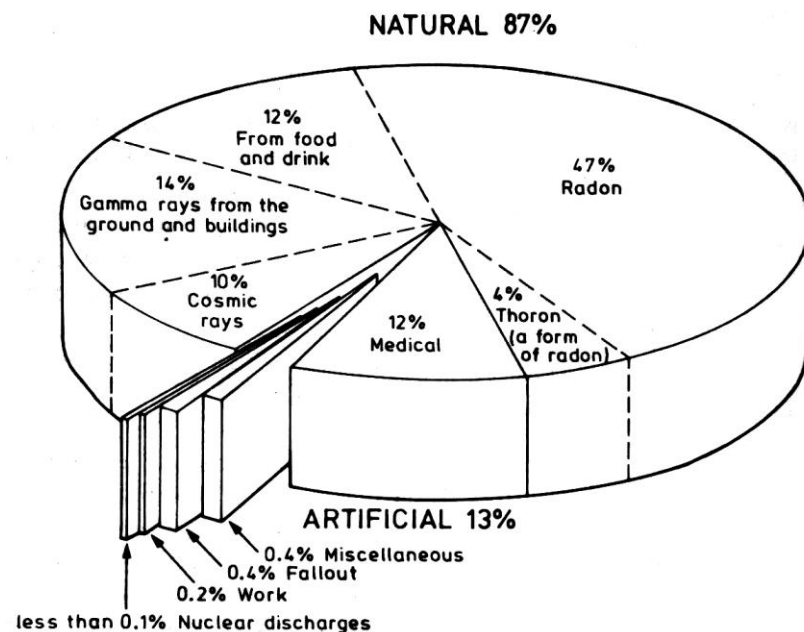
External radiation from:

- cosmic rays 30
- radioactive ores, etc. 30
- radon gas 200
- med X-rays/CAT scan 55

Internal exposure from:

- radioactive material (ingested into body) 45
- smoking ~150

Total: **360 (non-smoker)**
510 (smoker)





Relative hazard of ionizing radiations

The biological hazard varies with type of radiation and if the radiation is internal (ingested, inhaled, or injected) or external.

External	Radiation type	Internal
most damaging	fast neutrons	least damaging
	thermal neutrons	
	x rays and γ rays	
	beta radiation	
least damaging	alpha radiation	most damaging

The diagram includes an orange arrow pointing upwards from 'least damaging' to 'most damaging' on the left, and a red arrow pointing downwards from 'least damaging' to 'most damaging' on the right. The terms 'most damaging' and 'alpha radiation' are circled in the diagram.



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Radiation Chemistry:

Pulse Radiolysis/Flash Photolysis

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$$\text{Energy } E = h\nu = h(c/\lambda)$$

where h = Planck's constant

λ = wavelength

c = speed of light

Longer wavelengths = less energy

Bond	E (kJ·mol ⁻¹)	λ (nm)
O-H	465	257
C-H	415	288
N-H	390	307
C-O	360	332
C-C	348	344
C-Cl	339	353
Br-Br	193	620
O-O	146	820

**Light hitting
earth's surface
 $\lambda = 290\text{-}600\text{nm}$**



Lambert-Beer Law

$$A \equiv \log \frac{I_o(\lambda)}{I(\lambda)} = [\alpha(\lambda) + \varepsilon(\lambda)C]l$$

where:

A = absorbance

I = light intensity (emerging vs. incident)

λ = wavelength

α = absorption coefficient of the medium

ε = absorption coefficient of the compound

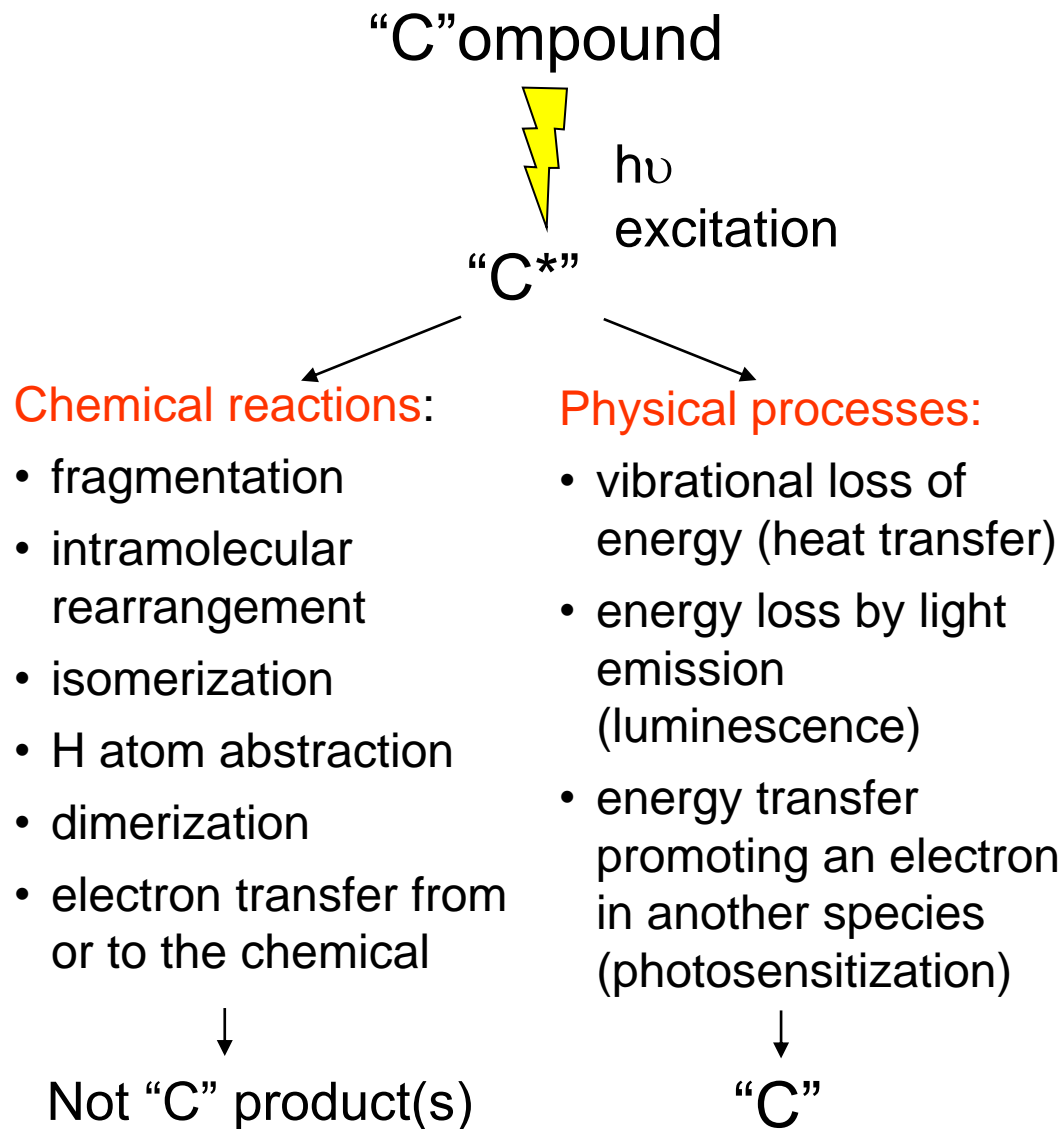
l = path length



Fate of Excited Species

Quantum yield: $\Phi_r(I)$
depends on chemical
structure, solvent, pH,
ionic strength, etc.

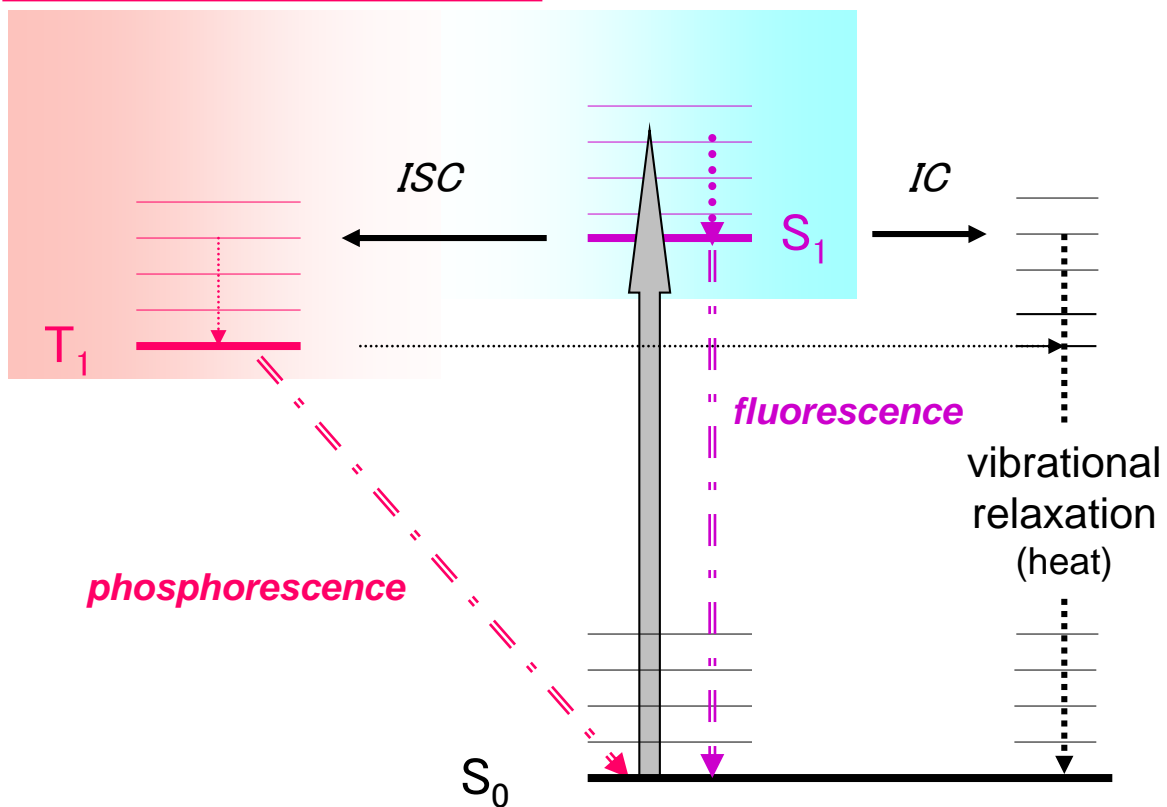
low activation energies:
 $10\text{-}30 \text{ kJ}\cdot\text{mol}^{-1}$ in solution



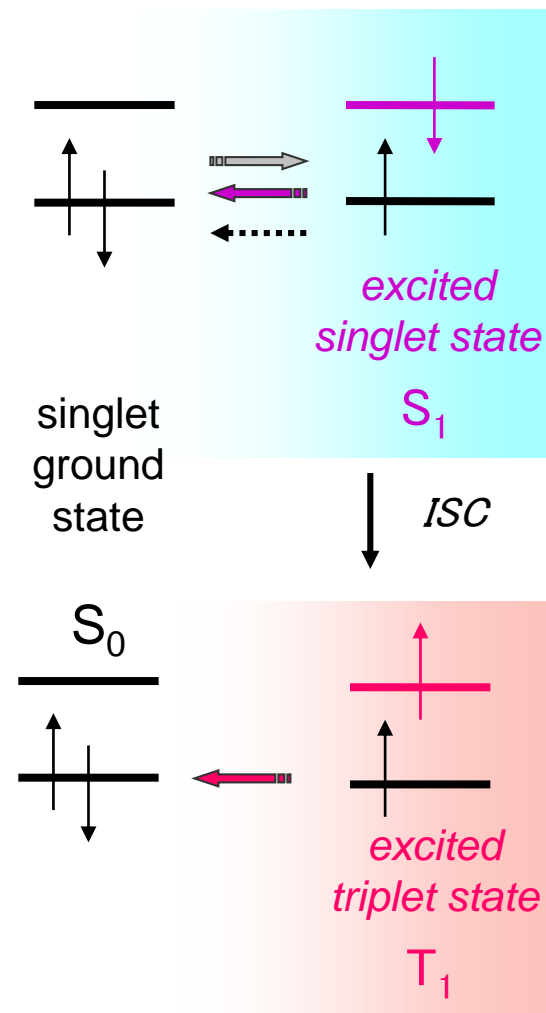


Photochemistry

Jablonski - diagram



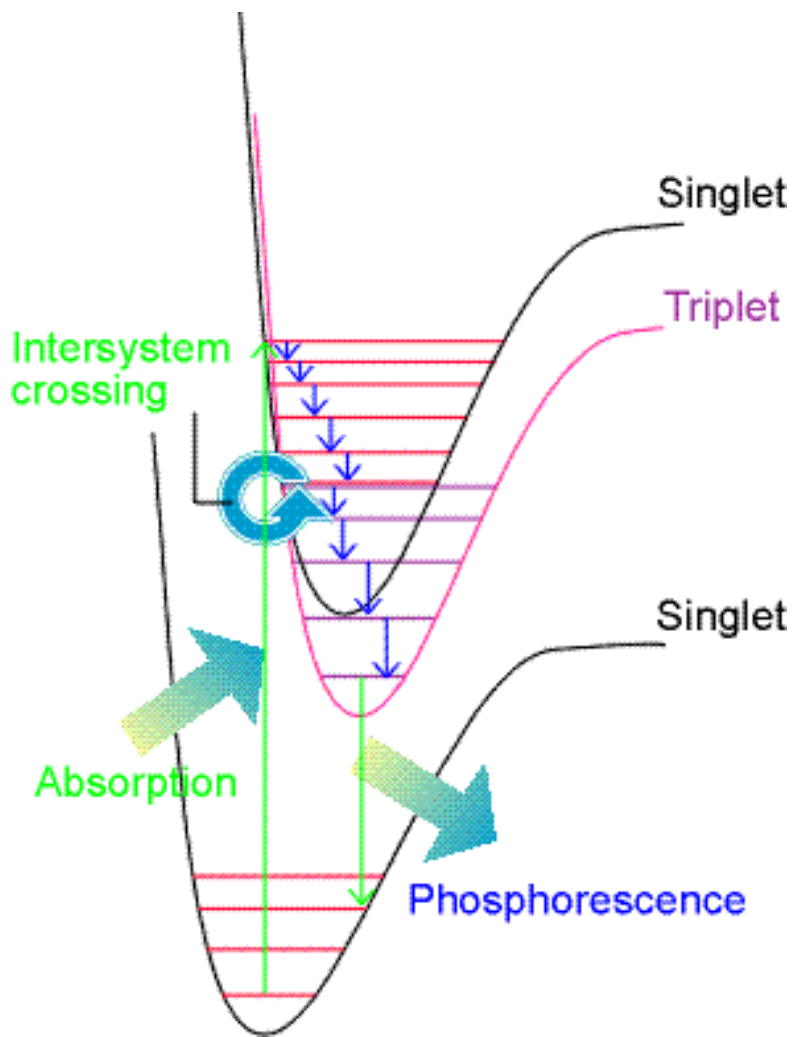
State Picture



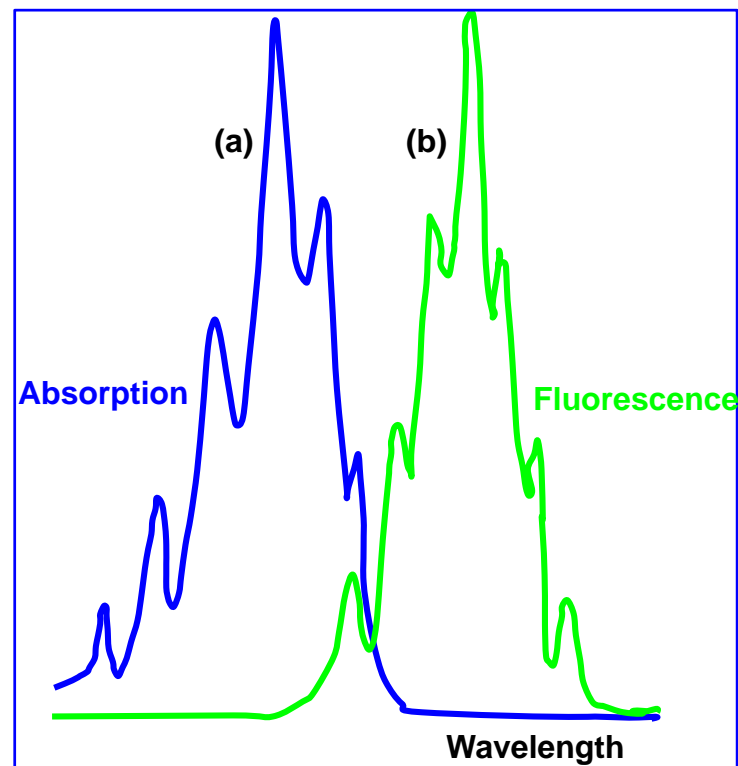
Orbital Picture



Radiationless Transitions Showing Nuclear Contributions



$$E = hc / \lambda$$

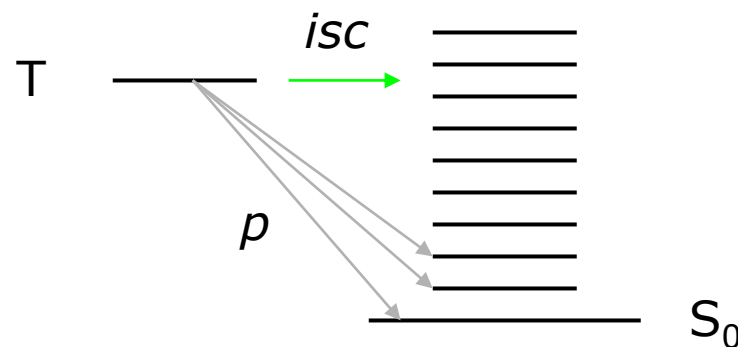




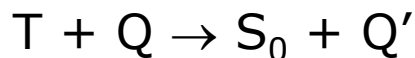
Lifetimes & Quantum Yields

- Triplet states have much longer lifetimes than singlet states
- In solutions, singlets live on the order of nanoseconds or 10's of nanoseconds
- Triplets in solution live on the order of 10' or 100's of microseconds
- Triplets rarely phosphoresce in solution (competitive kinetics)

Intramolecular decay channels



Intermolecular decay channels



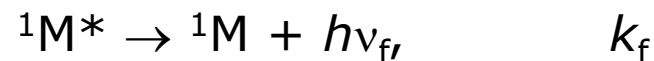
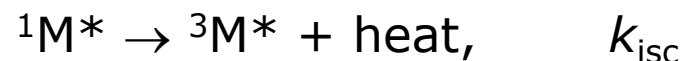
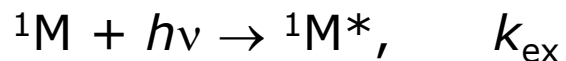
$$\frac{d[T]}{dt} = -k_{isc}[T] - k_p[T] - k_q[Q][T]$$

$$[T] = [T]_0 \exp\left\{-\left(k_{isc} + k_p + k_q[Q]\right)t\right\}$$



Competitive Kinetics – Singlet/Triplet State

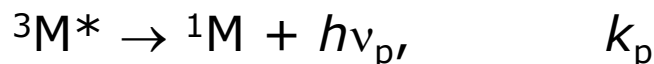
- Singlet State



$$k_{\text{S}} = k_{\text{pc}} + k_{\text{isc}} + k_{\text{ic}} + k_{\text{f}}$$

$$\Phi_{\text{T}} = k_{\text{isc}}/k_{\text{S}}$$

- Triplet State

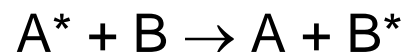


$$k_{\text{T}} = k'_{\text{pc}} + k'_{\text{isc}} + k_{\text{p}}$$

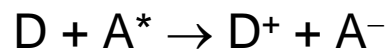
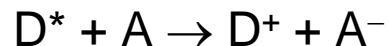


Intermolecular Excited-State Reactions

- Energy Transfer



- Electron Transfer



- Atom (Hydrogen) Abstractions

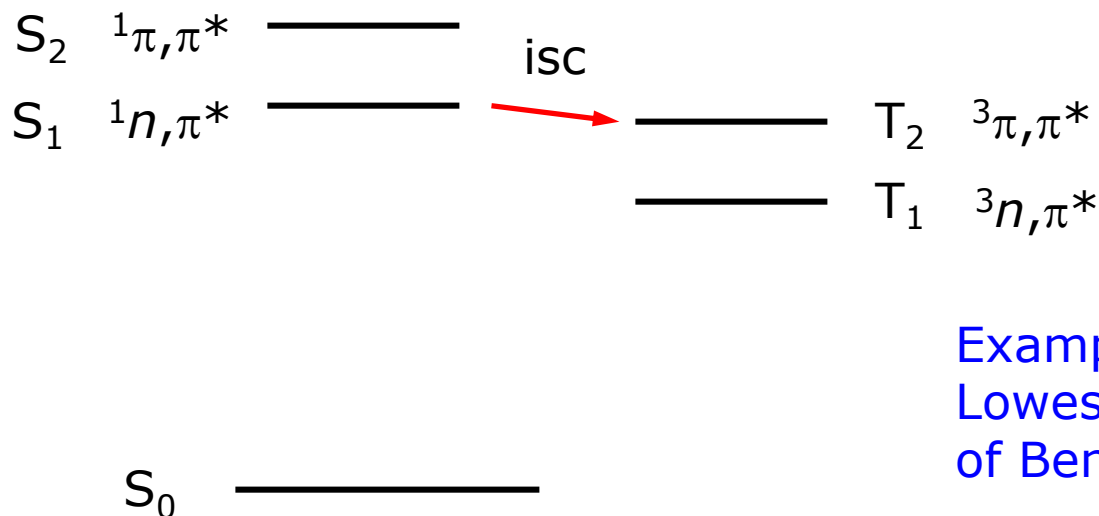
Note:
Need to have excited states that live long enough to find quenching partner by diffusion



Important Types of Organic Excited States

Relevant for chemical reactions are the nature of the excited state of the molecules present in the medium submitted to irradiation. Two type of excited are relevant for organic molecules:

- π, π^* states, particularly in aromatics and polyenes
- n, π^* states, particular in carbonyls



Example:
Lowest electronic states
of Benzophenone



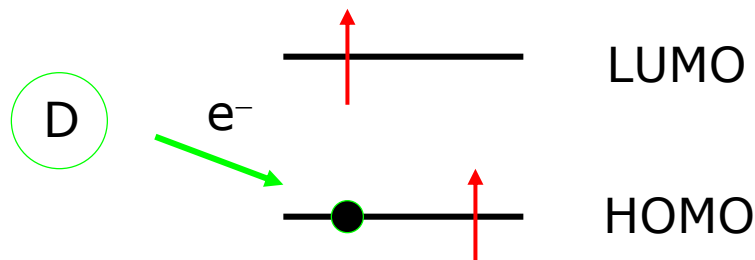
Weak Spin Interactions

- Triplet states, spin interactions are weak, so excited triplet states can live for some time
- But they have lower energy than their corresponding singlet states with the same orbital configurations
- By Pauli Exclusion principle - no two electrons in the same system can have the same quantum numbers
- By Pauli Exclusion principle like spins avoid each other – correlation hole around each electron
- **Photochemistry of Triplet States**
 - ${}^3n,\pi^*$ states are particularly good in H-abstractions: they act like free radicals
 - Molecules in excited states are generally more reactive in electron-transfer reactions than are their ground states

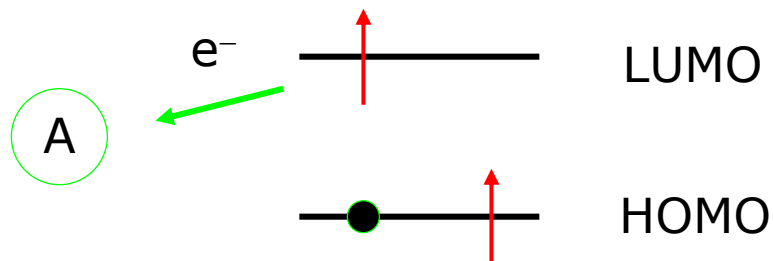


Excited-State Electron Transfer

- Because of the “hole” in the HOMO of the ground state, the excited states have a low-lying orbital available for **accepting** electrons

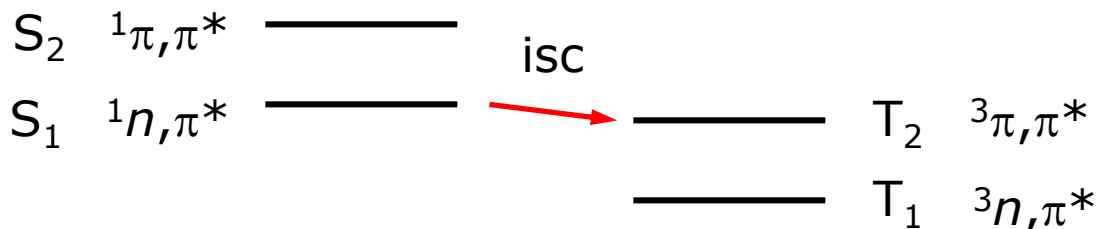


- Because of the electron in the highly excited orbital, e.g. the LUMO of the ground state, the excited state is a good **donor** for elect. transfer





Why Triplet Quantum Yield is high in Benzophenone?



Lowest electronic states
of Benzophenone



- (1) $1n, \pi^*$ states have small k_{rad} because of small orbital overlap
- (2) k_{isc} is large because of low-lying $3\pi, \pi^*$ and El-Sayed's Rule



El-Sayed's Rule

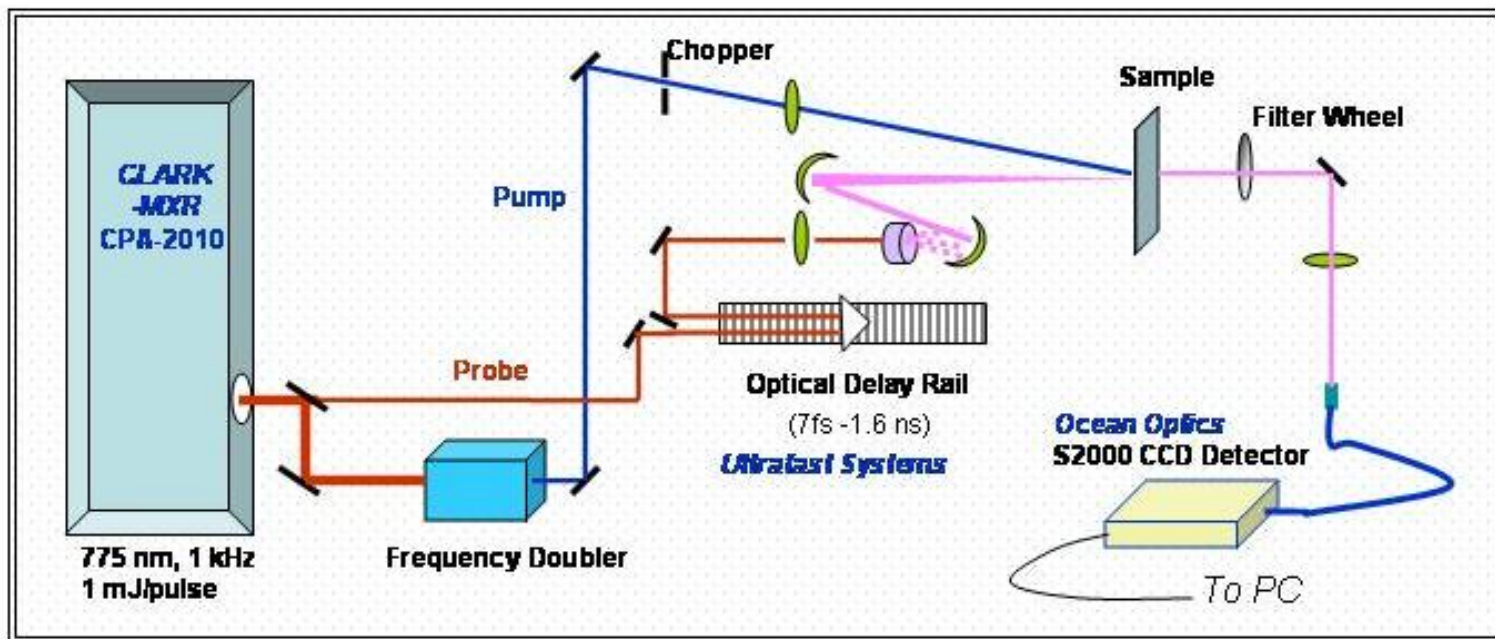
- Selection Rule for Intersystem Crossing
- Transitions between a singlet state and a triplet state of the **same orbital configurations** are slower than that between states having different orbital configurations.
- Examples, ISC transition $^1n,\pi^* \rightarrow ^3\pi,\pi^*$ is much faster than $^1\pi,\pi^* \rightarrow ^3\pi,\pi^*$

Characteristics of Radiationless Transitions

- Kasha's Rule
- El-Sayed's Rule
- Deuterium Effect
- Wavelength Independence of Luminescence
- Energy Gap Law
- Competitive First-Order Kinetics



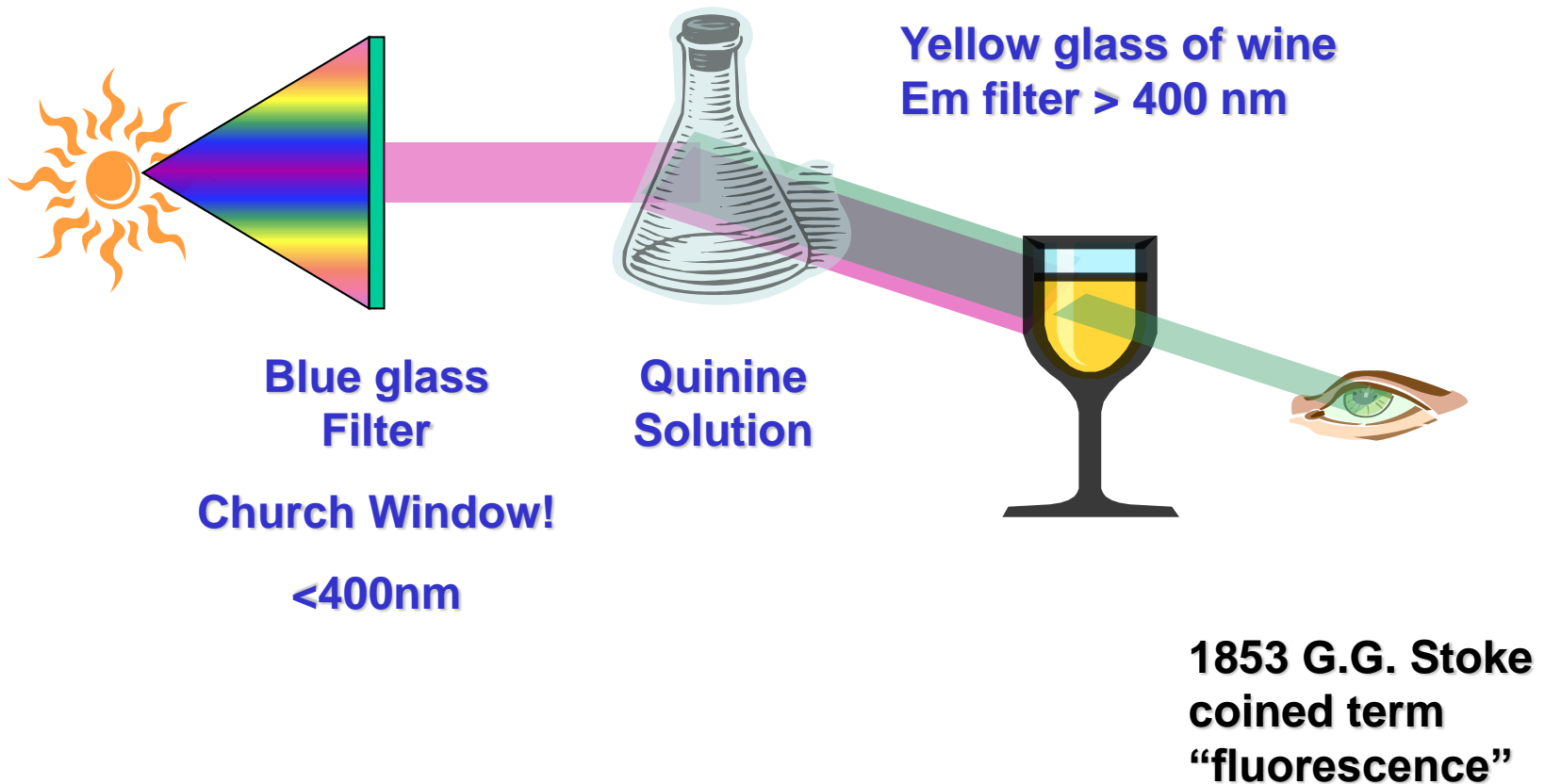
Pump-Probe Femtosecond Laser





Fluorescence: a Type of Light Emission

- First observed from quinine by Sir J. F. W. Herschel in 1845

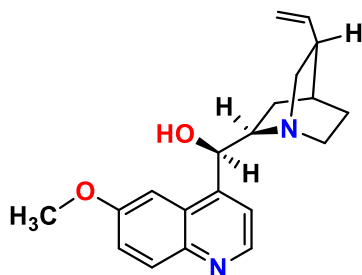




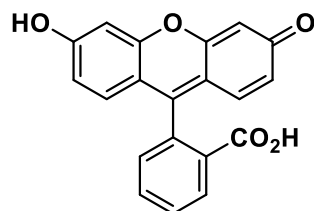
Common Fluorophores

Typically, Aromatic molecules

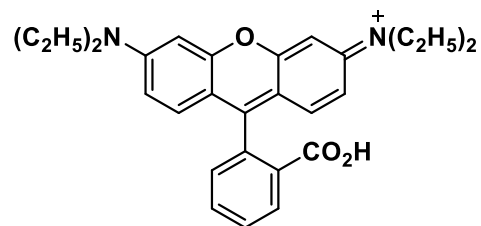
- Quinine, ex 350/em 450
- Fluorescein, ex 485/520
- Rhodamine B, ex 350/em 450
- Acridine Orange, ex 330/em 500
- POPOP, ex 360/em 420
- Coumarin, ex 350/em 450
- Acridine Orange, ex 330/em 500



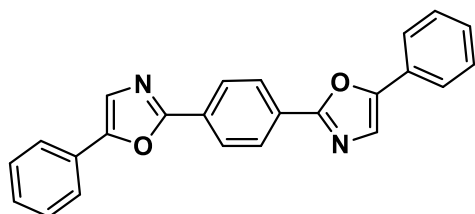
Quinine



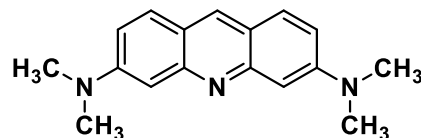
Fluorescein



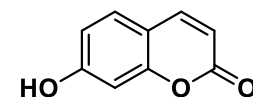
Rhodamine B



POPOP



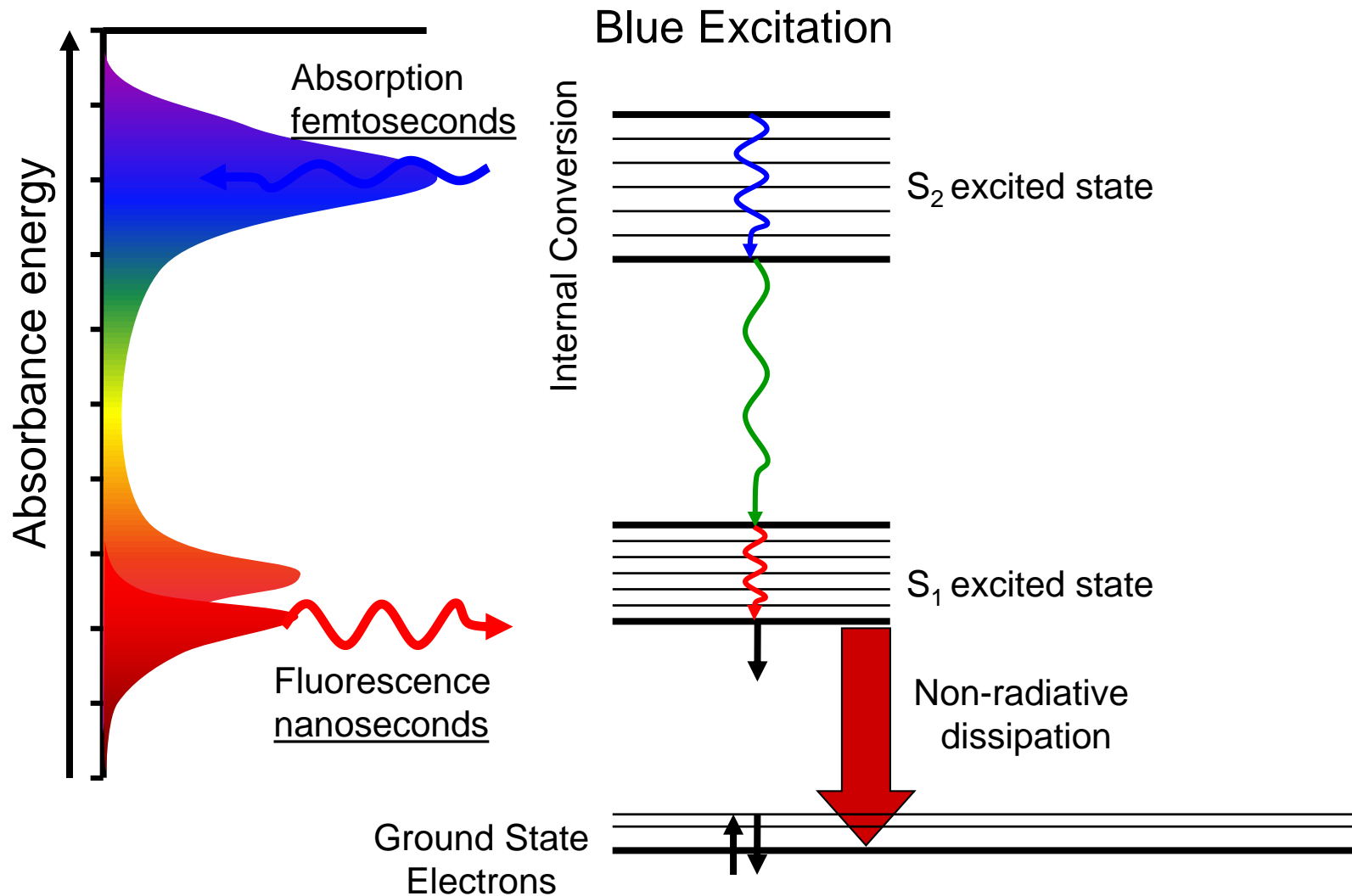
Acridine Orange



7-hydroxy coumarin
(Umbelliferone)



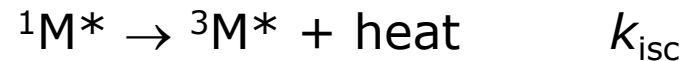
Fluorescence



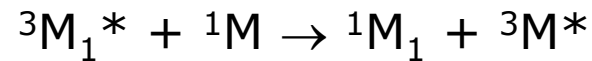


Creation of Triplets

(1) Intramolecular radiationless transitions



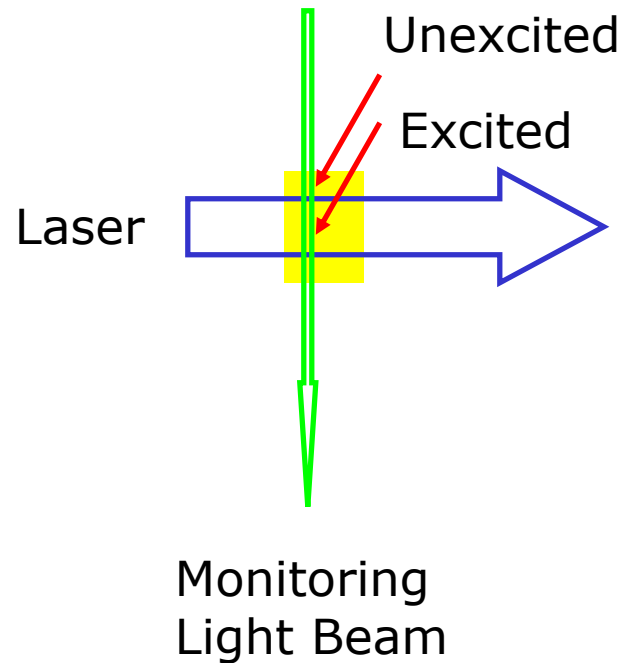
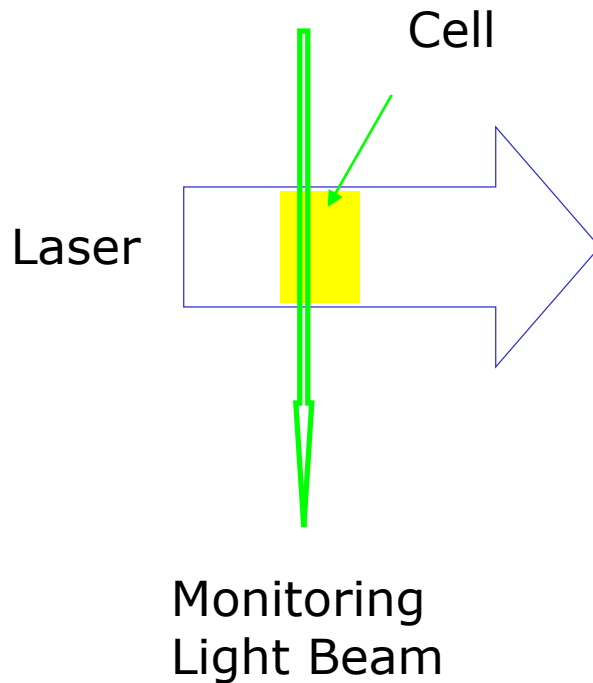
(2) Intermolecular energy transfer



(3) Transfer from solvent triplets in radiolysis of benzene.



Spatial Overlap of Laser and Monitoring Beam



Proper alignment:
Sample is excited along the
entire optical path length

Improper alignment:
Sample is not excited along the
entire optical path length



Relative Actinometry

- This is a two cell experiment.
- In one cell there is a compound of unknown $\varepsilon_T^*(\lambda_1)$, but with a known intersystem crossing yield $\Phi_T(T)$
- In the other cell there is a compound of known $\varepsilon_R^*(\lambda_2)$, and also with a known intersystem crossing yield of $\Phi_T(R)$
- If the optical densities at the respective wavelengths are the same, then the number of photons absorbed by each cell is exactly the same and

$$\varepsilon_T^*(\lambda_1) = \varepsilon_R^*(\lambda_2) \cdot \frac{\Delta OD_T \cdot \Phi_T(R)}{\Delta OD_R \cdot \Phi_T(T)}$$

- This is a consequence of Beer's Law
- The monitor beam must also be fixed relative to the cell and the laser



Relative Actinometry and Φ_{isc}

- Rearranging formula from one of the preceding slides

$$Q_T(T) = \Phi_T(R) \cdot \frac{\Delta OD_T(\lambda_1) \varepsilon_R^*(\lambda_2)}{\Delta OD_R(\lambda_2) \varepsilon_T^*(\lambda_1)}$$

- This is one of the most popular ways to measure triplet yields
- Need two extinction coefficients and the reference triplet yield



Detection Methods of Radical with Radiation Sources

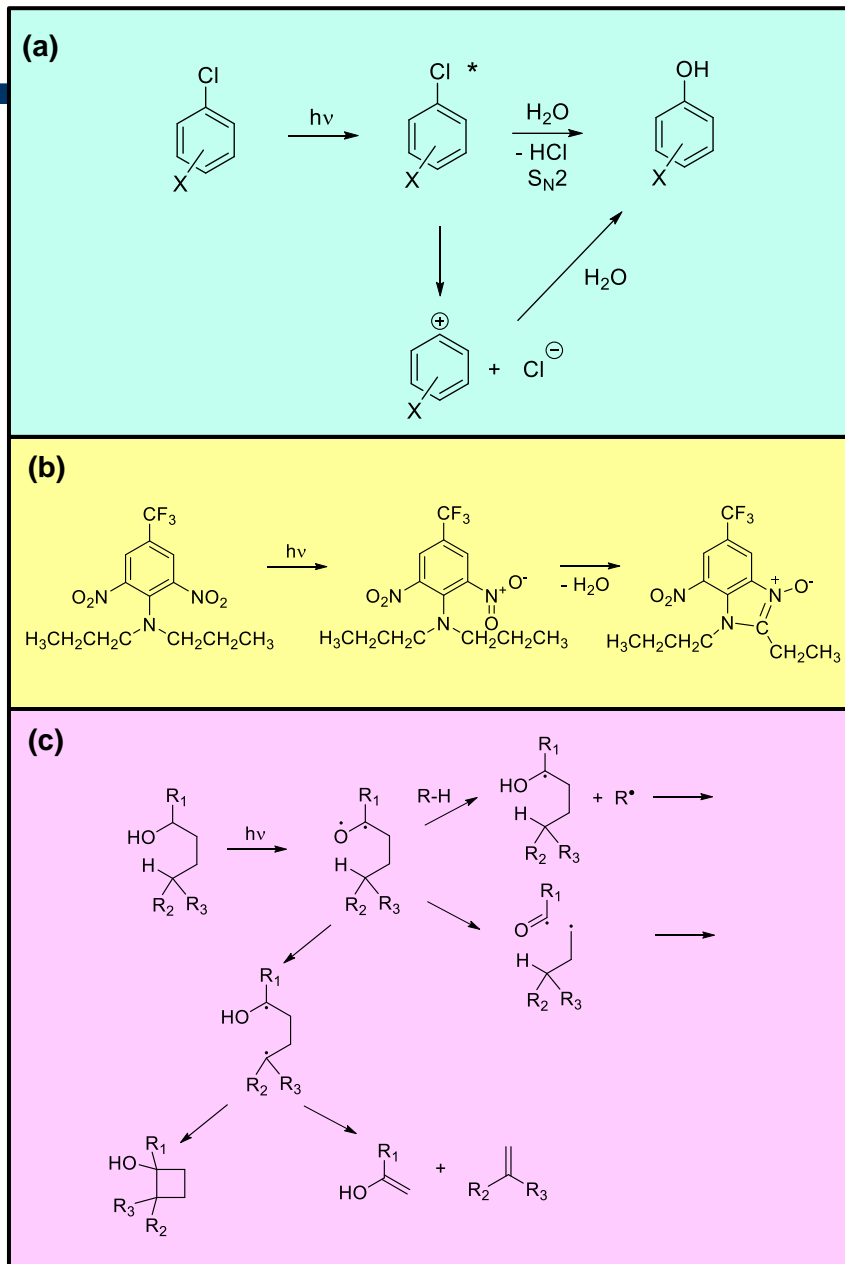
- Absorption spectra (free radical and excited states have generally broad and featureless absorption spectra)
- Conductivity (a non-specie specific method and additive with respect to ionic content of the cell)
- Resonance Raman
- Electron-Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR)



Chemical Processes

Examples:

- a) Aromatic substitution
- b) Intramolecular substitution
- c) Fragmentation, intramolecular hydrogen-abstraction, cyclization





Reaction Rates for Direct Photolysis in Water:

$$k_a^0(\lambda) = 2.3 \cdot W(\lambda) D^0(\lambda) \varepsilon(\lambda)$$

Light absorption rate (\neq rate constant!)

Where:

W = incident light intensity

D = distribution function describing average path length of light vs. depth of concern (z_{mix})

ε = absorption coefficient for compound of interest

all at a specific wavelength (λ)



Rate Constant from Light Absorption Rate

The specific light absorption rate must be adjusted to give a rate constant. First account for light scattering in the water:

$$k_a = \sum k_a^0(\lambda)S(\lambda) \quad S = \text{light-screening factor}$$

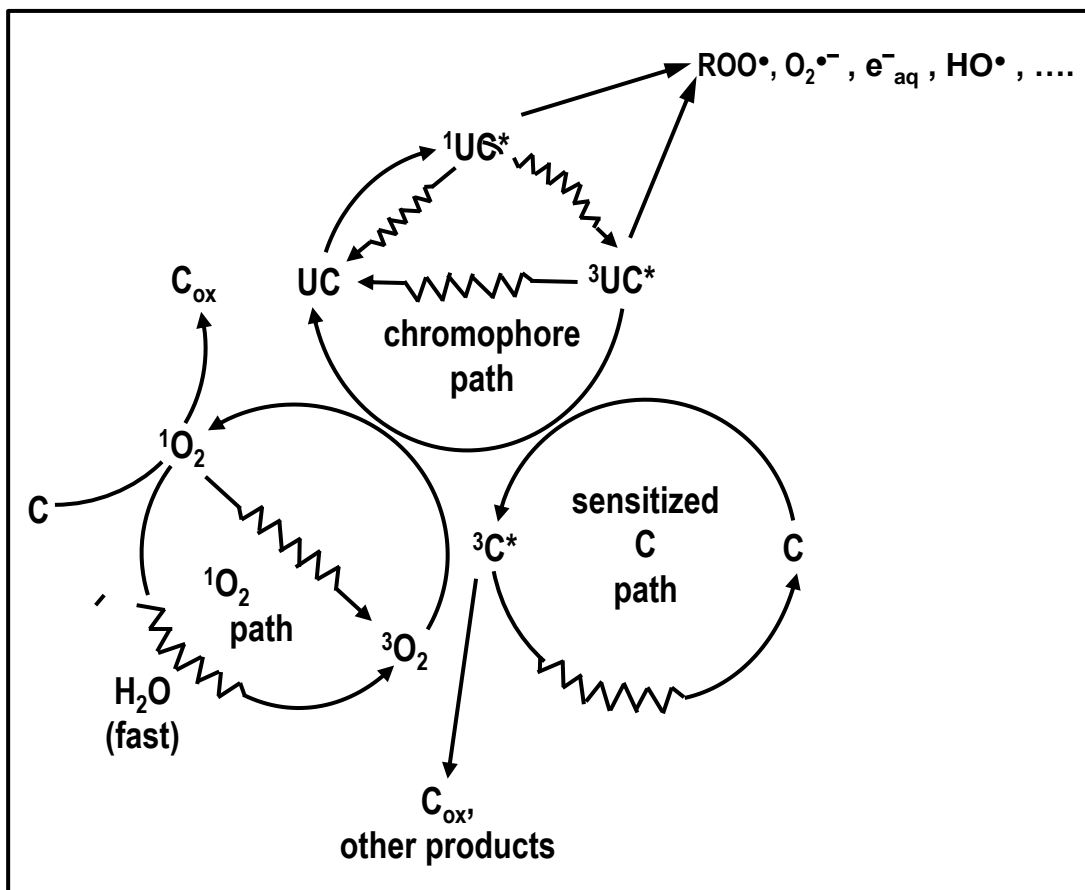
Then for quantum yield (Φ):

$$-\left(\frac{dC}{dt}\right)_{p,\lambda} = \Phi_r k_a(\lambda)C$$

First order process for dilute solutions.



Indirect Photolysis



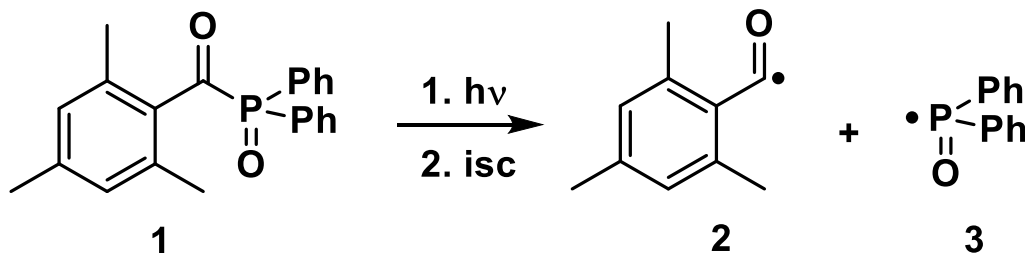
Important reactants
(electrophiles):

- ✓ Singlet oxygen (¹O₂)
- ✓ Peroxy Radicals (ROO[•])
- ✓ Hydroxyl radicals

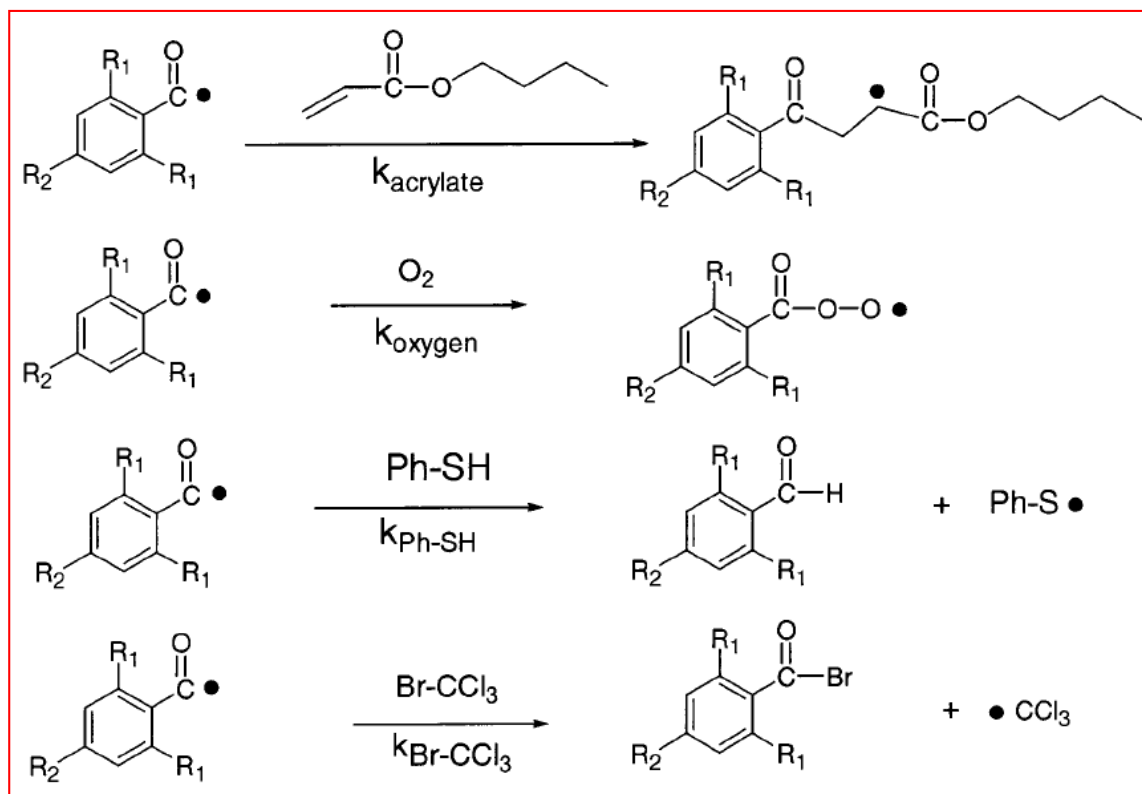
Figure 13.12 – Pathways for indirect photolysis of organic chemical (C). UC refers to unknown chromophores. Wavy arrows symbolize radiationless transition from Zafiriou et al. 1984)



Addition and Atom Abstraction Reactions Studied by Flash Photolysis



Investigated reactions by laser flash photolysis with different transient detection methods (IR, UV, EPR,)





Transient IR Absorption Kinetics in the Photolysis of Irgacure 819

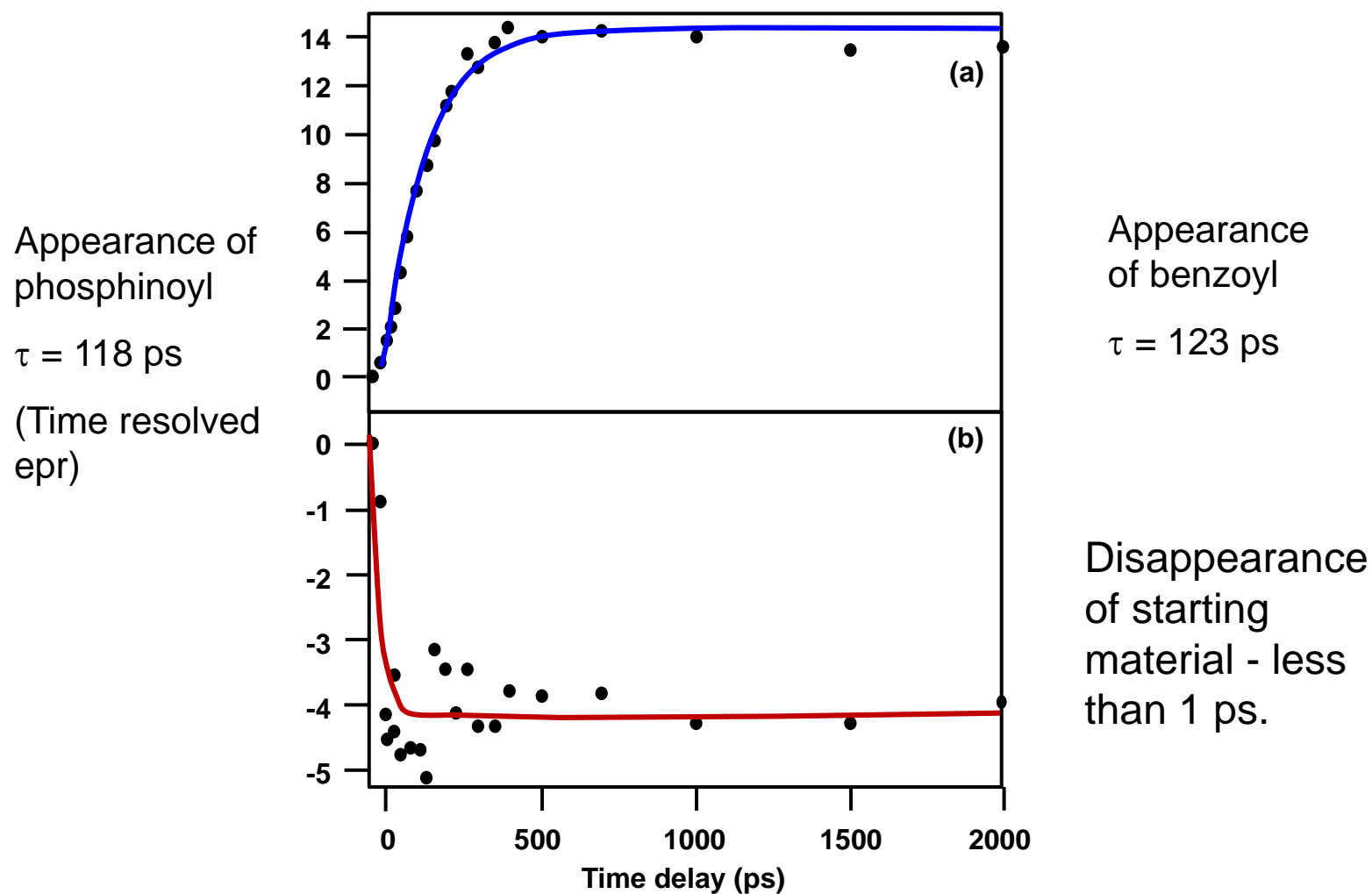
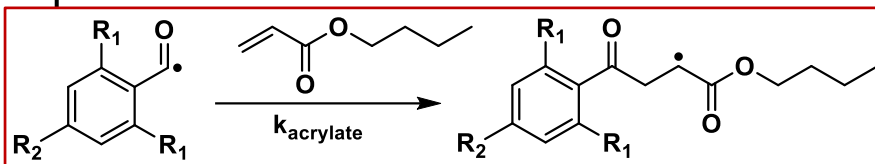
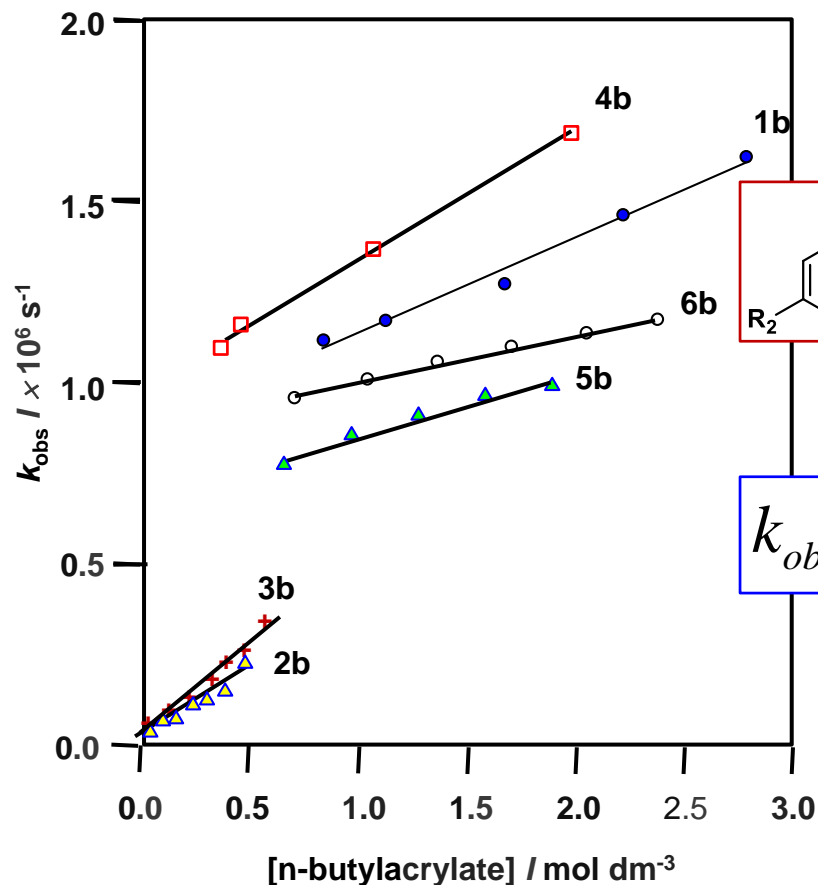


Figure 5. Transient IR absorption kinetics observed following picosecond excitation (400 nm, 1 ps) of **5a** in argon saturated acetonitrile solution. monitored at (a) 1800 cm^{-1} and (b) 1670 cm^{-1} .

Pseudo first order rate constants for the disappearance of benzoyl radicals from Irgacures with butyl acrylate



$$k_{obs} = k_0 + k_{acrylate} [\text{acrylate}]$$

Figure 6. Pseudo-first-order decay rate constants (k_{obs}) of the benzoyl radical **1b-6b** versus n -butylacrylate concentration, measured following laser flash photolysis (355 nm, 8 ns) of argon-saturated acetonitrile solutions of **1a-6a** in the presence of different n -butylacrylate concentrations. The rate constants for **2b** and **3b** were determined at Columbia University, and those for **1b** and **4b-6b**, at Nottingham.³⁴

Turro et al. *Macromolecules*, **1998** 31 7992



Transient Radicals Detection by IR and UV

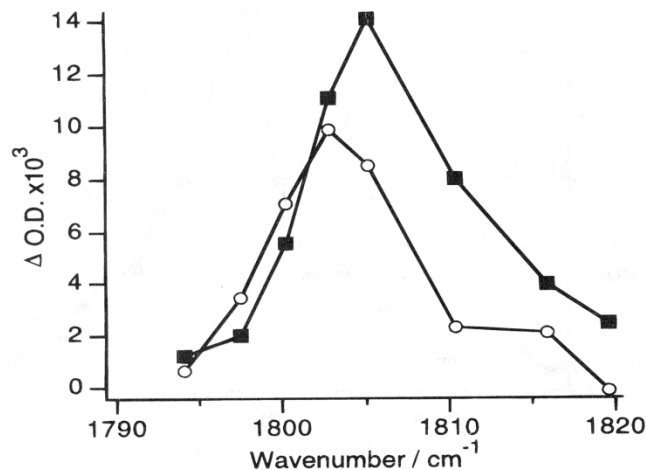


Figure 3. Time-resolved IR spectra, recorded (■) 1 μ s and (○) 40 μ s following the laser pulse, from laser flash photolysis (355 nm excitation) of a 0.02 M solution of **1** in deoxygenated *n*-heptane containing 0.005 M bromotrichloromethane.

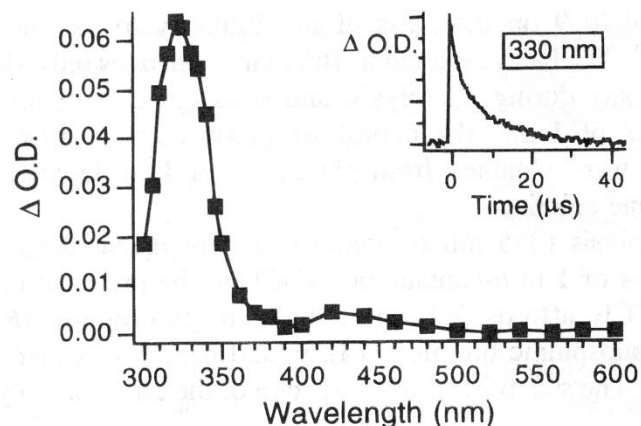


Figure 4. Transient UV absorption spectrum recorded 0.1–1.0 μ s following laser flash photolysis (355 nm excitation) of a 0.001 M solution of **1** in deoxygenated hexane. The inset shows a transient decay measured at a monitoring wavelength of 330 nm.

A major reason to use IR spectroscopy for these experiments is because the extinction coefficients of benzoyl radicals are low in the UV spectra. In this case, in the absence of quenchers, decay rates are about the same measured by either technique

Pseudo-first-order Decay Rate of Radical $(\text{Ph})_2(\text{O})\text{P}^\bullet$ versus Quencher Concentration

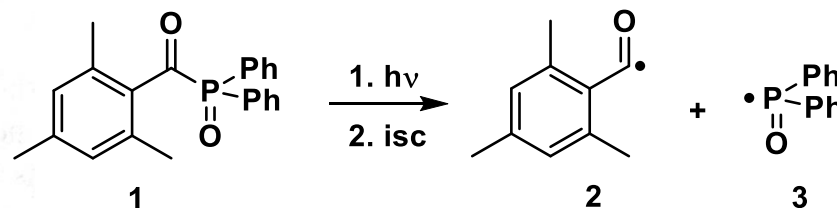
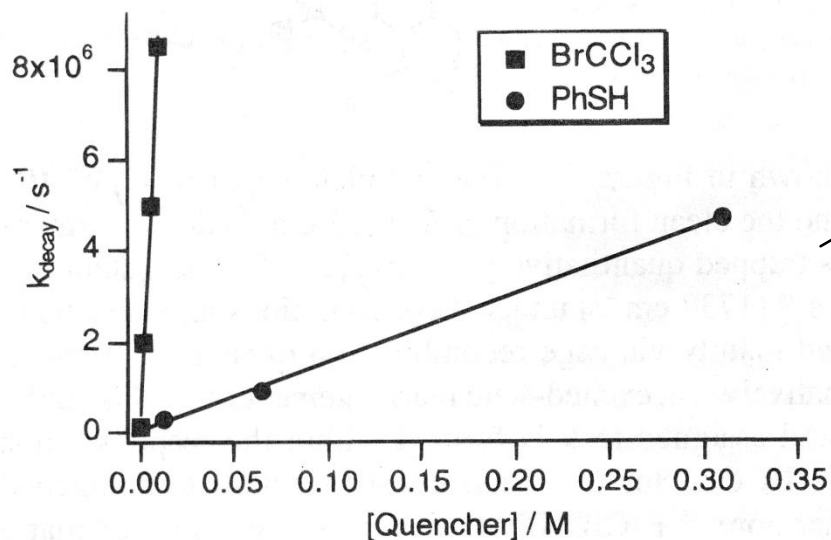


Table 1. Rate Constants for Reaction of 2,4,6-Trimethylbenzoyl (**2**) and Diphenylphosphonyl (**3**) Radicals with Bromotrichloromethane (BrCCl_3), Thiophenol (PhSH), and Benzhydrol (Ph_2CHOH) in Alkane Solution at $23 \pm 2^\circ\text{C}^a$

reagent	k_q (10^{-8} Ms)	
	2	3
BrCCl_3	1.7	8.3
PhSH	0.13	0.15
Ph_2CHOH	$<0.005^b$	$<0.005^b$

^a Errors are ca. $\pm 10\%$. ^b Dichloromethane solution.



Rate Constants of Radicals from Irgacures

Frequencies (ν_{CO}) and Bimolecular Rate Constants for Reactions of Benzoyl Radicals (**1b-6b**) and Their Counterradicals (**1c-6c**)

radical	ν_{CO} (cm ⁻¹)	$k_{acrylate}$ (M ⁻¹ s ⁻¹)	k_{PhSH} (M ⁻¹ s ⁻¹)	k_{BrCCl_3} (M ⁻¹ s ⁻¹)	k_{O_2} (M ⁻¹ s ⁻¹)
1b	1818	2.7×10^5	1.8×10^7	1.8×10^8	
1c		1.3×10^7 ^b			5.4×10^9 ^b
2b	1805	3.5×10^5			
2c		1.3×10^7 ^b			6.6×10^9 ^b
3b	1805	5.5×10^5			
3c		6.1×10^6 ^b			4.3×10^9 ^b
4b	1789	3.6×10^5	5.4×10^7	5.8×10^8	
4c		6.1×10^6 ^b			4.3×10^9 ^b
5b	1800	1.8×10^5	3.9×10^6		3.0×10^9
5c		2.8×10^7 ^c	4.2×10^6 ^c	6.9×10^8 ^c	4.2×10^9 ^c
6b	1803	1.3×10^5	7.1×10^6	1.1×10^8	3.3×10^9
6c		1.5×10^7 ^c		2.4×10^8 ^c	2.6×10^9 ^c