Department CMIC
Lecture 13 – FR13

POLITECNICO DI MILANO

Free-Radicals: Chemistry and Biology

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
http://iscamap.chem.polimi.it/citterio/education/free-radical-chemistry/

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Radicals in Photochemistry

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

Introduction

1) Photochemistry

The branch of chemistry which deals with the study of chemical reaction initiated by light.

2) Energy of photon

The photon is quantized energy: light quantum

$$\varepsilon = h\gamma = h\frac{c}{\lambda} = hc\nu$$

Where *h* is the Plank constant, *c* the velocity of light in vacuum, λ the wave-length of the light, ν the wave number, and ε is the energy.

Electromagnetic Spectrum

3×10^{5} m; 3.98×10^{-7} J·mol^{-1}

3×10^{1} m; 3.98×10^{-3} J·mol^{-1}

6×10^{-4} m; 1.99×10^{2} J·mol^{-1}

3×10^{-5} m; 3.99×10^{3} J·mol^{-1}

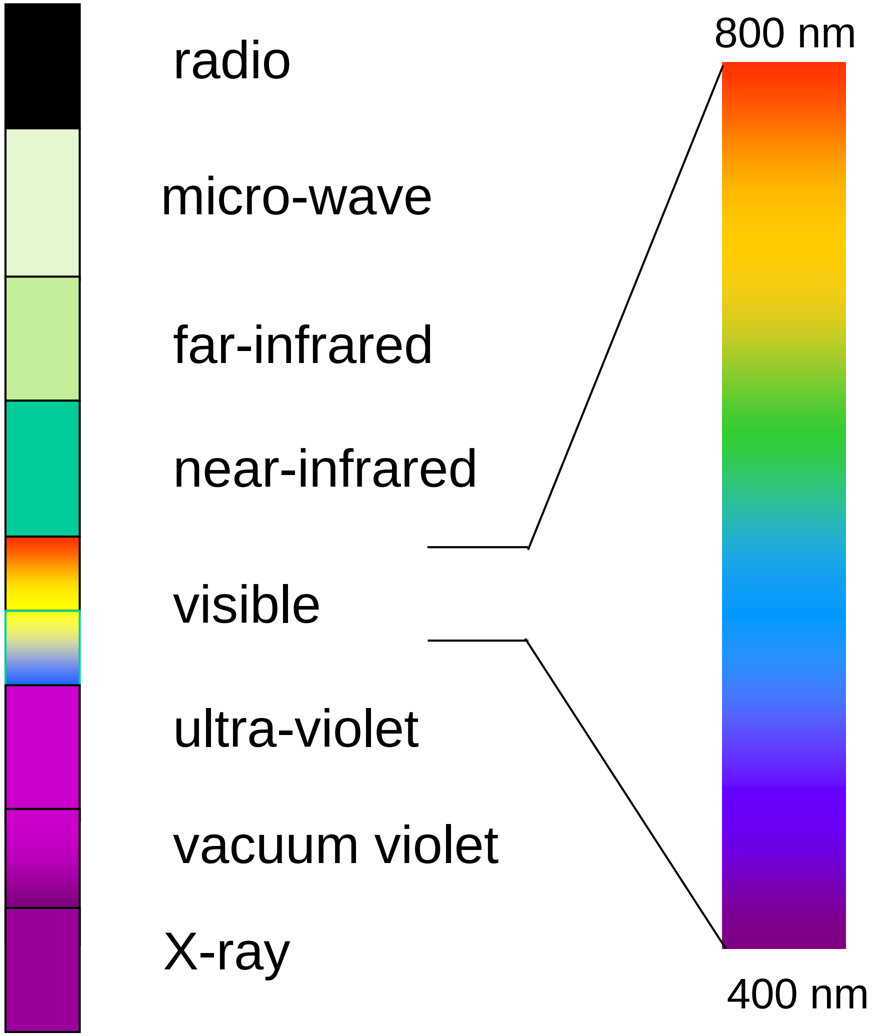
800 nm; 1.50×10^{5} J·mol^{-1}

400 nm; 2.99×10^{5} J·mol^{-1}

150 nm; 7.76×10^{5} J·mol^{-1}

5 nm; 2.39×10^{7} J·mol^{-1}

5 pm; 2.39×10^{10} J·mol^{-1}



radio

micro-wave

far-infrared

near-infrared

visible

ultra-violet

vacuum violet

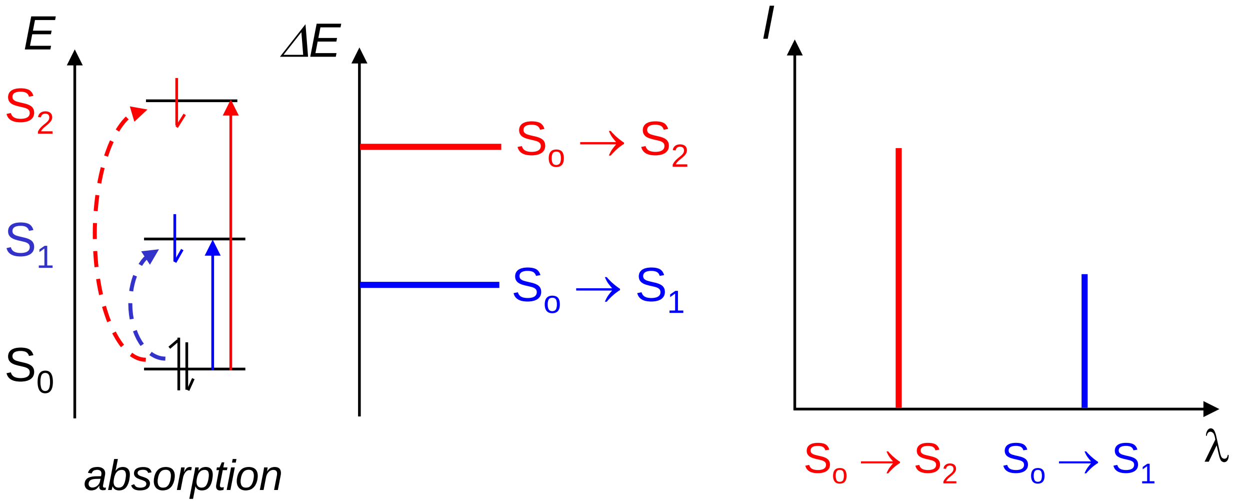
X-ray

800 nm

400 nm

Line Absorption and Emission Spectra of Atoms

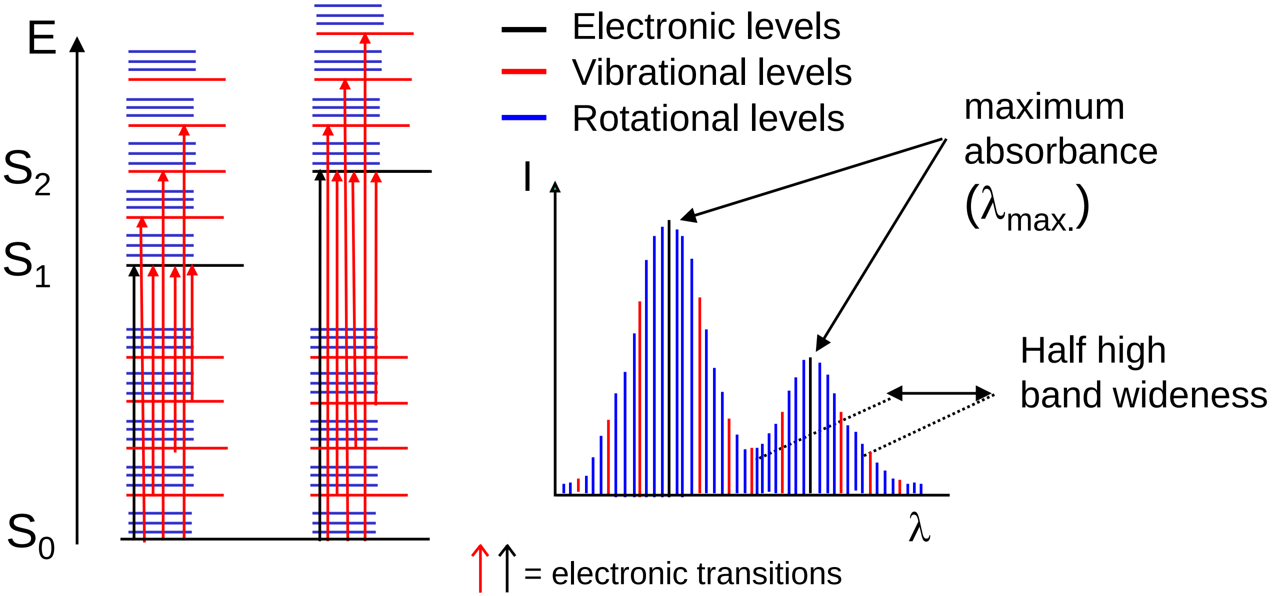
When an atom absorbs electromagnetic radiation, discrete electronic transitions occur and a *line absorption spectrum* is observed. When energy is provided, one or more electrons in an atom may be promoted from its ground state level S_0 to a higher energy state S_n. A *line emission spectrum* is thereby produced by decay from each excited state to the ground state.



Spectral lines in both absorption and emission spectra may be designated in terms of frequency ν or wavelength λ.

Electronic Transitions and UV-visible Spectra in Molecules

If a molecule absorbs an appropriate amount of energy, an electron from an occupied orbital (ground state, S_0) may be excited to an unoccupied or partially occupied orbital (excited state, S_1,S_2 …). Being electronic transition fast, it represent a “snapshot” of the molecule in a particular vibrational and rotational state at a particular moment in time. A broad band is therefore observed.



— Electronic levels
— Vibrational levels
— Rotational levels

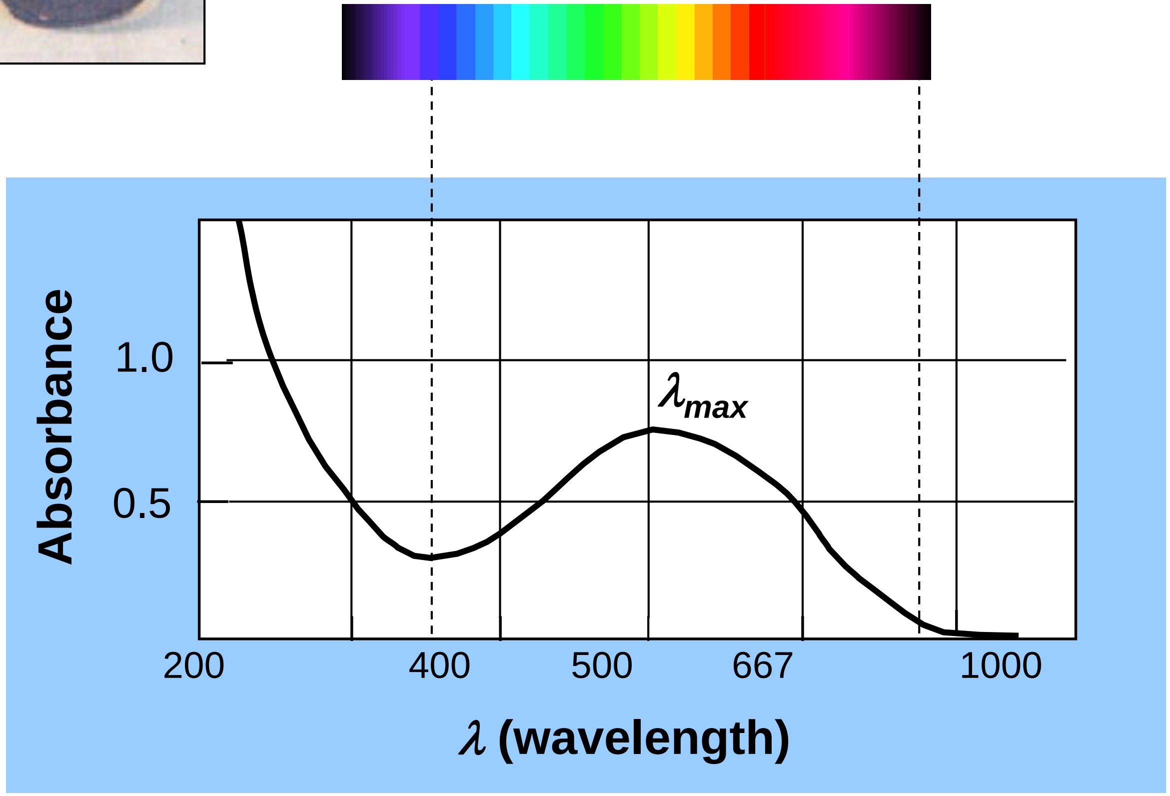
maximum absorbance ($\lambda_{max.}$)

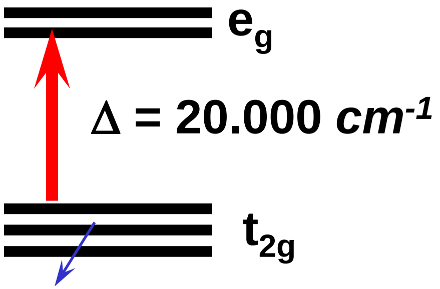
Half high band wideness

↑↑ = electronic transitions

Electronic Spectrum of an Aqueous Solution of 0.1 *M* $[Ti(H_2O)_6]^{3+}$ and related “color”

Color of absorbed light: yellow-green





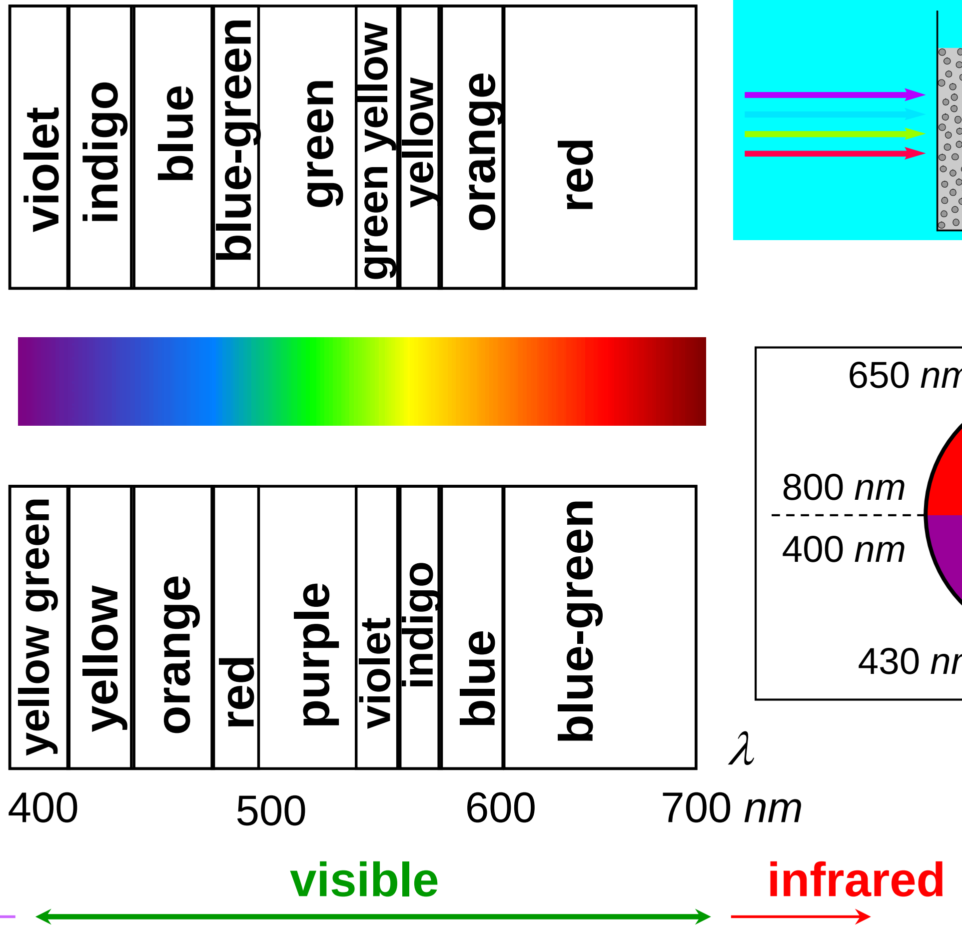
visible color : violet

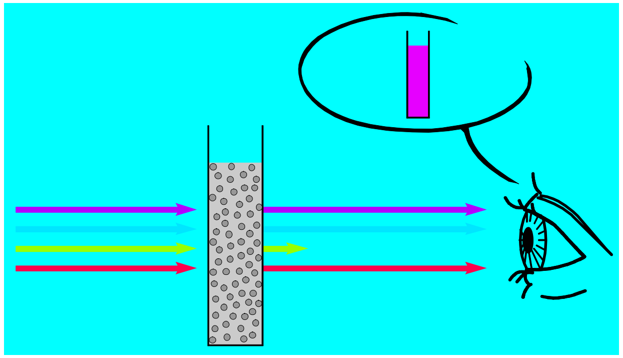
Color of Light: The human eye sees the complementary color to that which is absorbed

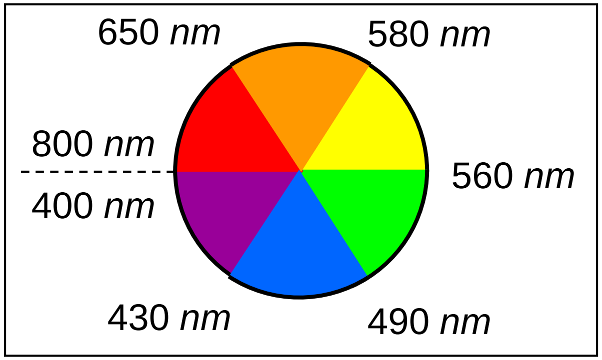
Emitted color from band of the indicated wavelength

radiation spectrum in the visible

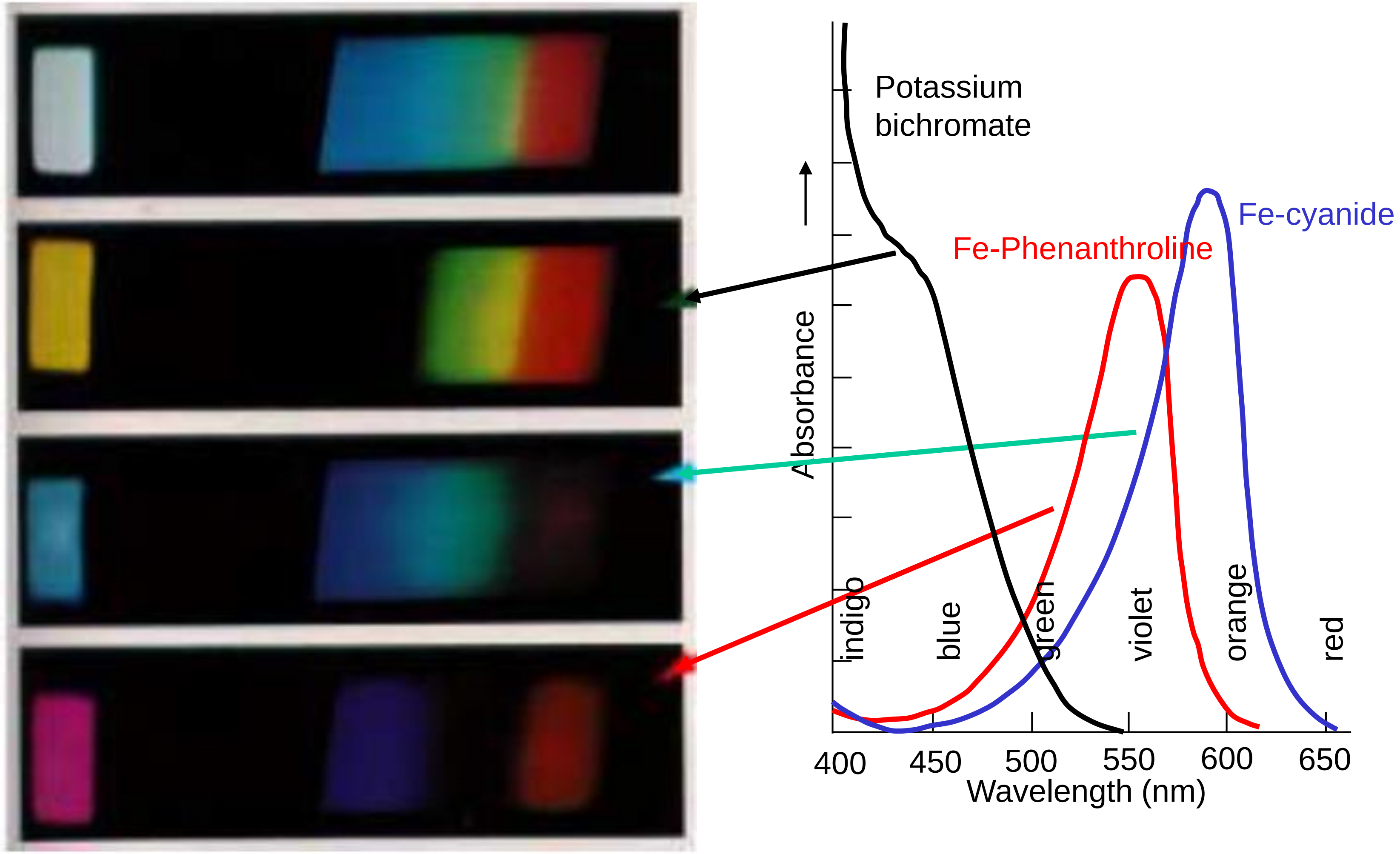
Visible color if the absorption of the upper band is full.



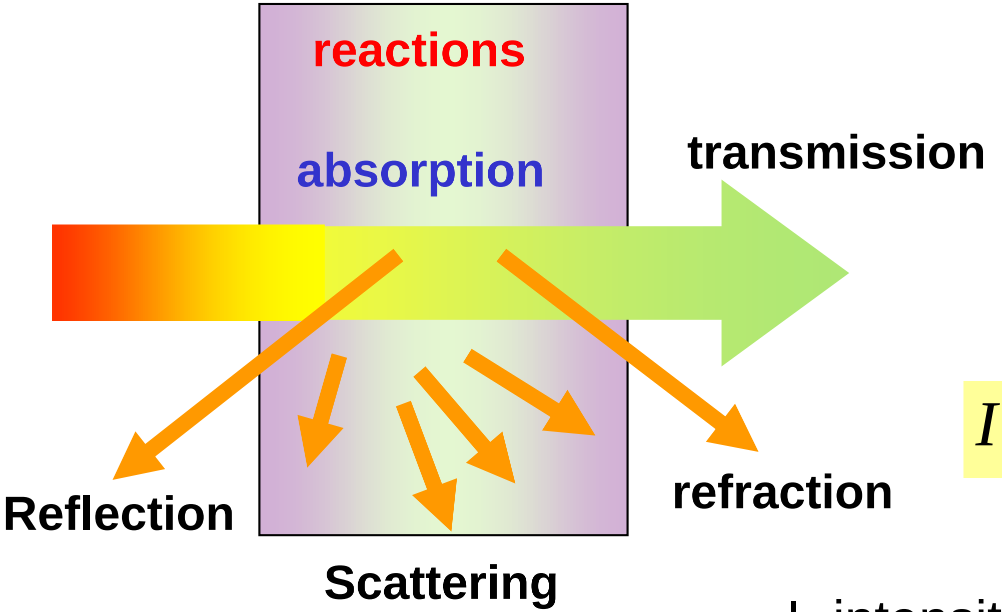




Visible Spectra of Iron Complexes



Absorption of Light Beam



$$-\frac{dI}{I} = a dx$$

$$I = I_0 \exp(-ax)$$

$$I_a = I_0 - I = I_0[1 - \exp(-ax)]$$

I- intensity of light, x the thickness of the medium, a the absorption coefficient.

Lambert's law:

when a beam of monochromatic radiation passes through a homogeneous absorbing medium, equal fraction of the incident radiation are absorbed by successive layer of equal thickness of the light absorbing substance

Transmittance and Absorbance

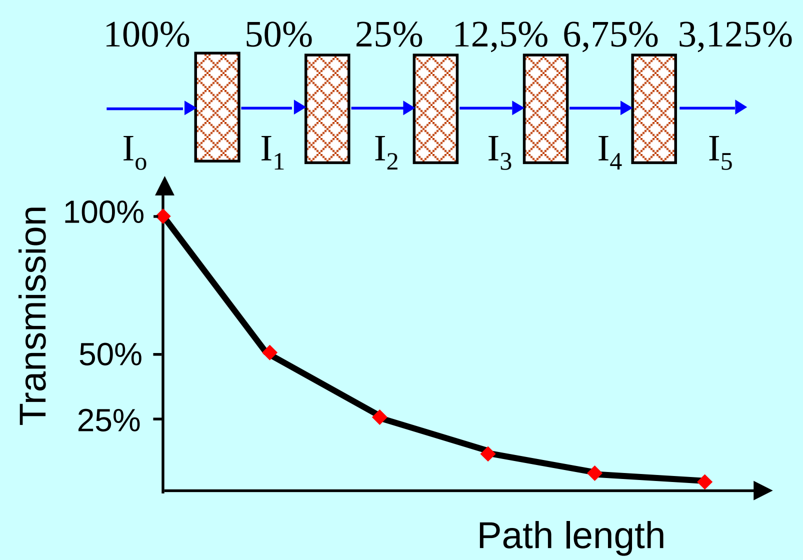
When light is absorbed by a sample or is reflected, the amount of absorbed light is the difference between the incident radiation, I_0, and the transmitted radiation, I. The light absorbed can be expressed as :

a) **Transmittance.** (normally in fractional term or as %) :

$$T = I / I_0 \quad o \quad \%T = I / I_0 \times 100$$

b) **Absorbance.** (normally expressed in logarithmic term) :

$$A = -\log_{10} T$$



Generally, A is proportional to concentration of absorbing specie in diluted solutions (10^{-4} M) in a narrow range of concentrations (**Lambert-Beer Law**) :

$$\boxed{T = I / I_0 = e^{-\varepsilon c l}}$$

ε = molar extinction coeff.

l = cell thickness (cm)

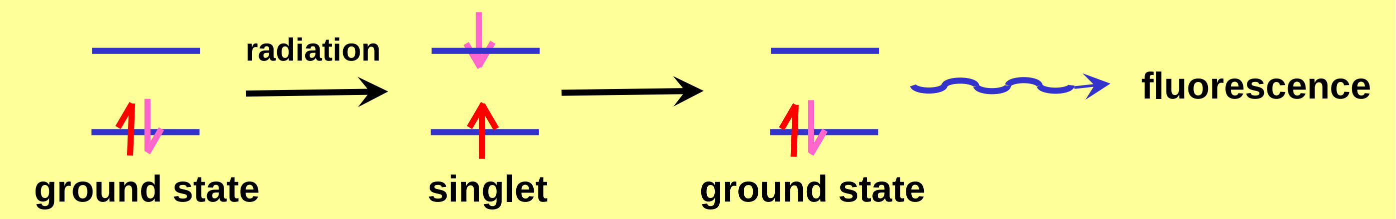
c = concentration ($mol \cdot l^{-1}$)

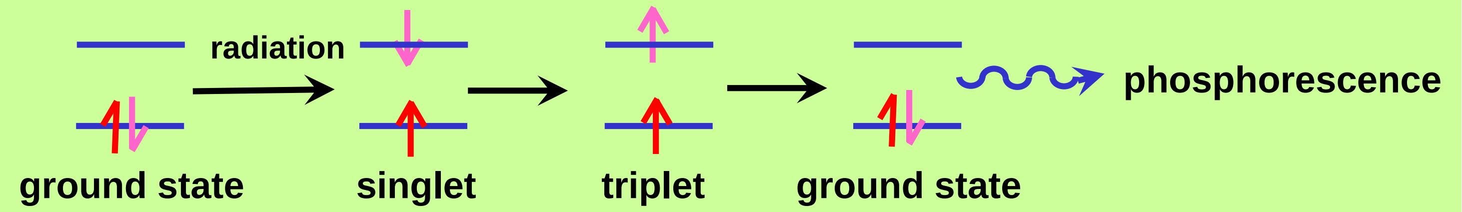
Photoexcitation

Upon photoactivation, the molecules or atoms can be excited to a higher electronic, vibrational, or rotational states.

$$\mathbf{A + \mathit{h\nu} \rightarrow A^*}$$

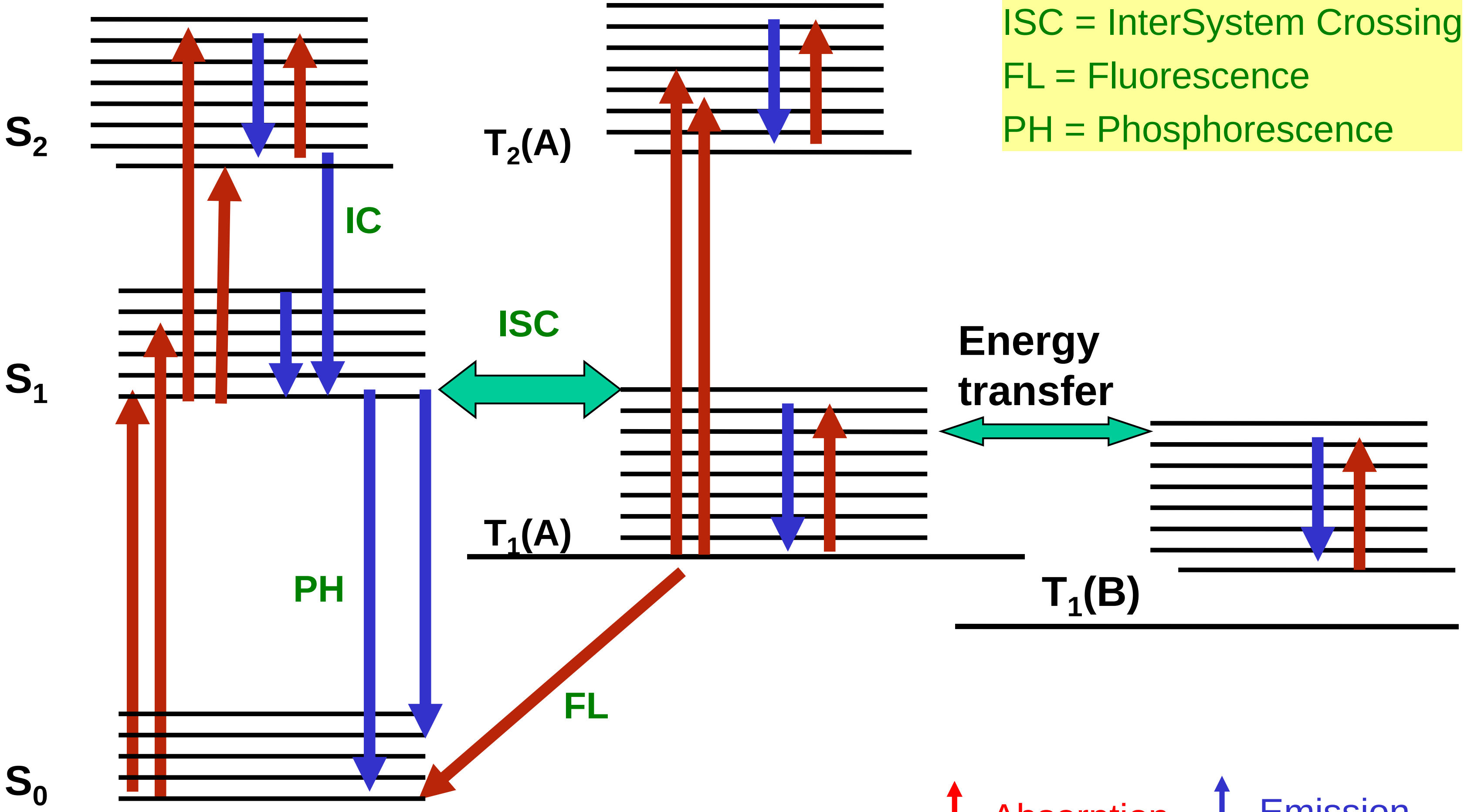
The lifetime of the excited atom is of the order of 10^{-8} s. Once excited, it decays at once.





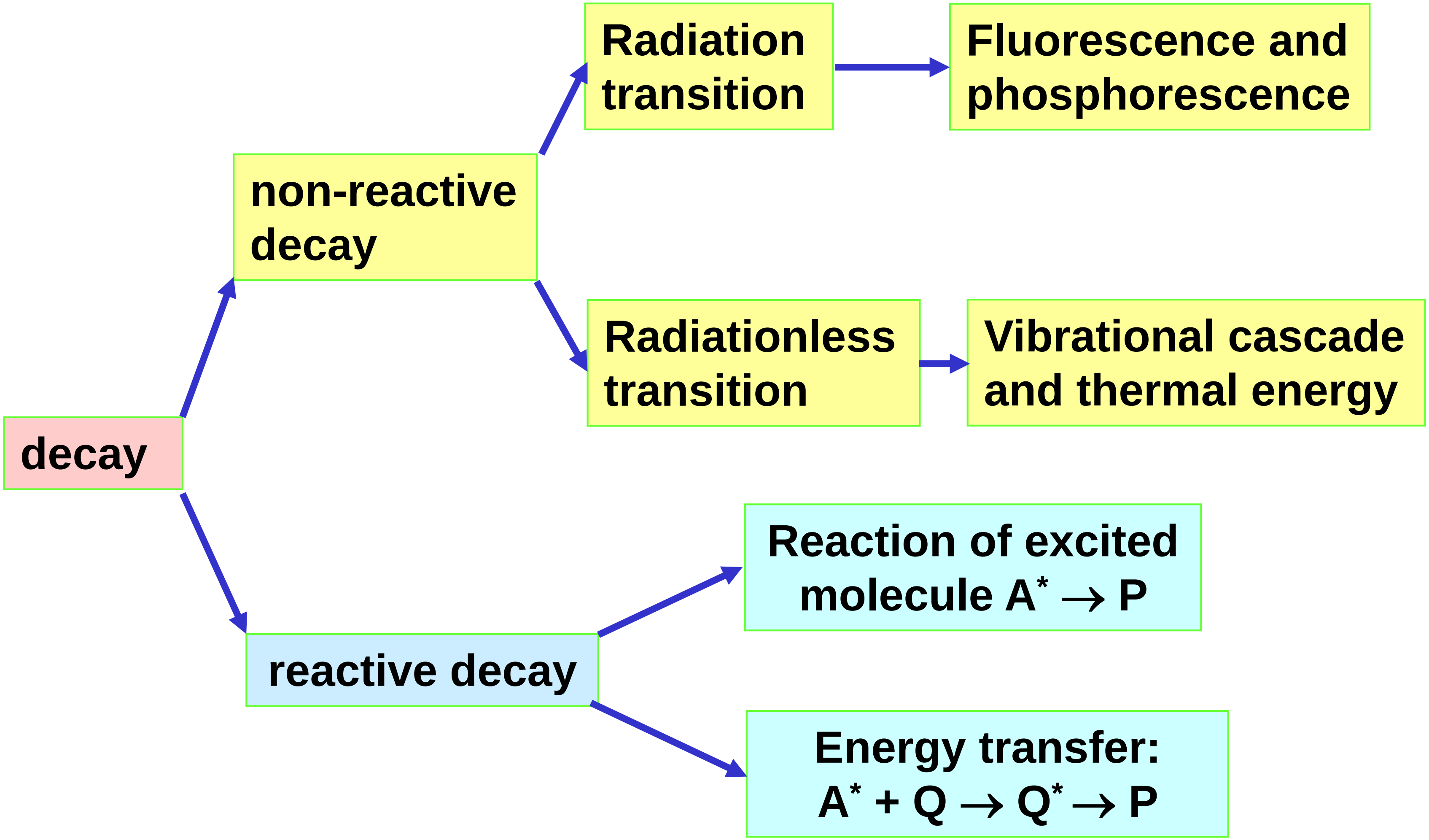
Excitation between different electronic level.

Jablonski Diagram



IC = Internal Conversion
ISC = InterSystem Crossing
FL = Fluorescence
PH = Phosphorescence

Decay of Photoexcited Molecules



decay

non-reactive decay

Radiation transition

Fluorescence and phosphorescence

Radiationless transition

Vibrational cascade and thermal energy

reactive decay

Reaction of excited molecule $A^* \rightarrow P$

Energy transfer: $A^* + Q \rightarrow Q^* \rightarrow P$

Photochemistry

The first law of photochemistry: (Grotthuss and Draper, 1818)

- Only the light that is absorbed by a substance is effective in producing a photochemical change.

The second law of photochemistry - The law of photochemical equivalence (Einstein and Stark, 1912)

- The quantum of radiation absorbed by a molecule activates one molecule in the primary step of photochemical process.

The activation of any molecule or atom is induced by the absorption of single light quantum.

$$\mu = Lh\nu = 0.1196\ \nu\ \mathrm{J \cdot mol^{-1}}$$ (one einstein)

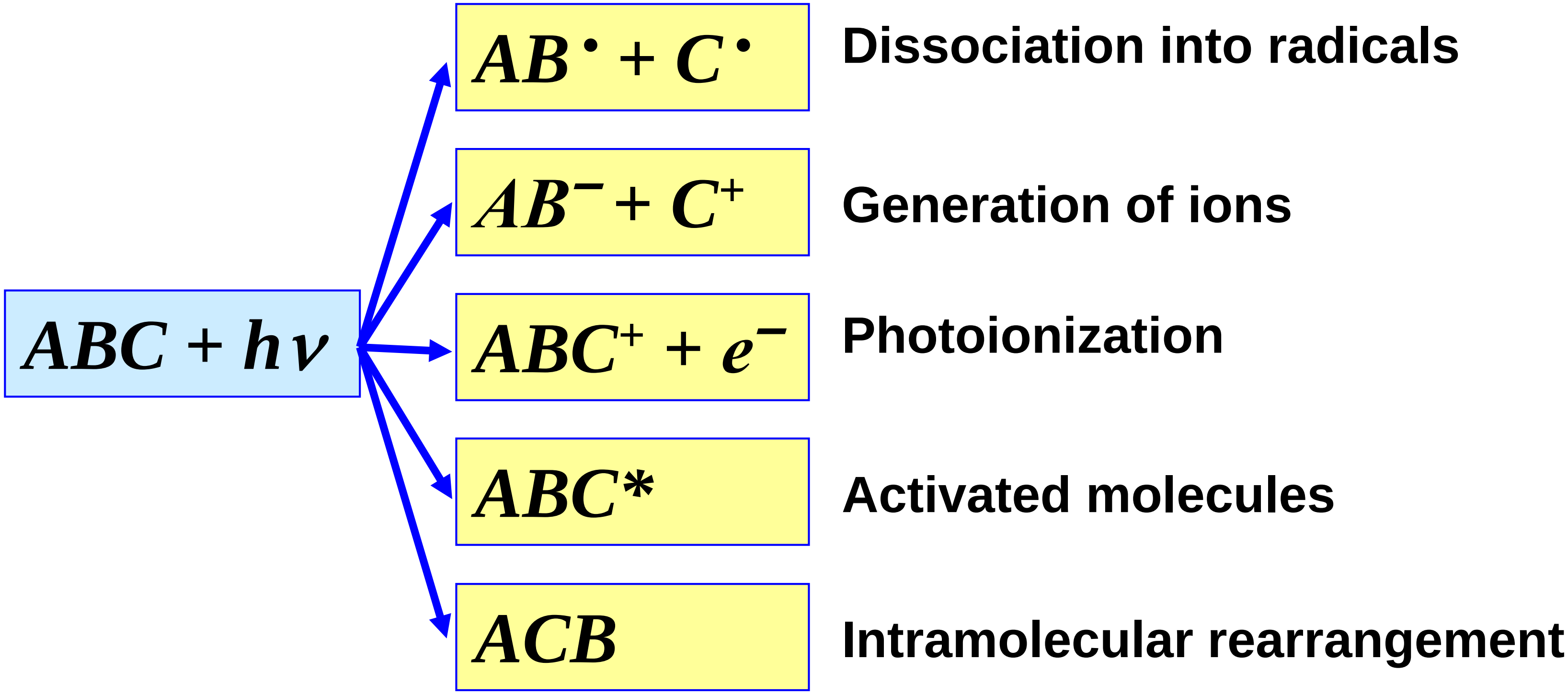
The probability of multiphoton absorption is rare, unless under high intensive radiation.

The Primary Photochemical Process

A chemical reaction wherein the photon is one of the reactant.

$$S + h\nu \rightarrow S^*$$

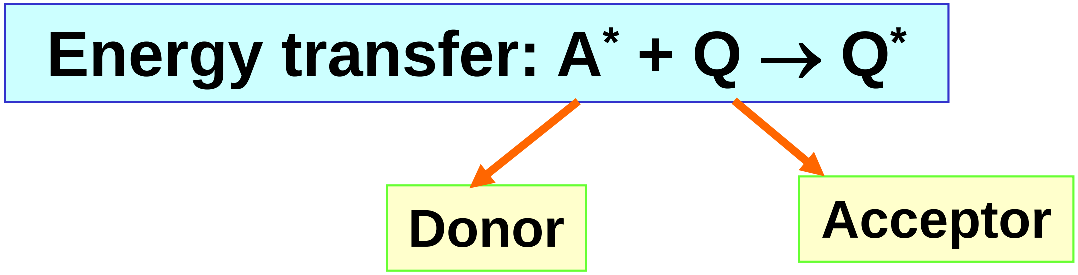
Some primary photochemical process for molecules:



$ABC + h\nu$

$AB^\bullet + C^\bullet$	**Dissociation into radicals**
$AB^- + C^+$	**Generation of ions**
$ABC^+ + e^-$	**Photoionization**
ABC^*	**Activated molecules**
ACB	**Intramolecular rearrangement**

Secondary Photochemical Process



Energy transfer: $A^* + Q \rightarrow Q^*$

Donor

Acceptor

$Q^* \rightarrow P$ (sensitization), A^*: sensitizer

$Q^* + A$ (quenching), Q: quencher

Kinetics and Equilibrium of Photochemical Reaction

For primary photochemical process:

$$\mathrm{R} + h\nu \longrightarrow \mathrm{R^*} \longrightarrow \mathrm{P}$$

$$r = kI_a$$

Zeroth-order reaction

For secondary photochemical process:

$$\mathrm{HI} + h\nu \rightarrow \mathrm{H^\bullet} + \mathrm{I^\bullet} \qquad \mathrm{H^\bullet} + \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I^\bullet} \qquad \mathrm{I^\bullet} + \mathrm{I^\bullet} \rightarrow \mathrm{I_2}$$

$$-\frac{d[HI]}{dt} = kI_a + k_2[H][HI]$$

$$-\frac{d[H]}{dt} = kI_a - k_2[H][HI] = 0$$

$$-\frac{d[HI]}{dt} = kI_a + k_2[H][HI] = 2kI_a$$

Generally, the primary photochemical reaction is the r. d. s.

Opposing Reactions and Equilibrium

For a reversible process:

$$A \rightleftharpoons B$$

$$r_+ = k_+ I_a \qquad r_- = k_-[B]$$

At equilibrium

$$[B] = \frac{k_+}{k_-} I_a$$

The composition of the equilibrium mixture is determined by radiation intensity.

Quantum Yield and Energy Efficiency

Quantum yield or quantum efficiency (Φ):

$$\Phi = \frac{n}{\mu} = \frac{r}{I_a}$$

The ratio between the number of moles of reactant consumed or product formed for each einstein of absorbed radiation.

For $\mathbf{H_2 + Cl_2 \rightarrow 2HCl}$ $\quad \Phi = 10^4 \sim 10^6$

$\mathbf{H_2 + Br_2 \rightarrow 2HBr}$ $\quad \Phi = 0.01$

$\Phi < 1$, the physical deactivation is dominant

$\Phi = 1$, product is produced in primary photochemical process

$\Phi > 1$, initiate chain reaction.

Energy Efficiency

Energy Efficiency:

$$\eta = \frac{\text{Light energy preserved}}{\text{Total light energy}}$$

Photosynthesis:

$$6CO_2 + 6H_2O + nh\nu \rightarrow C_6H_{12}O_6 + 6O_2 \qquad \Delta G_{fr} = 2870\ \text{kJ}\cdot\text{mol}^{-1}$$

For formation of a glucose molecule, 48 light quanta was needed.

$$\eta = \frac{2870}{48 \times 167.4} = 35.7\%$$

red light with wavelength of 700 nm

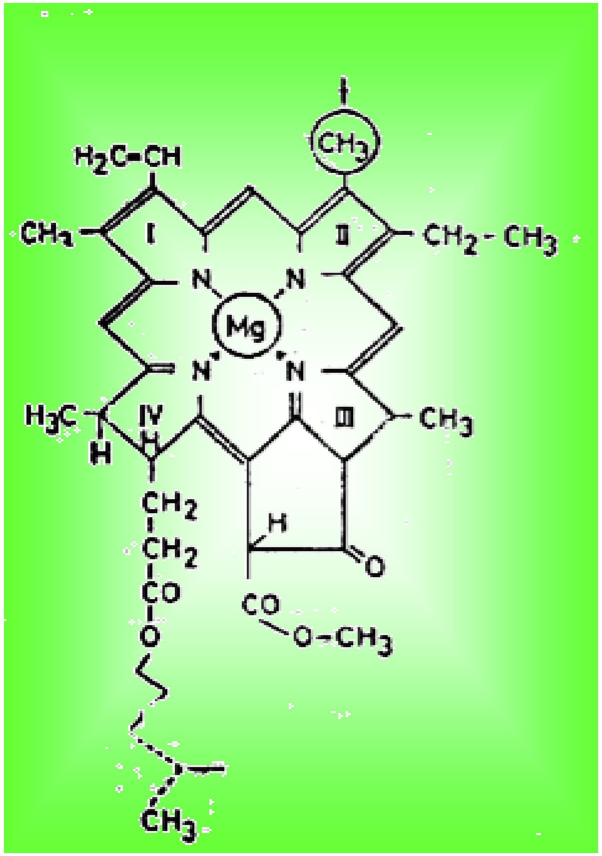
Photosensitive Reaction

Reaction initiated by photosensitizer.

When reactants themselves do not absorb light energy, photoensitizer can be used to initiate the reaction by conversion of the light energy to the reactants.

$$6CO_2 + 6H_2O + nh\nu \rightarrow C_6H_{12}O_6 + 6O_2$$

Chlorophyll A, B, C, and D



Magnesium Porphyrin complex

Photosynthesis Main Steps

Light reaction: the energy content of the light quanta is converted into chemical energy.

Dark reaction: the chemical energy was used to form glucose.

$$4Fd^{3+} + 3ADP^{3-} + 3P^{2-} \xrightarrow{8h\gamma} 4Fd^{2+} + 3ATP^{4-} + O_2 + H_2O + H^+$$

Fd is a protein with low molecular weight

$$3ATP^{3-} + 4Fd^{2+} + CO_2 + H_2O + H^+ \ 3P^{2-} \rightarrow (CH_2O) + 3ADP^{3-} + 3P^{2-} + 4Fd^{3+}$$

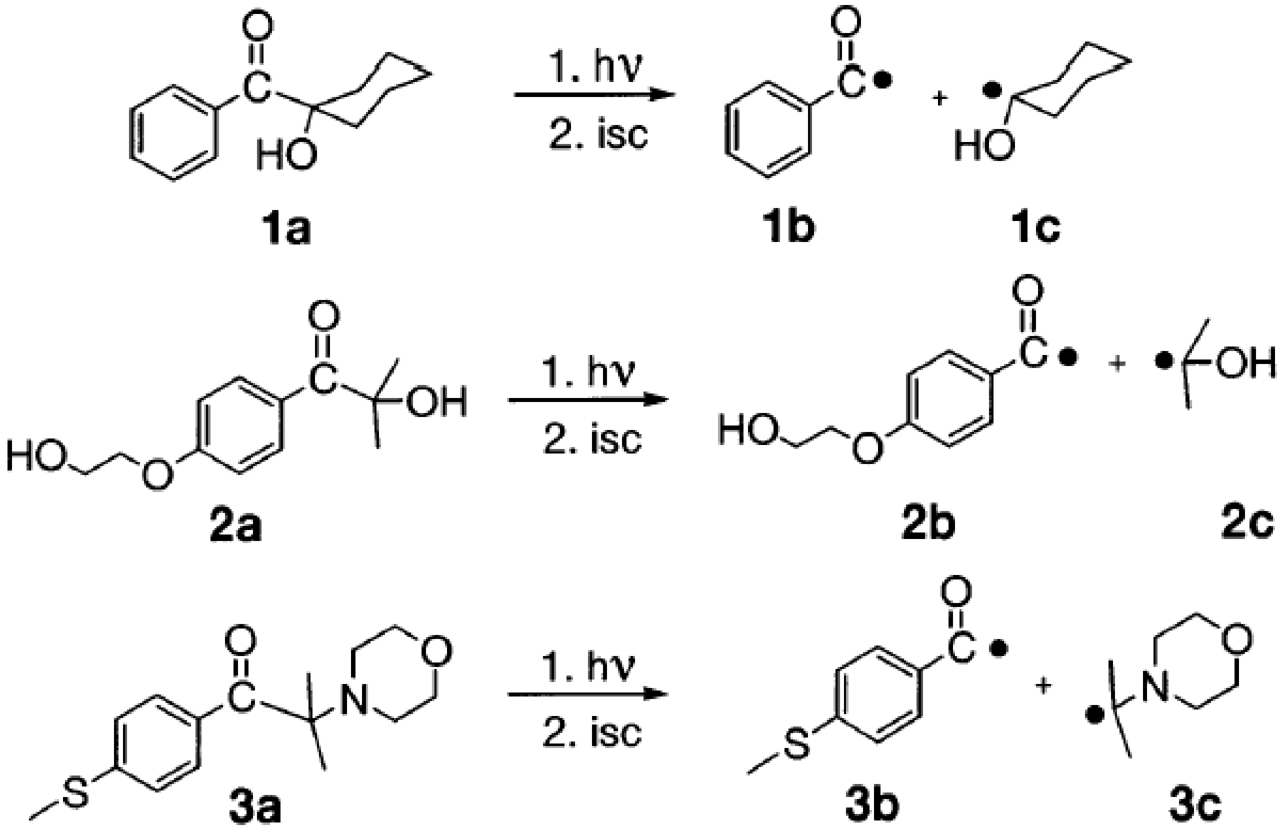
Photoinitiators (Norrish Type I)

Definitions:

- **Photoinitiator** - compound that generates radical, cationic, anionic or other chain polymerizations after the absorption of light.
- **Photosensitizer** - energy transfer donor (see the Jablonski diagram).
- **Quencher** - energy transfer acceptor (the energy transfer donor is 'quenched').

- Free radical polymerization is responsible for about 90% of the 'energy cure' business; the remaining 10% comes from cationic cure. There are no commercial anionic cure, Ziegler Natta, or other commercial chain processes.
- Free radical reaction 'energy cure' mostly involves acrylates; 90% of it is UV; the remainder is e-beam.
- 75% of all photoinitiators for UV energy cure are Norrish Type I photoinitiators.
- With a few notable exceptions, the initiating radical from most Norrish Type I initiators is the benzoyl radical, ØC(•)=O. (However see the data that follows).

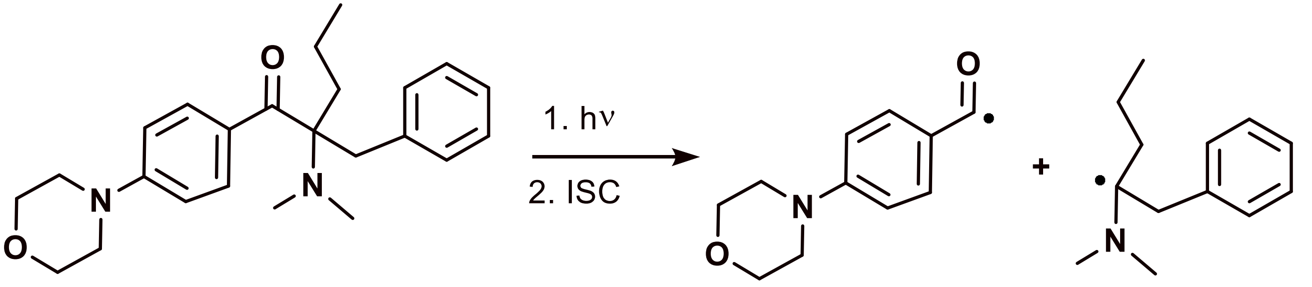
Some Commercial Norrish Type I Initiators



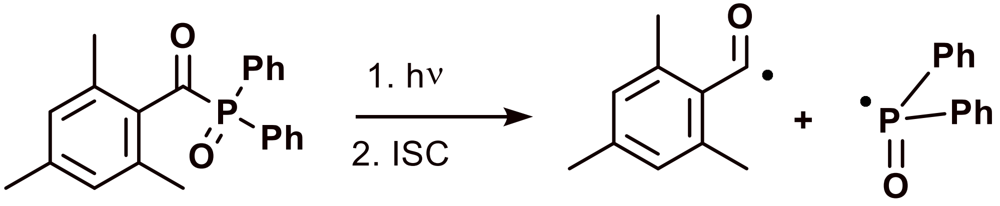
"Irgacure" Ciba trade name

Turro, et al. JACS **2002**, *124* 14952

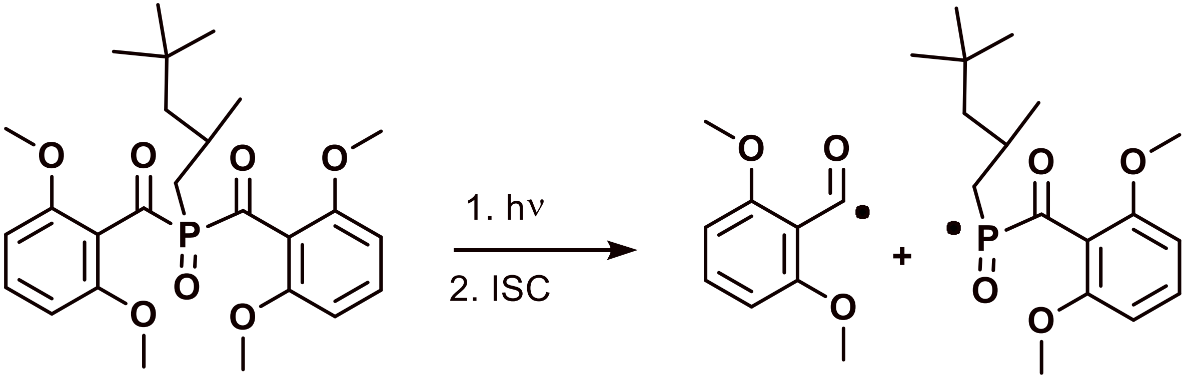
Additional Irgacures



4a **4b** **4c**

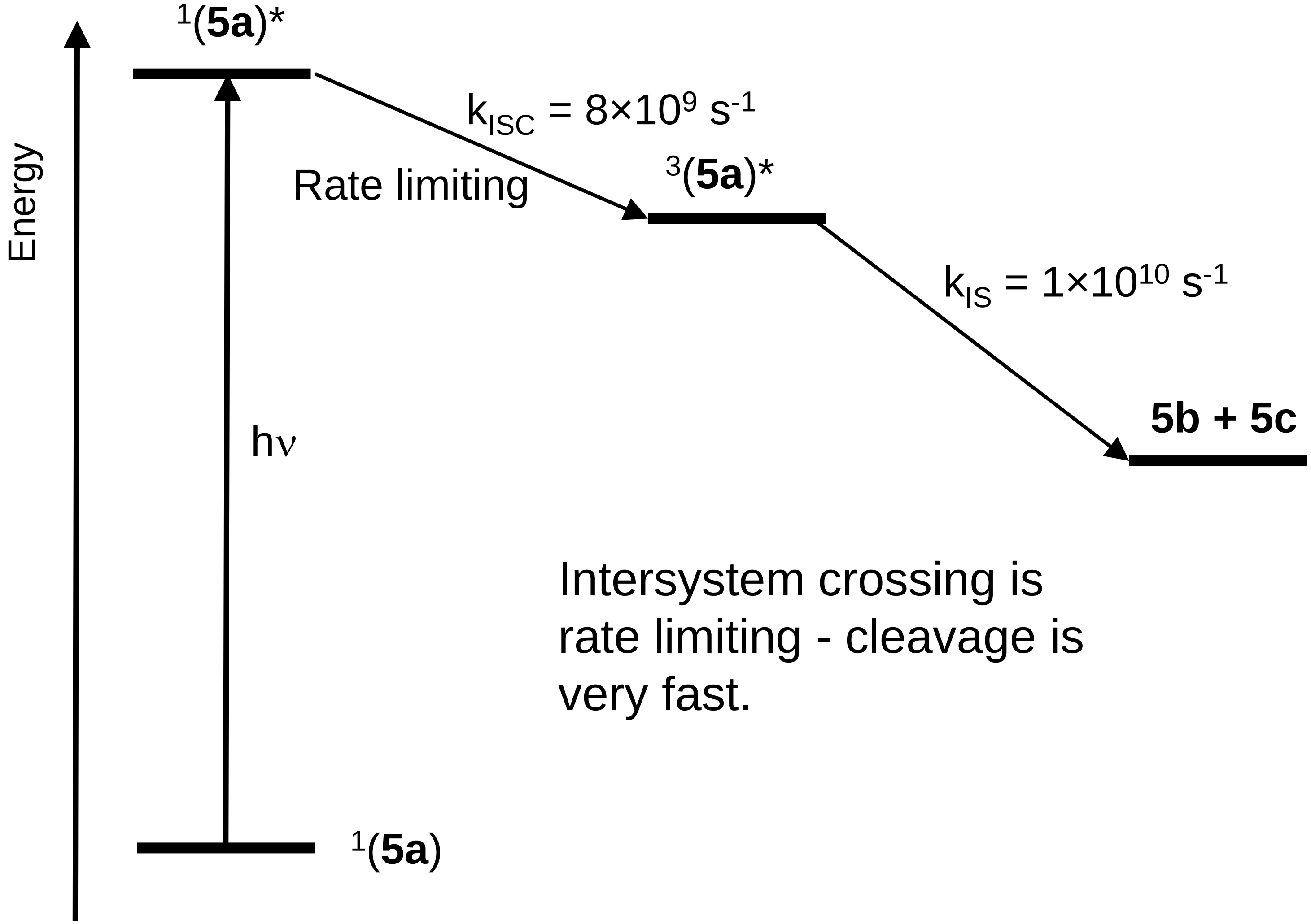


5a **5b** **5c**



6a **6b** **6c**

Energy Level Diagram for the a-Cleavage of Irgacure 5a



Energy

^{1}(**5a**)*

$k_{ISC} = 8\times10^{9}\ s^{-1}$

Rate limiting

^{3}(**5a**)*

$k_{IS} = 1\times10^{10}\ s^{-1}$

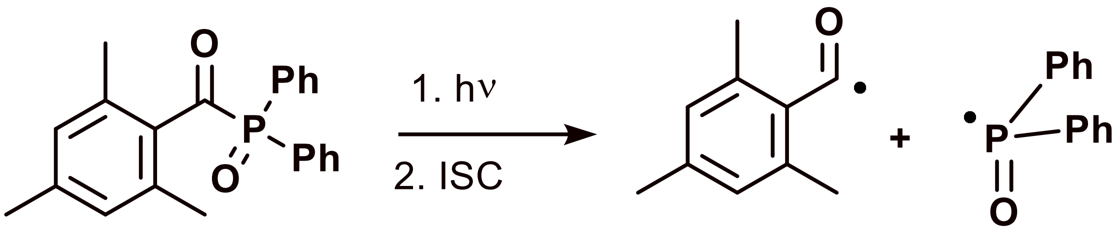
5b + 5c

hν

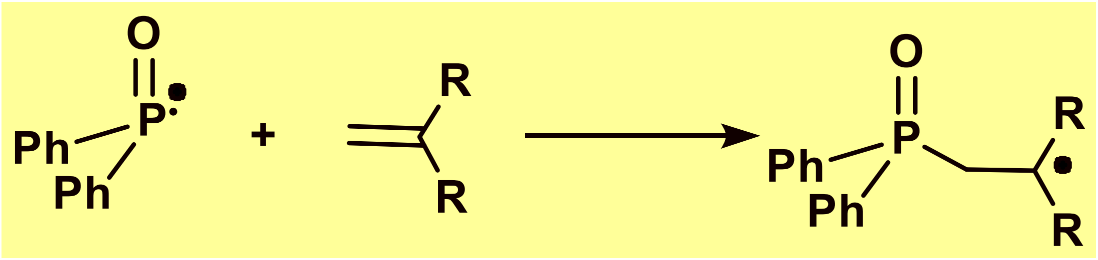
^{1}(**5a**)

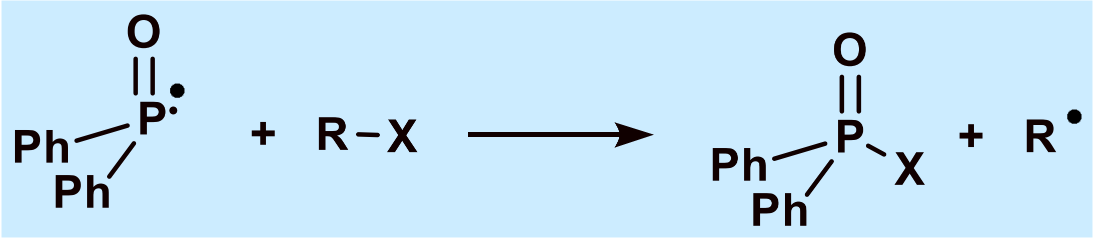
Intersystem crossing is rate limiting - cleavage is very fast.

Photo Generation of Carbon Free Radicals

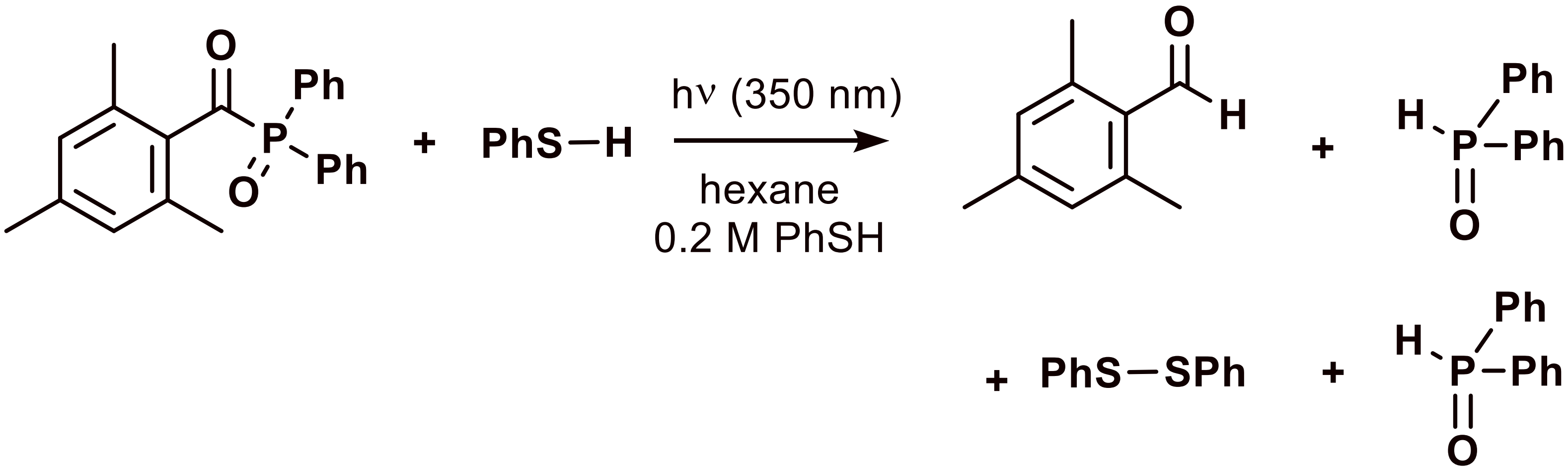


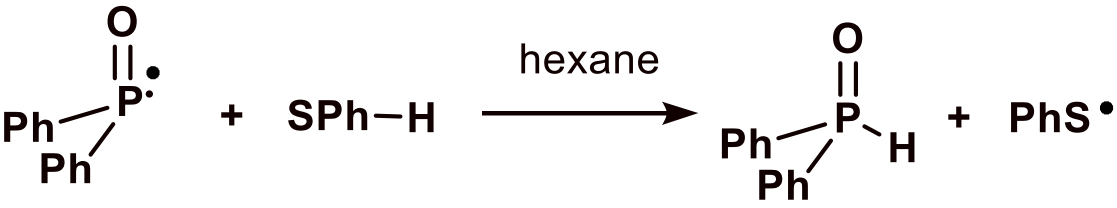
5a **5b** **5c**





Quenching with Thiophenol - Products





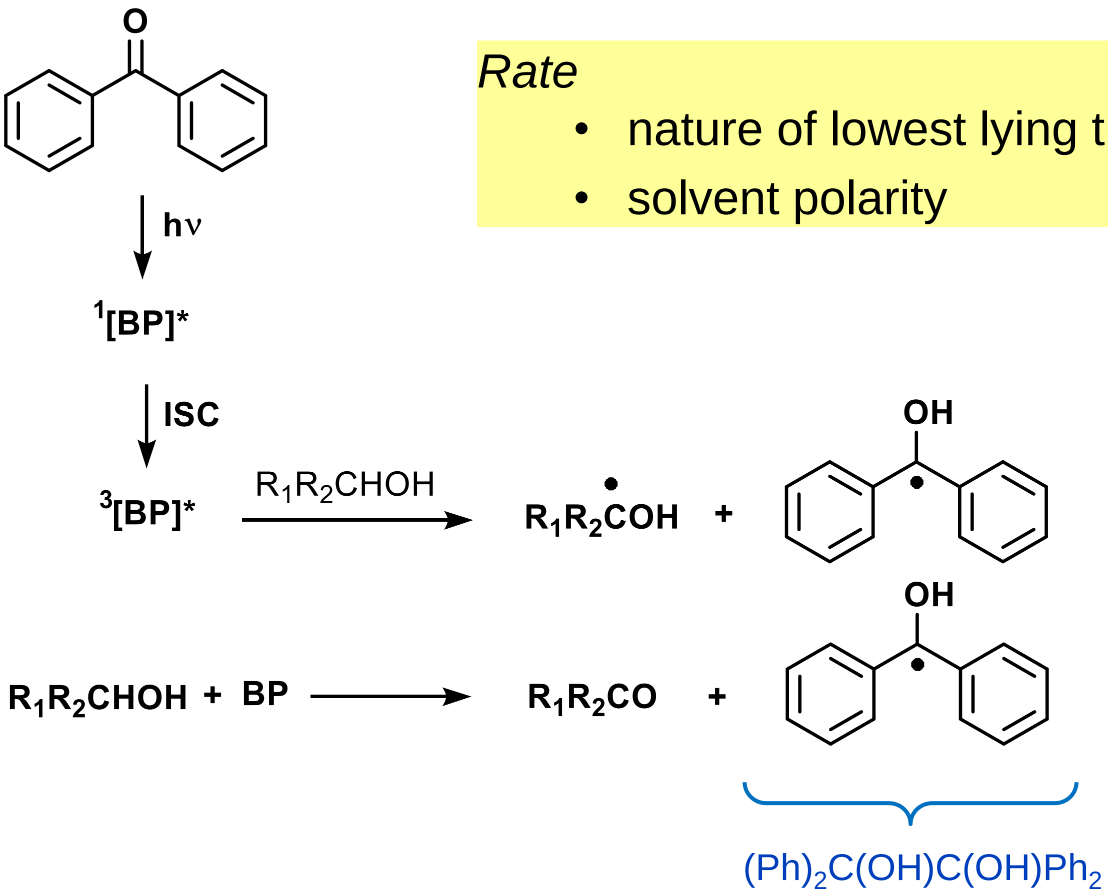
330 nm

450 nm

Photoreduction of Aromatic Carbonyl Compounds

Rate

- nature of lowest lying triplet state (n,π^*; π,π^*)
- solvent polarity

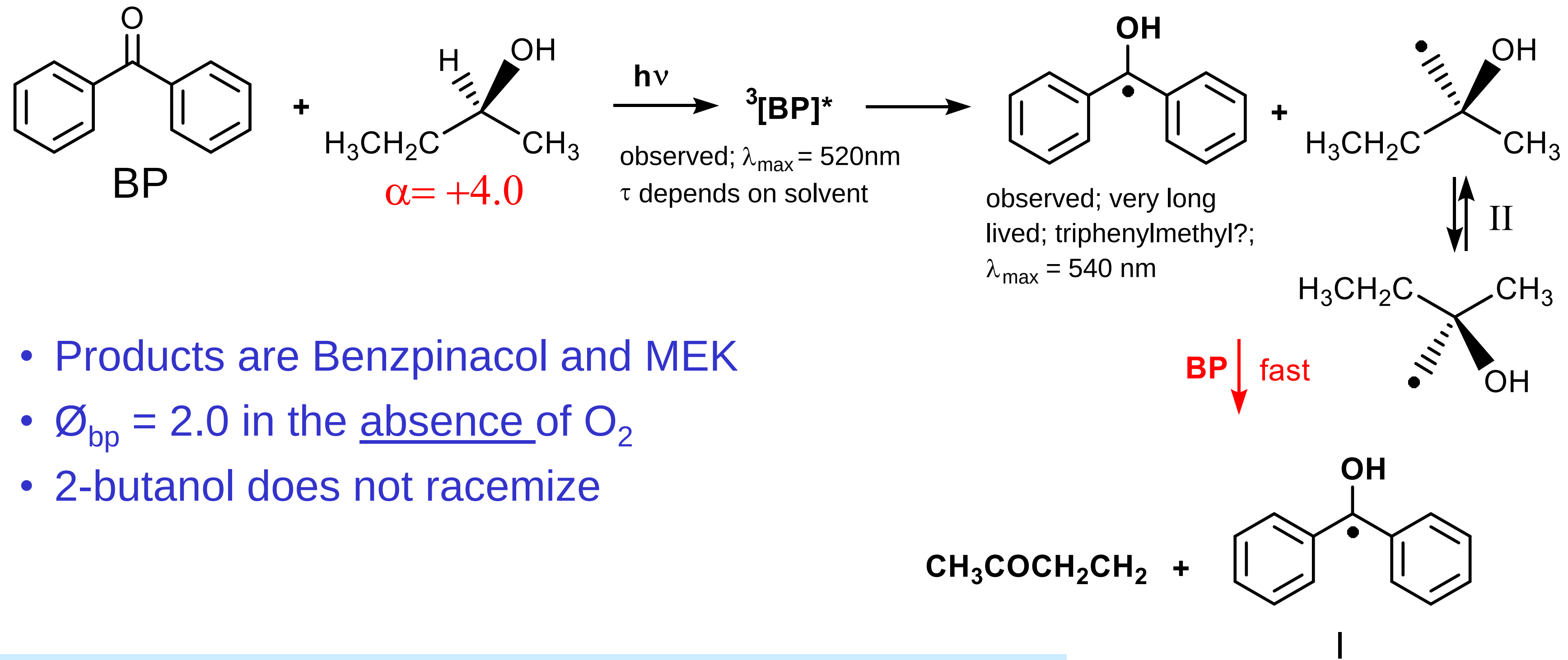


benzophenone ketyl radical

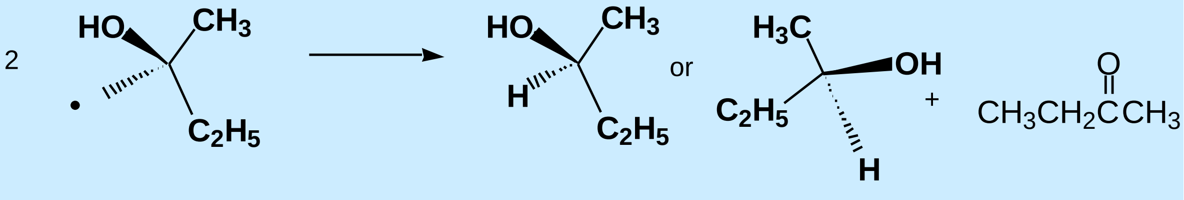
benzpinacol

Ciamician, G.; Silber P. Chem. Ber., 33, 2911, 1900.
Cohen, W. D., *Rec. Trav. Chim. Pays-Bas, 39, 243, 1920.*

Hydrogen Abstraction



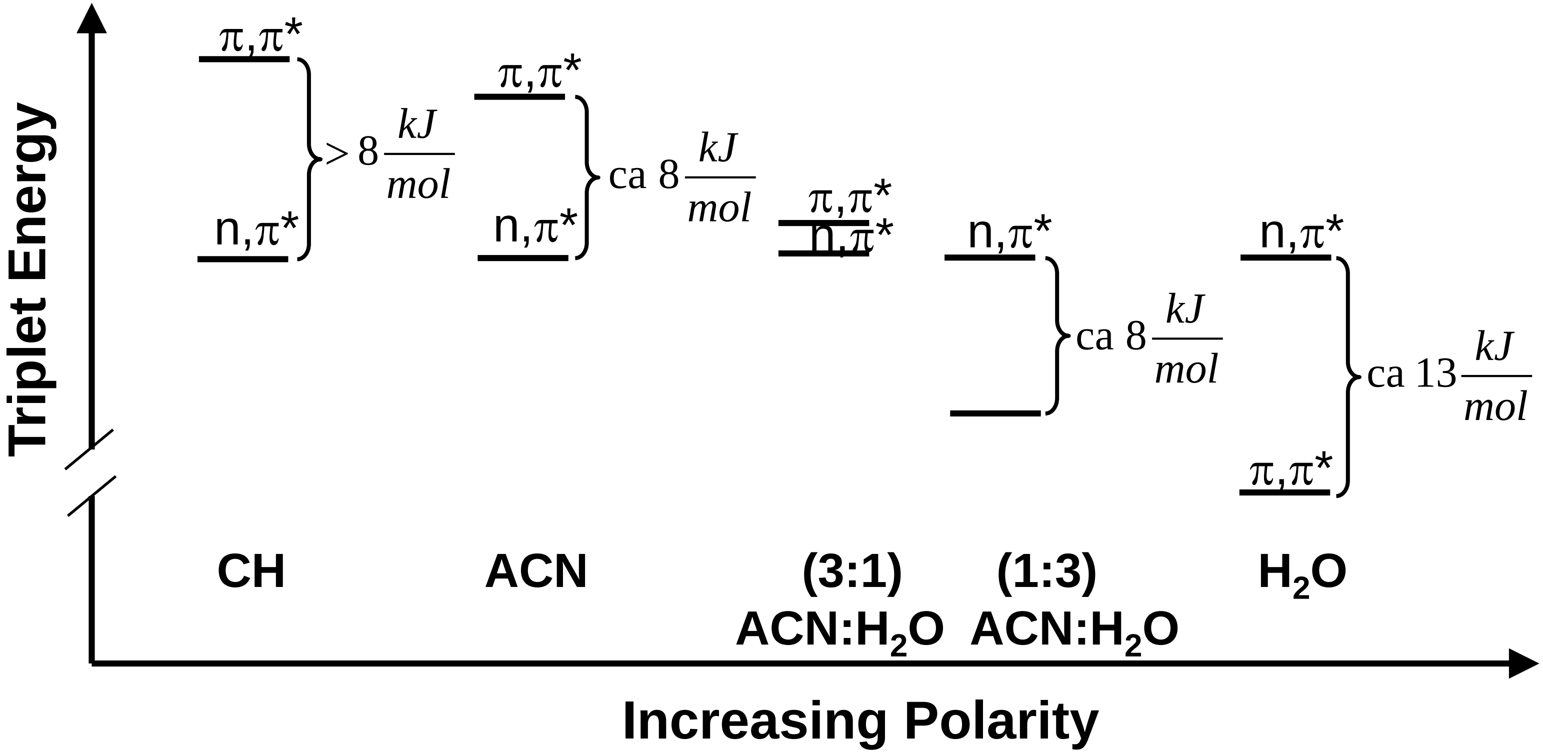
- Products are Benzpinacol and MEK
- $\varnothing_{bp}$ = 2.0 in the absence of O_2
- 2-butanol does not racemize



Disproportionation leads to racemization

Pitts, J. N., Letsinger, R. L., Taylor, R. P. Patterson, J. M., Rechtenwald, G., Martin, R. B. J. Amer. Chem. Soc., 1959, 80, 1068; Bäckström, H. L. J., Sandros, K. Acta. Chem. Scand. 1960, 14, 48.

Energetic Diagram



Energetic diagram for the lowest triplet states of 4-MeBP in solvents of different polarity.

Electron Transfer: Photochemical Oxidation Reduction

Electron transfer, or photochemical oxidation reduction, also leads to radicals - but invariably via **radical ions**:

$$\mathbf{D \rightarrow D^*}$$

$$\mathbf{D^* \rightarrow D^{+\bullet} + e^-}$$

radical cations

or

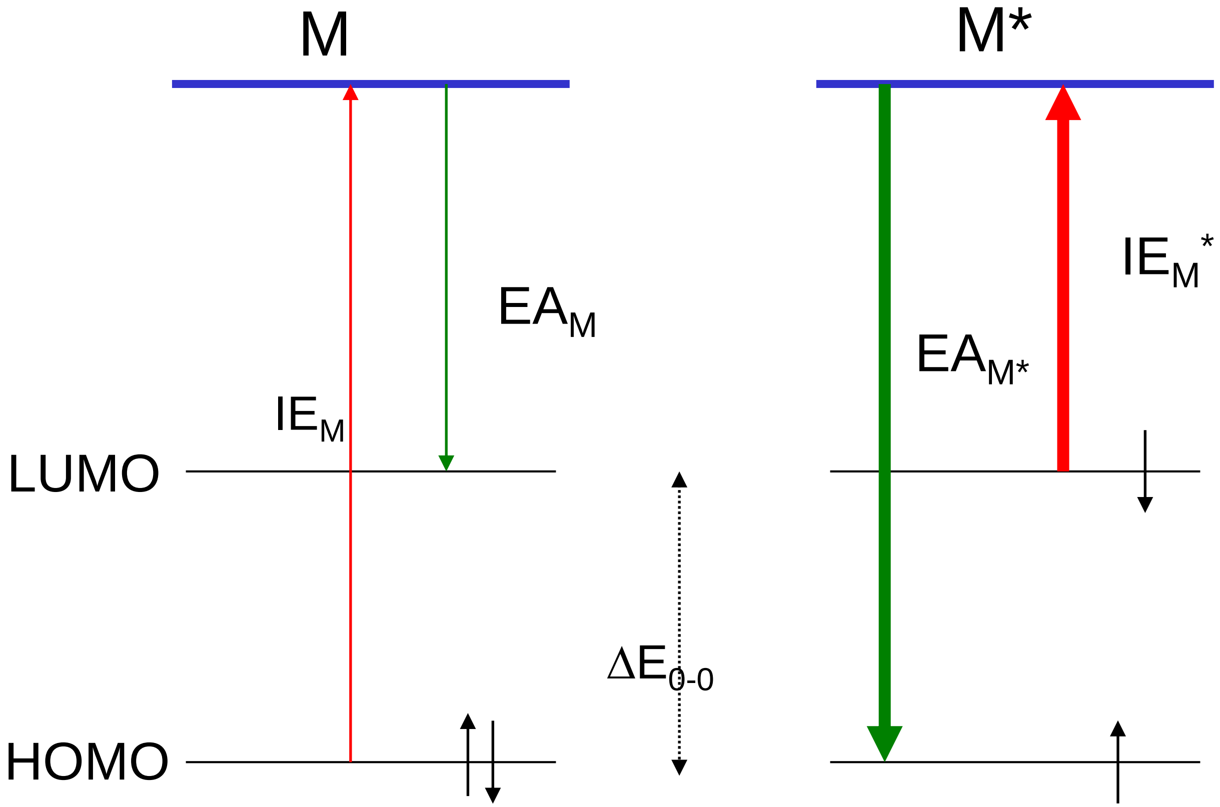
$$A \rightarrow A^*$$

$$A^* + e^- \rightarrow A^{\bullet -}$$

radical anions

Spontaneity of Electron Transfer

Ionization energy and electron affinities - ground state and excited electronic states of molecule, M. The ionization energy is reduced; electron affinity increased in the excited state relative to the ground state.



Rehm Weller Equation

In the gas phase the total change in Gibbs free energy associated with ionization of Q (→ $Q^{+\bullet}$) and the addition of an electron to M (→ $M^{-\bullet}$) is given by

$$IE_Q - EA_M = \Delta G$$

In solution one has to account for the solvent - (∂ term) relative to excited state energies however the values are small so they are usually ignored.

$$\text{Convention } M^{-\bullet} \rightarrow M \quad E(M^{-\bullet}/M)$$
$$Q \rightarrow Q^{+\bullet} \quad E(Q/Q^{+\bullet})$$

$$\Delta G = E(Q/Q^{+\bullet}) - E(M^{-\bullet}/M) - \Delta E_{0\text{-}0} + \partial$$

so-called Rehm Weller equation.

Rehm, D.; Weller, A.; *Israel J. Chem.* **1974**, *8* 259

Redox Potentials vs. SCE

Compound	**$E(M^{-\bullet}/M)$/ eV**	**$E(M/M^{+\bullet})$/ eV**	**ΔE_{0-0} eV**
Acetophenone	-1.85		3.41
Benzophenone	-1.68		3.23
9,10-dicyanoanthracene	-0.89		2.86
Anthracene	-1.93	1.16	3.28
Naphthalene	-2.29	1.60	3.99
N,N-dimethylaniline		0.81	3.85
Triethylamine		0.76	3.90
Triphenylamine		0.98	
Methyl viologen	-0.45		

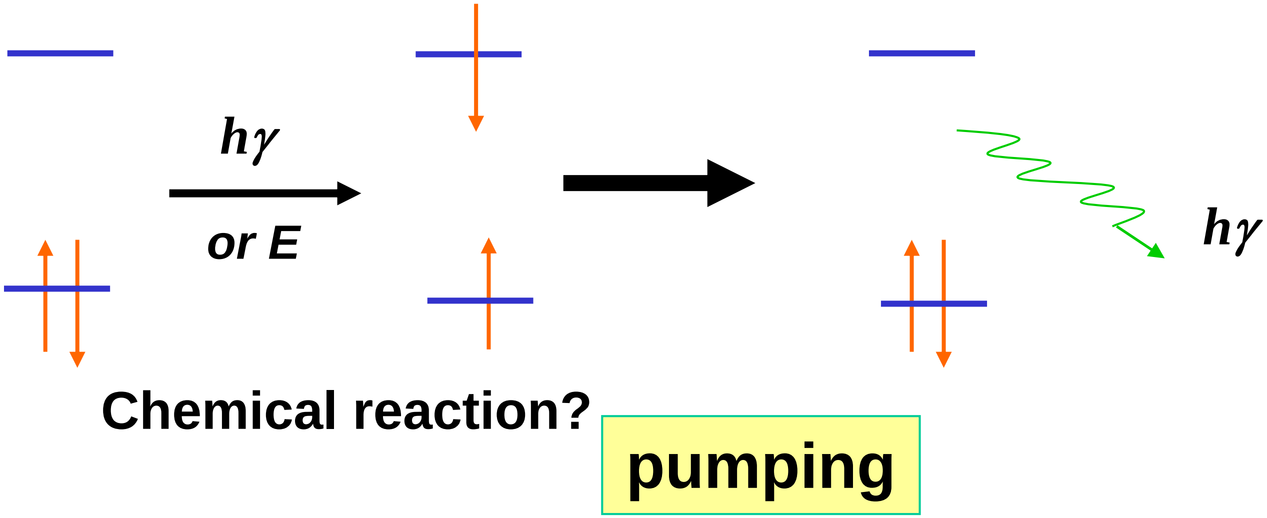
POLITECNICO DI MILANO

LUMINESCENCE

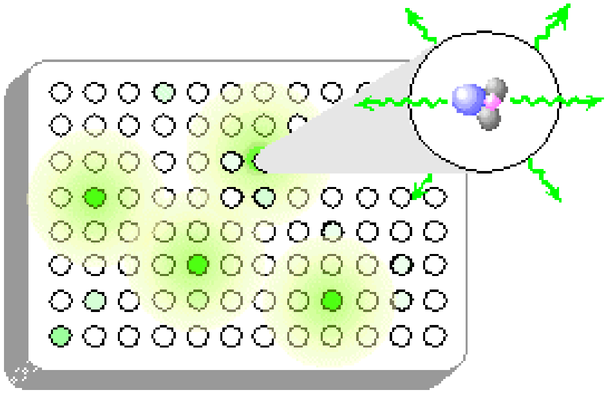
Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

Light Emission: the Way to Produce Light



- Photoluminescence
- Electroluminescence
- Chemiluminescence
- Electrochemiluminescence
- Light-emitting diode



Chemi(bio)luminescence

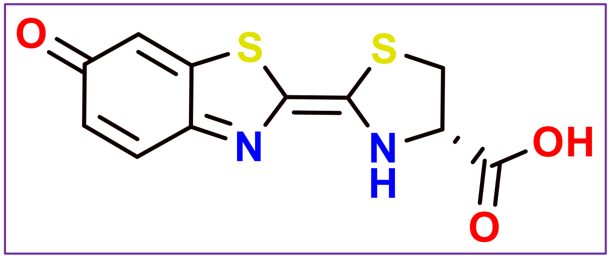
- ***Bioluminescence***
  - Fireflies,
  - Luminescent bacteria

- ***Chemiluminescence***
  - Luminol,
  - Cold light sticks

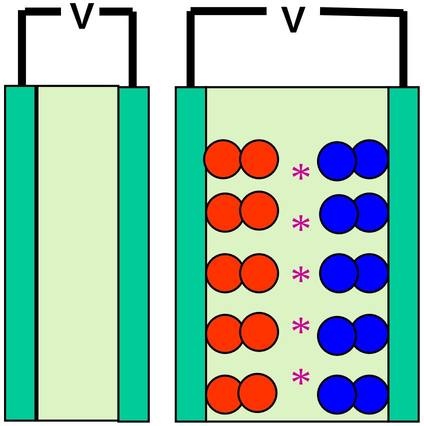
- An unstable species in a highly oxidized state is produced, and its decomposition leads to energy in the form of emitted light.

- The basic chemistry in every case is that of a four membered ring of atoms, two of which are oxygens.

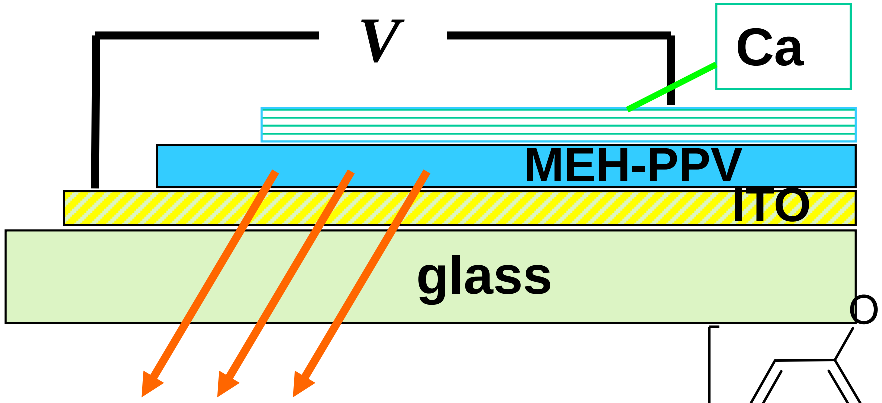
Bio-luminescence and Chemi-luminescence



Luciferase: can send out chemiluminescence in $10^{-13} \sim 10^{-15}$ mol dm^{-3} ATP.

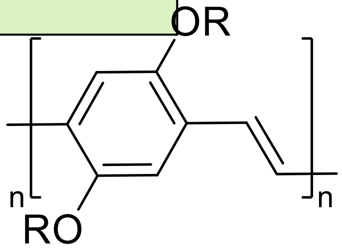


PPV+PEO+$LiCF_3SO_3$



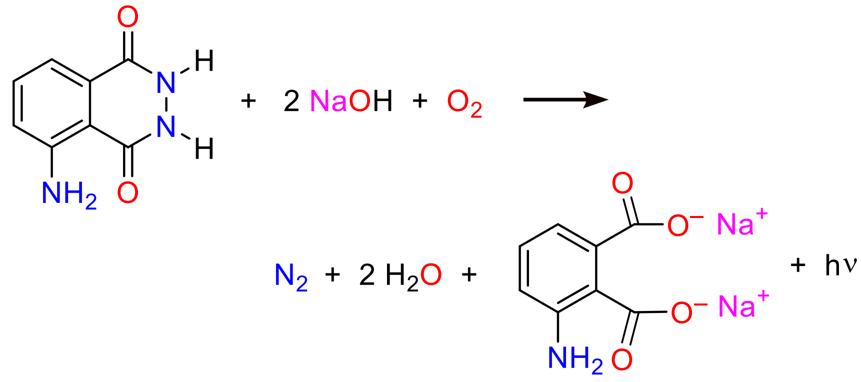
LED

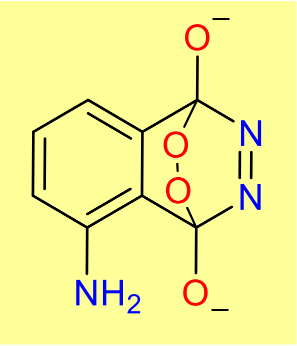
MEH-PPV

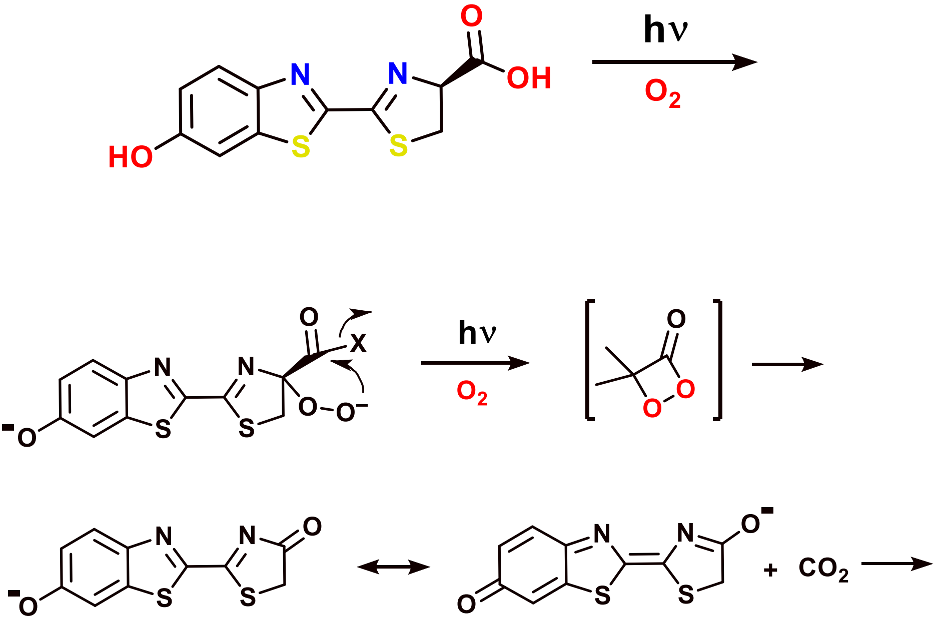


Luminescence

- Luminol
- Firefly



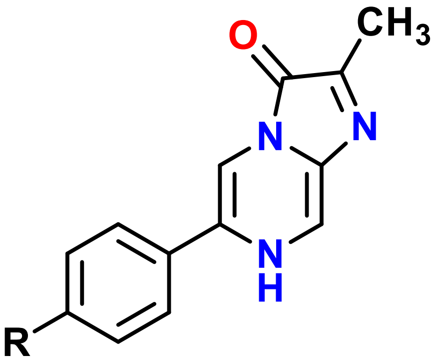




RED light

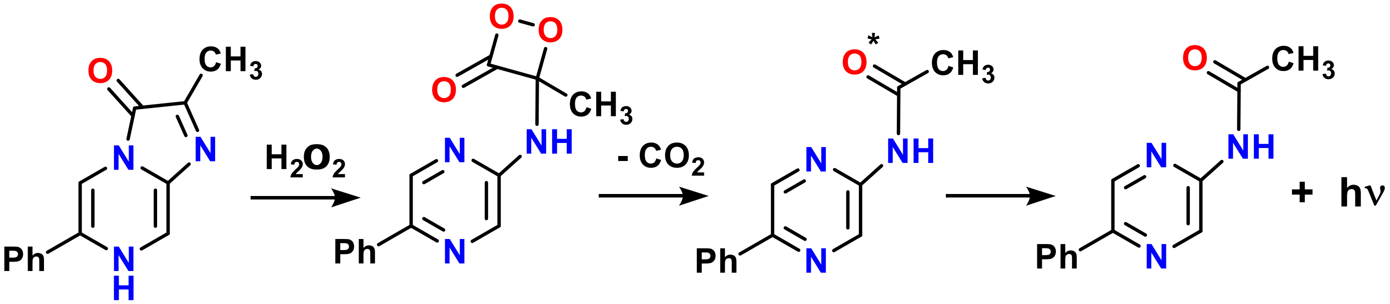
Cypridina: Luciferin Analog

Cypridina dentata (small planktonic crustaceans)



CLA; R = H

MCLA; R =CH_3O

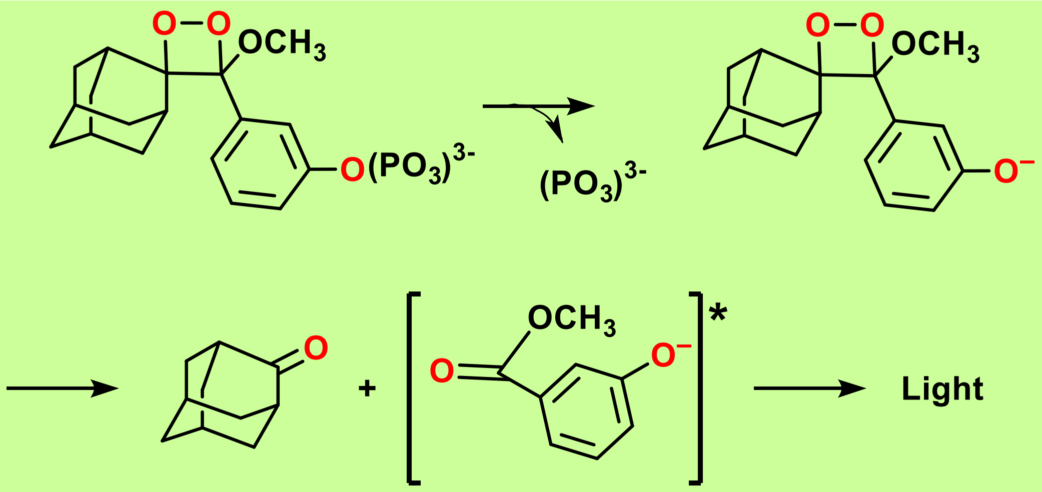


Ref: K. Akutsu et al., 1995: J. Chem. Soc. Perkin Trans. 2, 1699-1706

Chemiluminescence of 1,2-Dioxetane Phosphates as Bioanalyte

The use of 1,2-dioxetane chemiluminescent substrates with alkaline phosphatase (AP) enzyme labels provides highly sensitive detection for numerous immunoassay and nucleic acid detection formats. Current applications include membrane-based detection of proteins and nucleic acids, immunoassays, microplate-based nucleic acid detection and, increasingly, array-based detection.

Adamantyl-1,2-dioxetane phosphates that are direct substrates for alkaline phosphatase have been successfully used for bioanalyte and enzyme detection. Hydrolytic dephosphorylation of adamantyl-1,2-dioxetane phosphate substrates by AP results in the formation of a metastable anion, which fragments further to form an excited-state anion that emits light



POLITECNICO DI MILANO

Photo Reactions : Photochemistry

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”

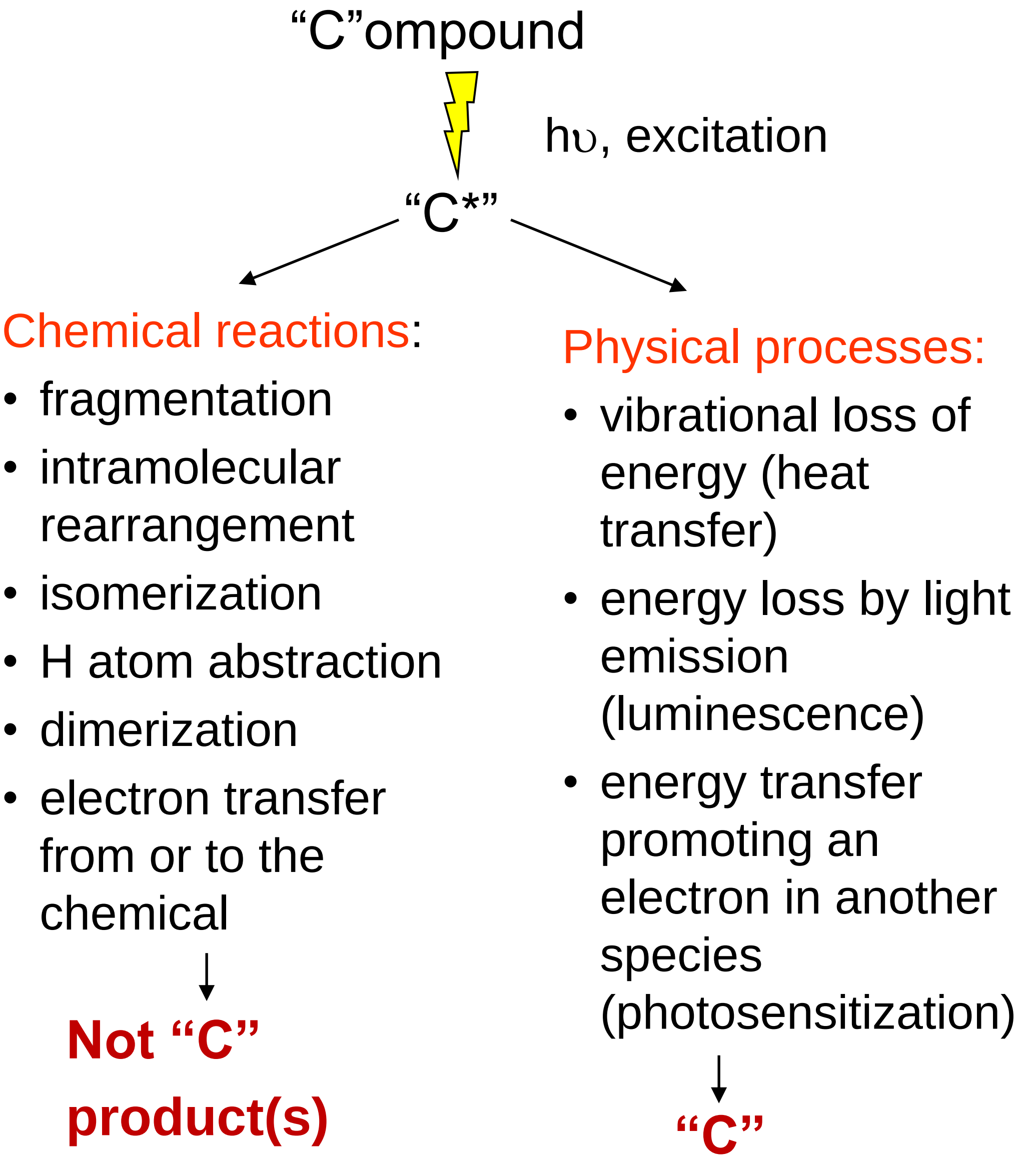
Excited State Reactions

- Reactions of electronically excited states occur initially on a potential energy surface which is not the ground state of the system.
- Reaction fastest if it can proceed in adiabatic manner – reactants and products correlate
- Hence likely to have different transition state and primary products.
- However potential surface crossings may also lead to ground state products
- Photon excitation not equivalent in general to heating
- Redox reactions more probable than in ground state

Fate of Excited Species

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

low activation energies: 10-30 kJ·mol^{-1} in solution



“C”ompound

hυ, excitation

“C*”

Chemical reactions:

- fragmentation
- intramolecular rearrangement
- isomerization
- H atom abstraction
- dimerization
- electron transfer from or to the chemical

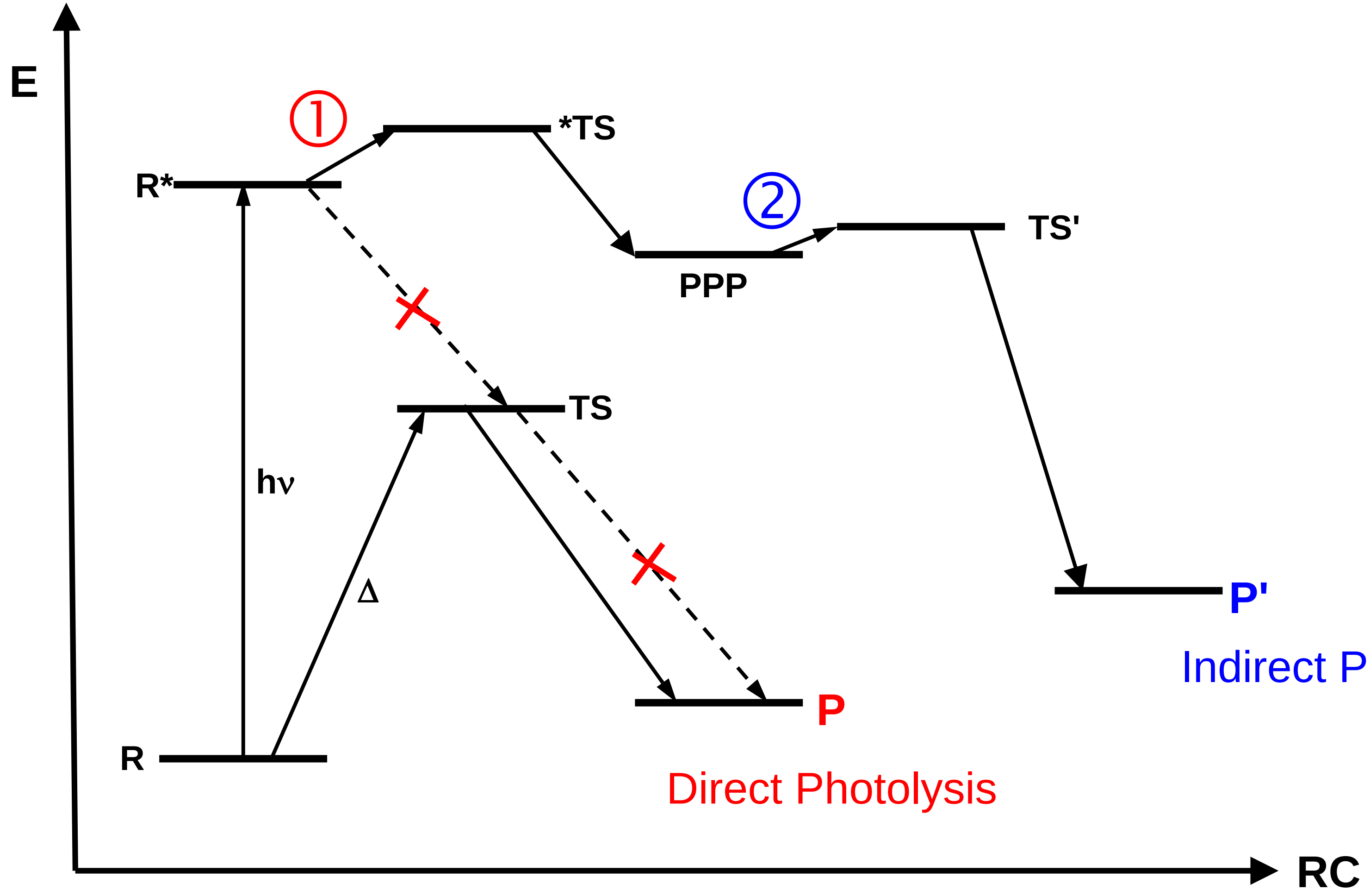
Not “C” product(s)

Physical processes:

- vibrational loss of energy (heat transfer)
- energy loss by light emission (luminescence)
- energy transfer promoting an electron in another species (photosensitization)

“C”

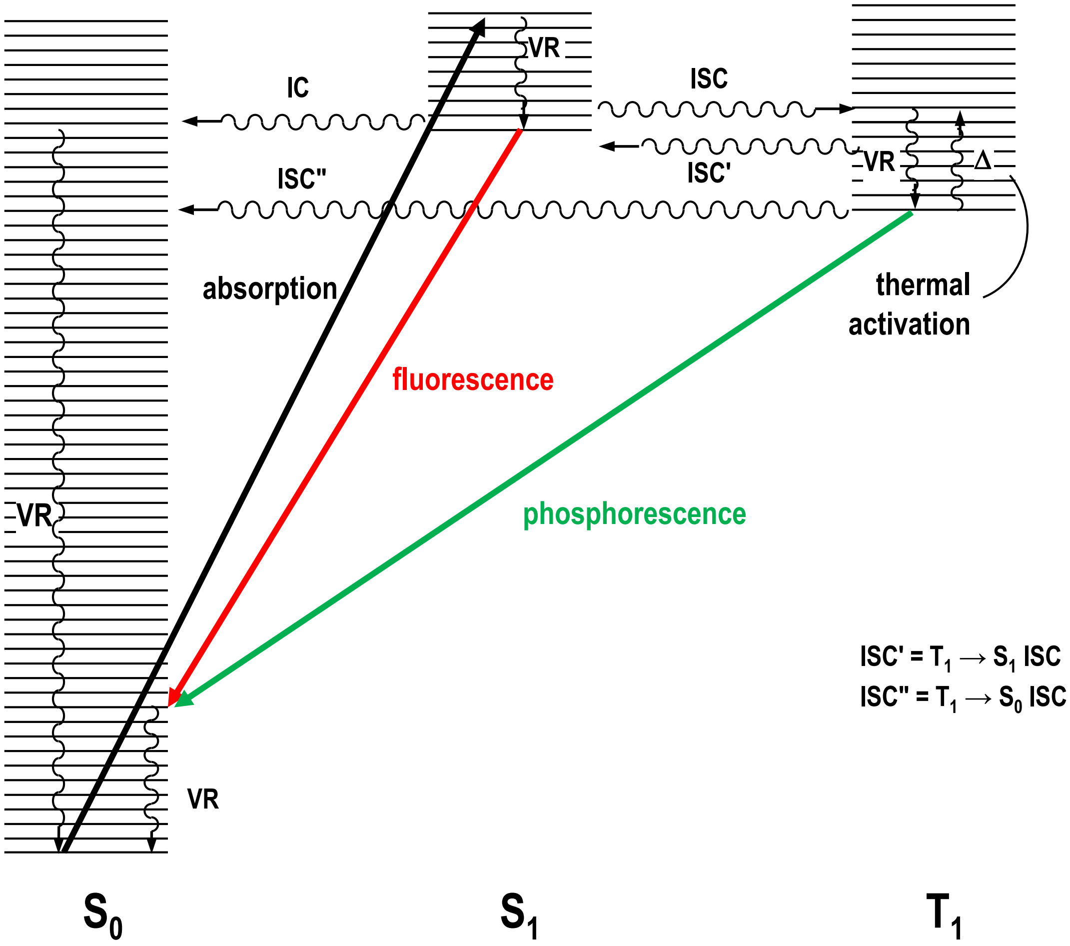
Schematic of Photochemical Process



Indirect Photolysis

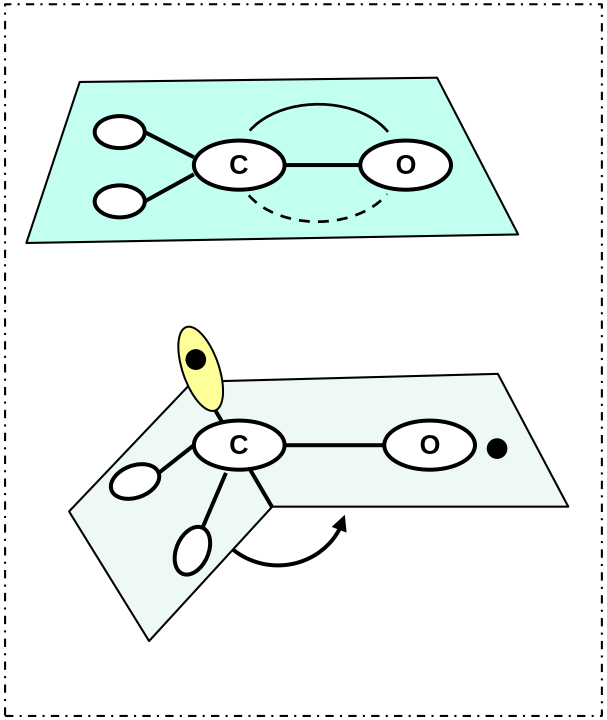
Direct Photolysis

Effects of Competing Processes



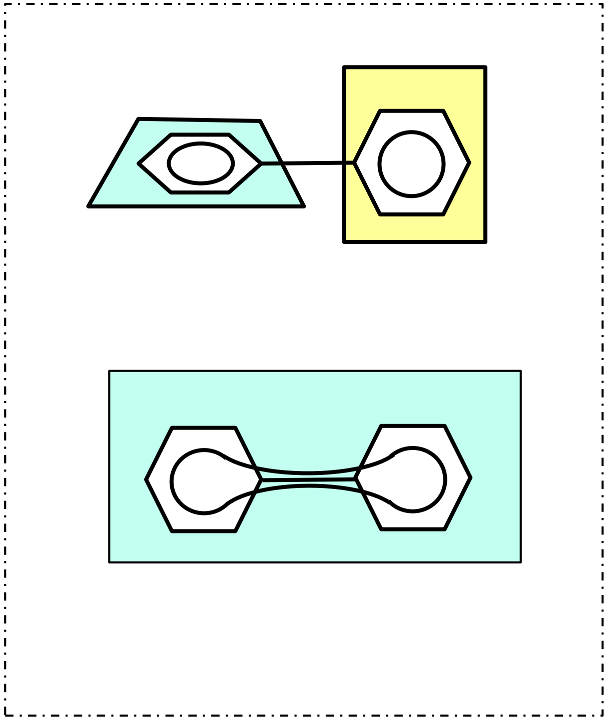
Slow phosphorescence and possibly slow T_1-S_0 means that in many cases triplet state may have greatest role in photochemistry

Geometry Changes



M

M*



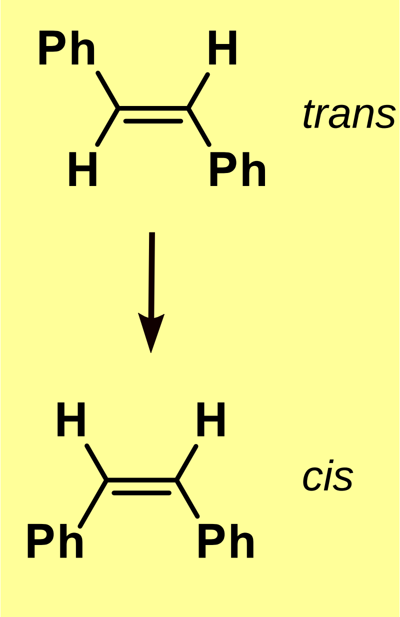
Biradical –

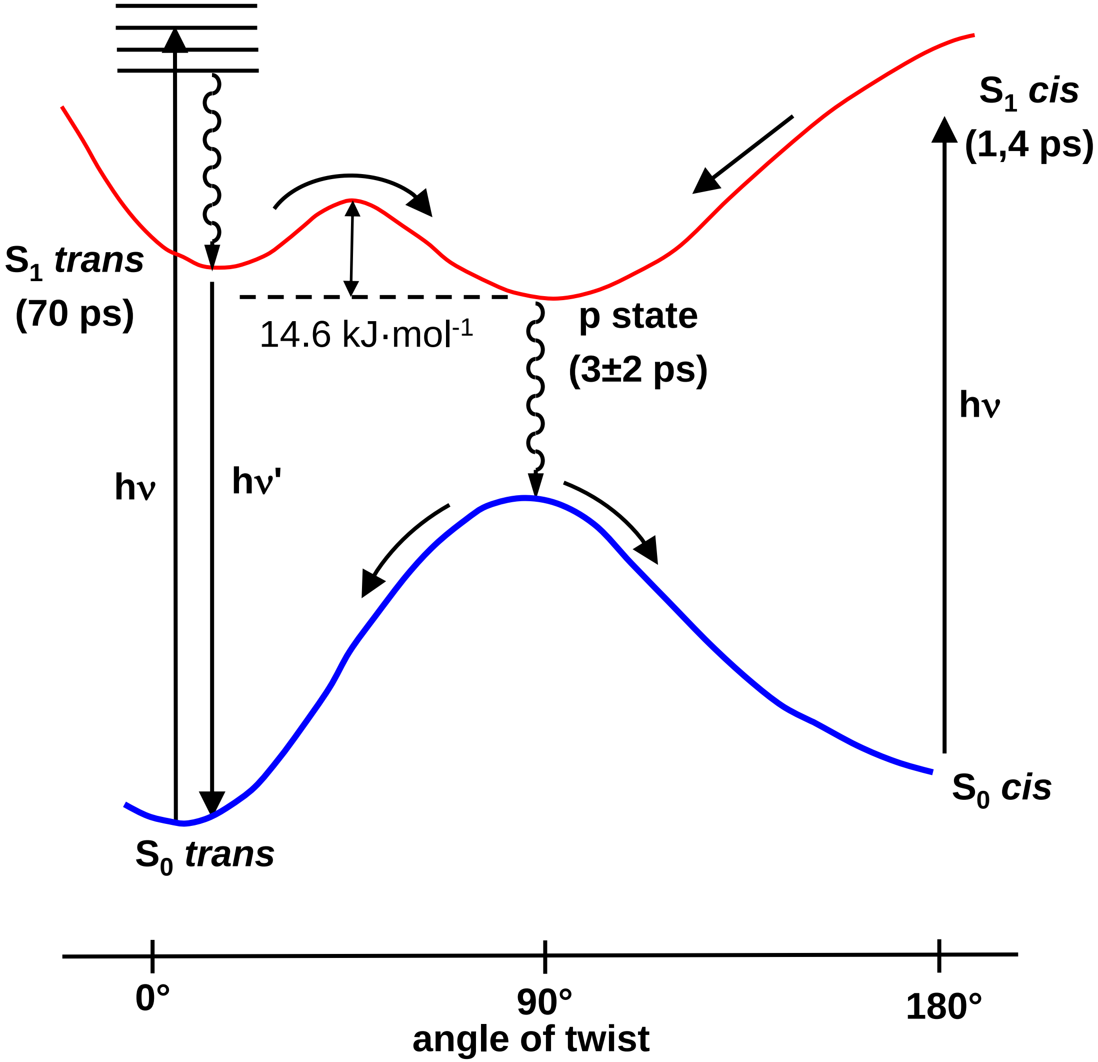
almost tetrahedral

Excimer like interaction between two rings.

Example of Effect of Geometry Change in Excited State: Isomerization of Stilbenes

Ph-CH=CH-Ph





Change of Dipole Moment

e.g., Formaldehyde

- S_0 state $\mu = 2.3D$
- $^1(n\pi^*)S_1$ state $\mu = 1.6D$

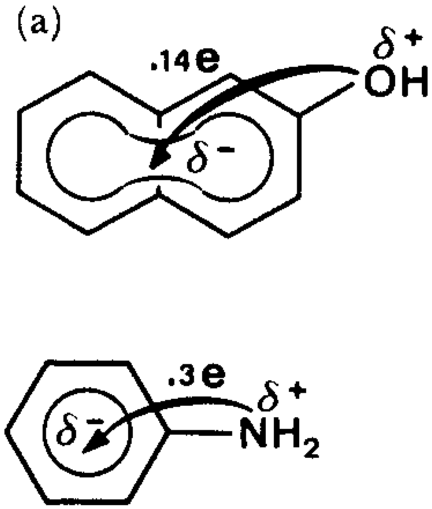
4-Nitroaniline

- S_0 state $\mu = 6D$
- S_1 state $\mu = 14D$

Indicate major changes in charge distribution (charge transfer) on excitation

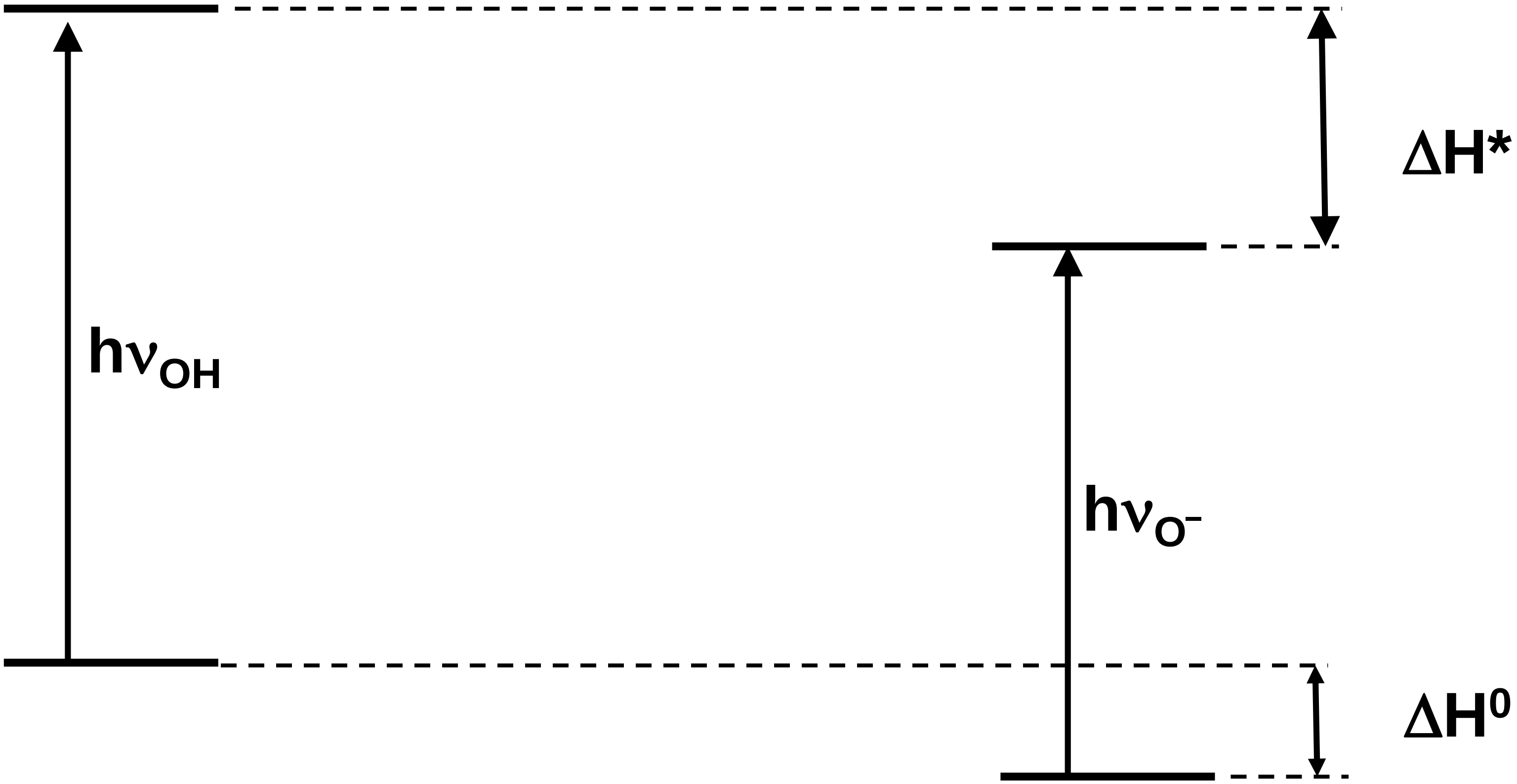
Acid-Base Behaviour

- Phenols – pK_a of excited singlet state up to 6 units smaller
- Amino-aromatics less basic in excited state



- Aromatic carboxylic acids pK_a up to 8 units higher in excited state
- Triplet states typically similar pK_a to ground state (zwitterionic character suppressed due to spin correlation)

Forster Cycle to Calculate pK$_a$

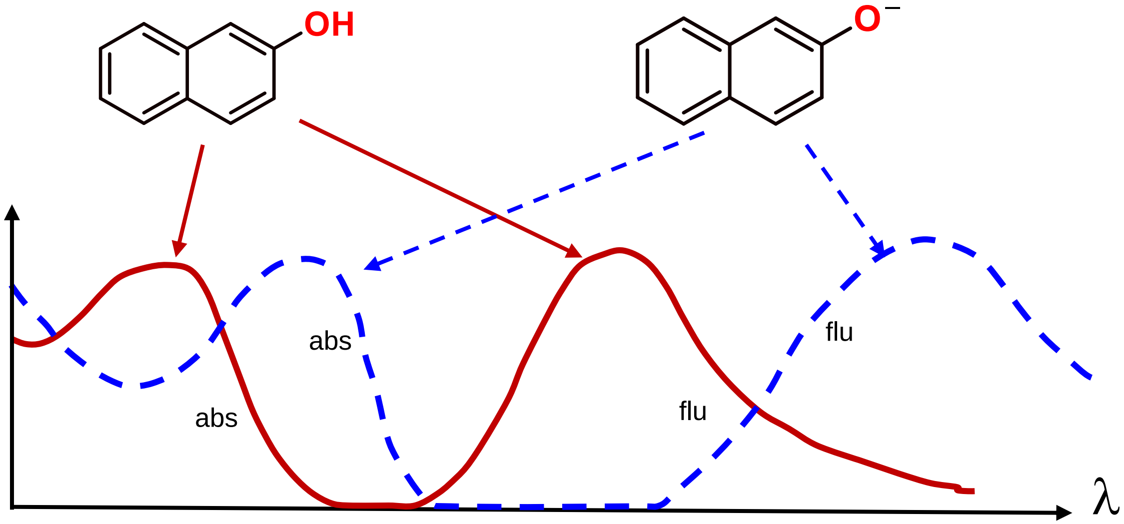


Forster Cycle for 2-Naphthol

$$\Delta G_1 - \Delta G_2 \approx \Delta H_1 - \Delta H_2 \approx N_A(h\nu_1 - h\nu_2) \approx -RT\ln\frac{K_{a1}}{K_{a2}}$$

$$= \frac{RT}{2.3}(pK_{a1} - pK_{a2})$$

$$pK_{a1} = -\log K_{a1} = -\frac{1}{2.3}\ln K_{a1}$$



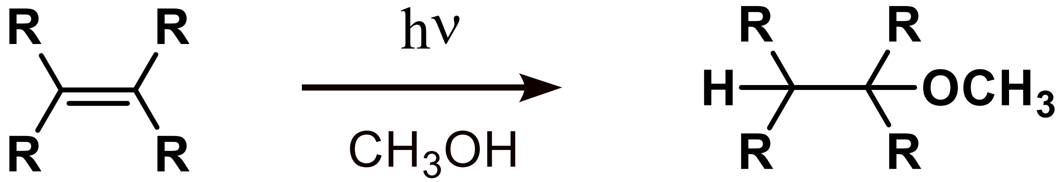
Shift of absorption and fluorescence spectra

Photochemically Induced Bimolecular Reactions

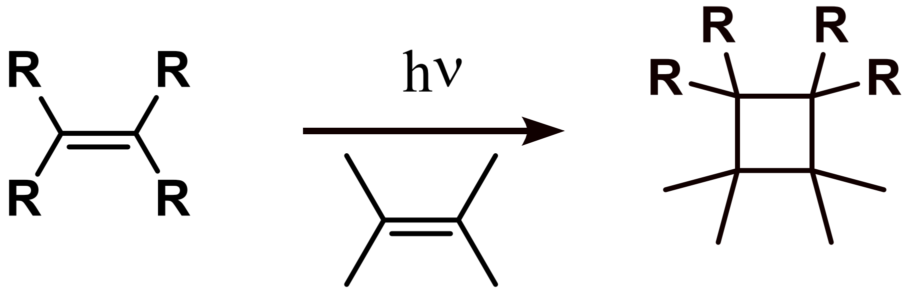
- **Additions** - Unsaturated molecule uses its weakened π-bond to form two new σ bonds
- Reductions by H atom extraction or electron transfer
- Oxygenations
- Substitutions

Photochemically induced Addition Reactions

a) Addition with σ-bond breaking

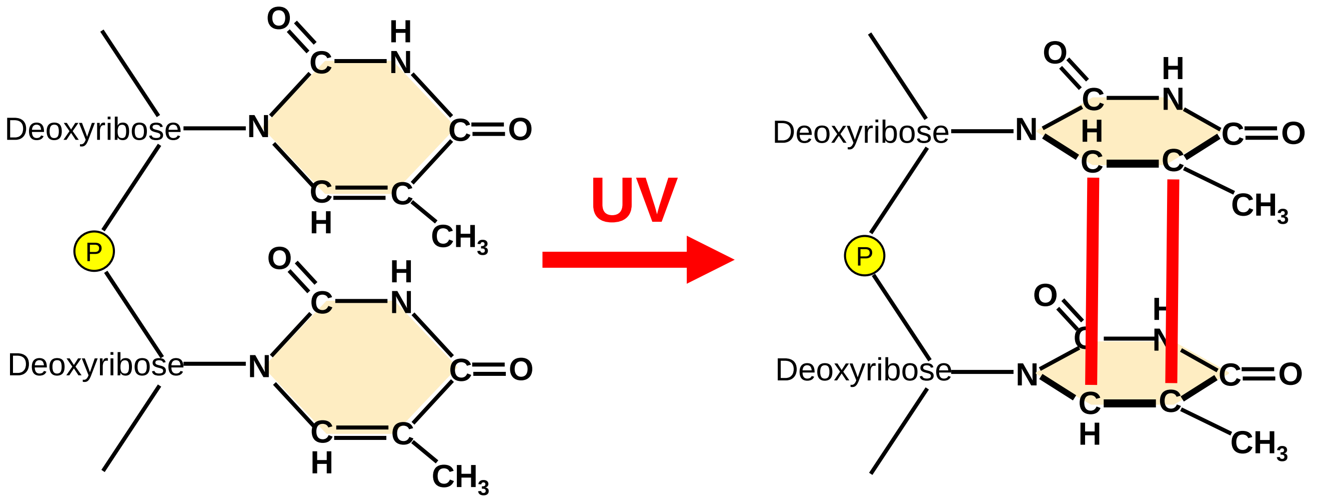


b) Addition with π-bond breaking (dimerization)



DNA: UV Photochemistry

Thymidine dimers are generated by exposure to UV light



Two thymine residues

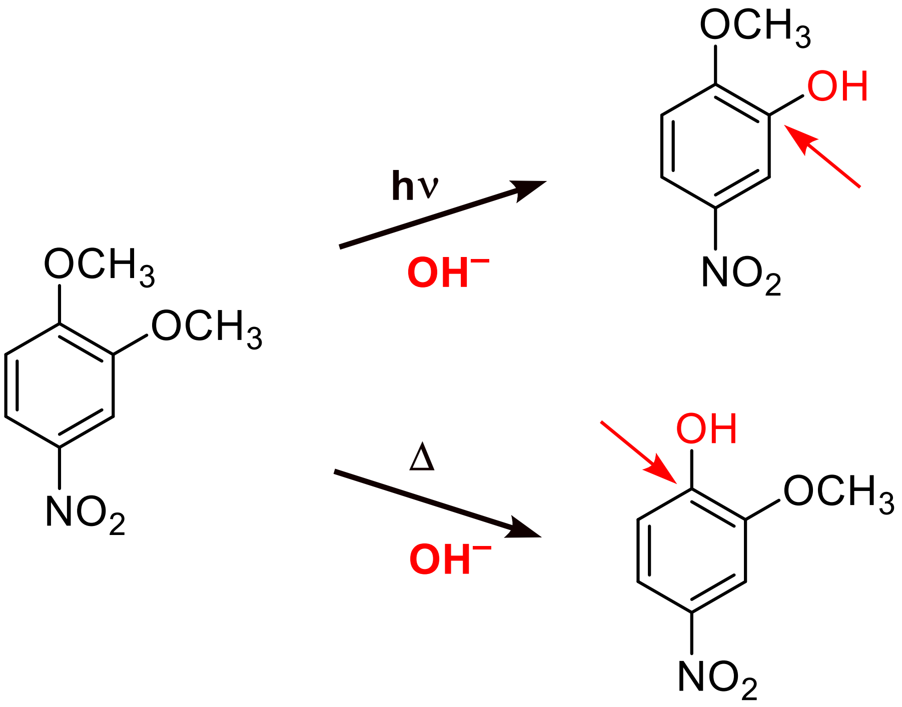
Thymine-thymine dimer residues

Two DNA bases lined together

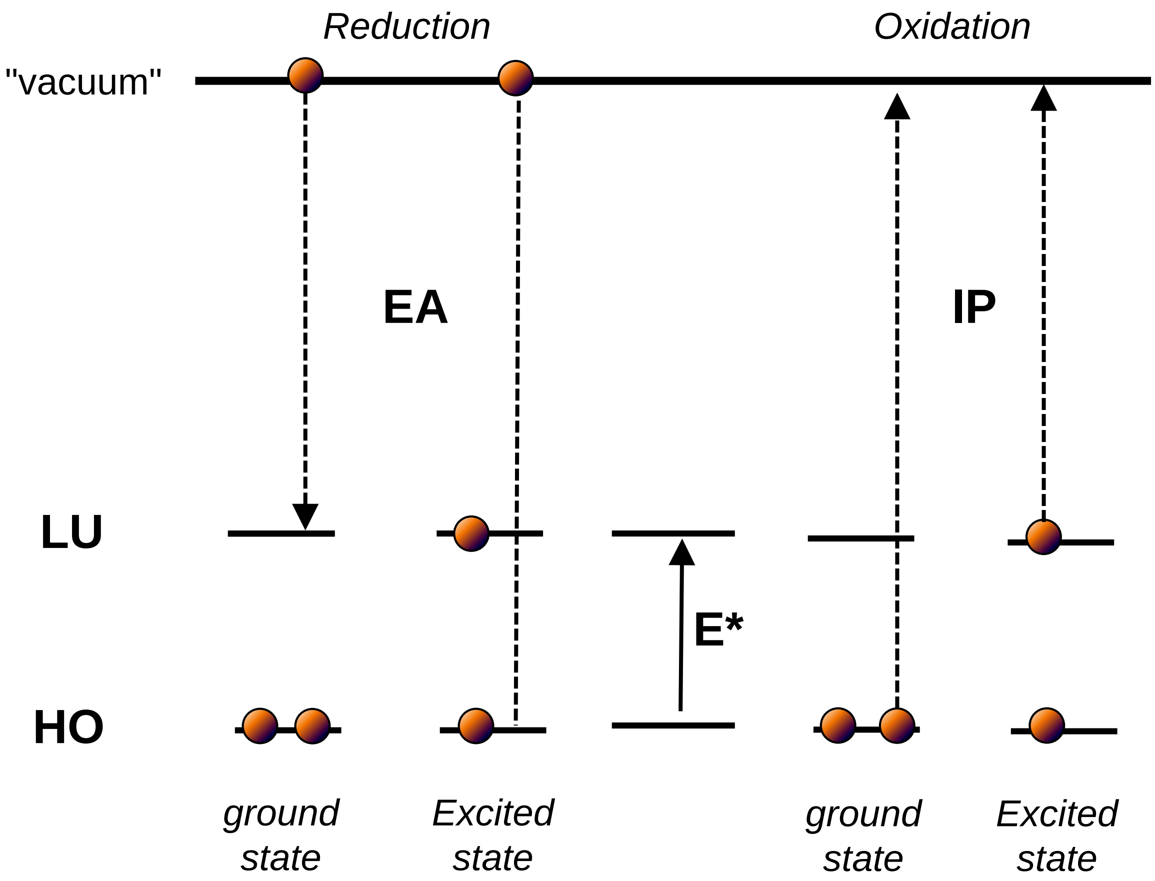
Photons cause two DNA bases to link: this kills the cells containing the irradiated DNA

Substitution

- Nucleophilic substitution at aromatic ring shows opposite trends to ground state
- e.g. electron withdrawing groups activate meta positions, electron-donating groups activate ortho and para positions.



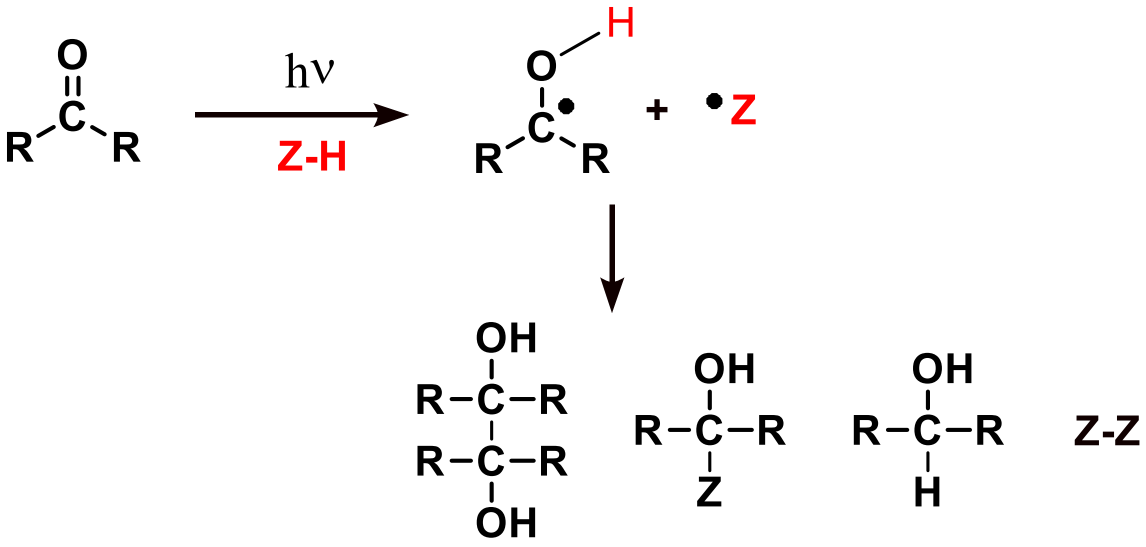
Redox Characteristics



- Electronically excited states are stronger reducing agents and stronger oxidising agents than the ground state

Photoreduction

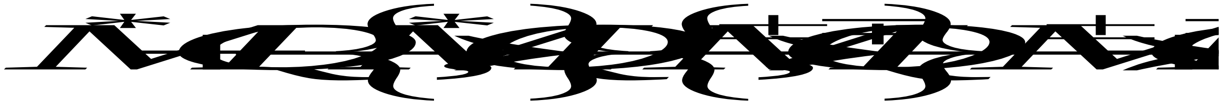
- Photoreduction of carbonyl compounds
- - Half filled n orbital on oxygen in excited state acts as strong electron acceptor



ZH = H atom donor
e.g., alcohols, ethers

Electron Transfer

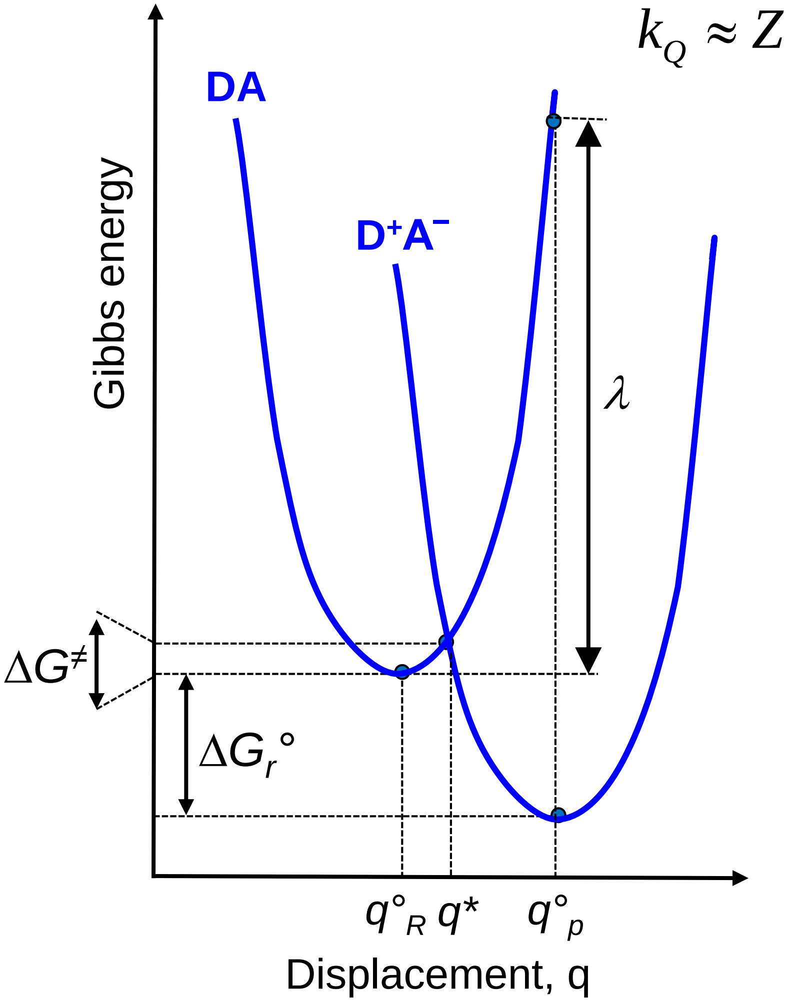
- In high polarity solvents, first step of photochemical process may involve electron transfer and ion pair formation



- Electron transfer takes place within intermediate complex

- Non-adiabatic process – effectively a change of electronic state within the complex.

Marcus Electron Transfer Theory



$$k_Q \approx Z \exp\left[-\frac{\Delta G^{\pm}}{RT}\right]$$

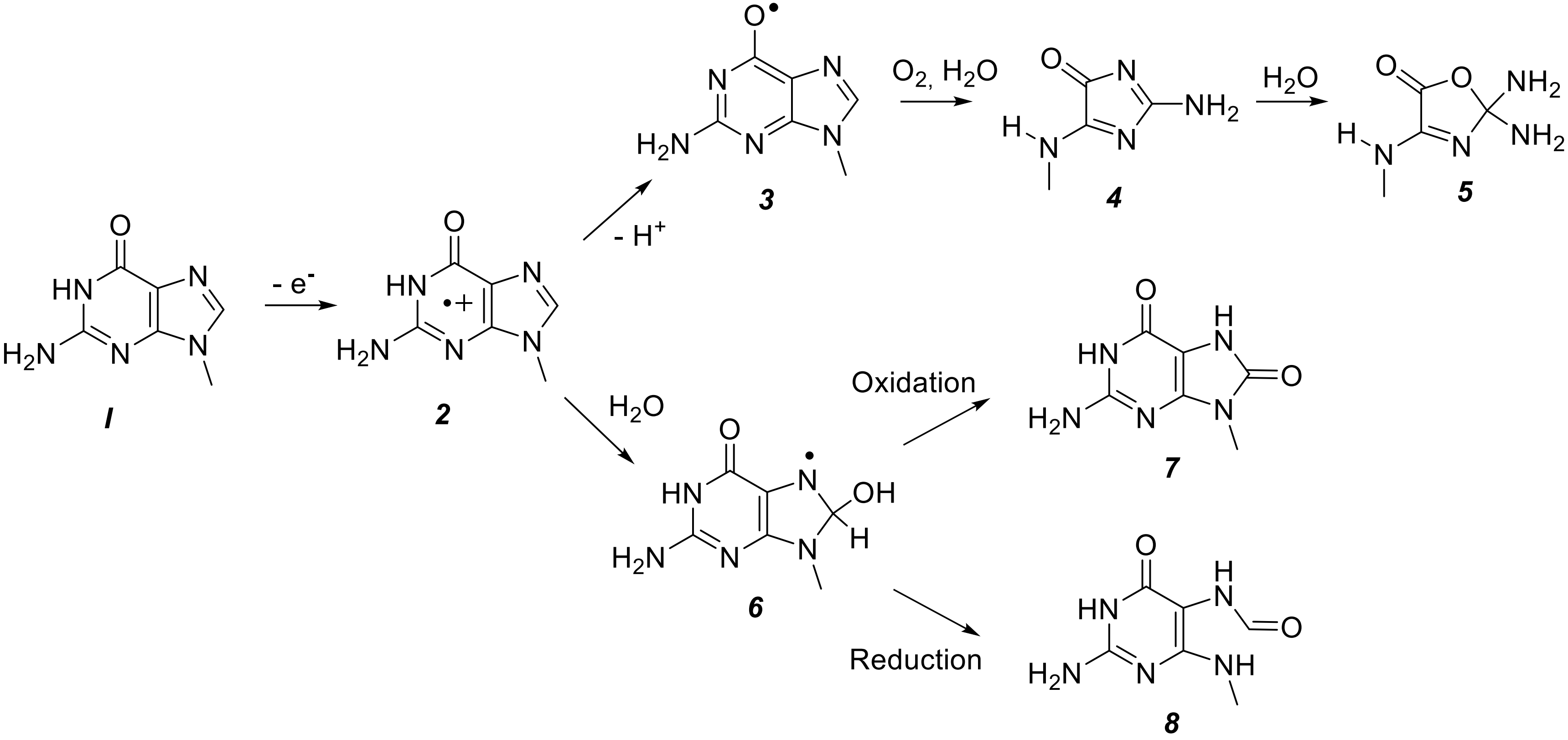
$$\boxed{k_Q \approx Z \exp\left[-\frac{\left(\Delta G^{\circ}+\lambda\right)^2}{4\lambda RT}\right]}$$

Solvent molecules in fluctuation – constant change in energy of donor-acceptor complex

At critical solvent configuration D*A complex has same free energy as D^+A^-

Gibbs energy of activation – Free energy required to reach this configuration.

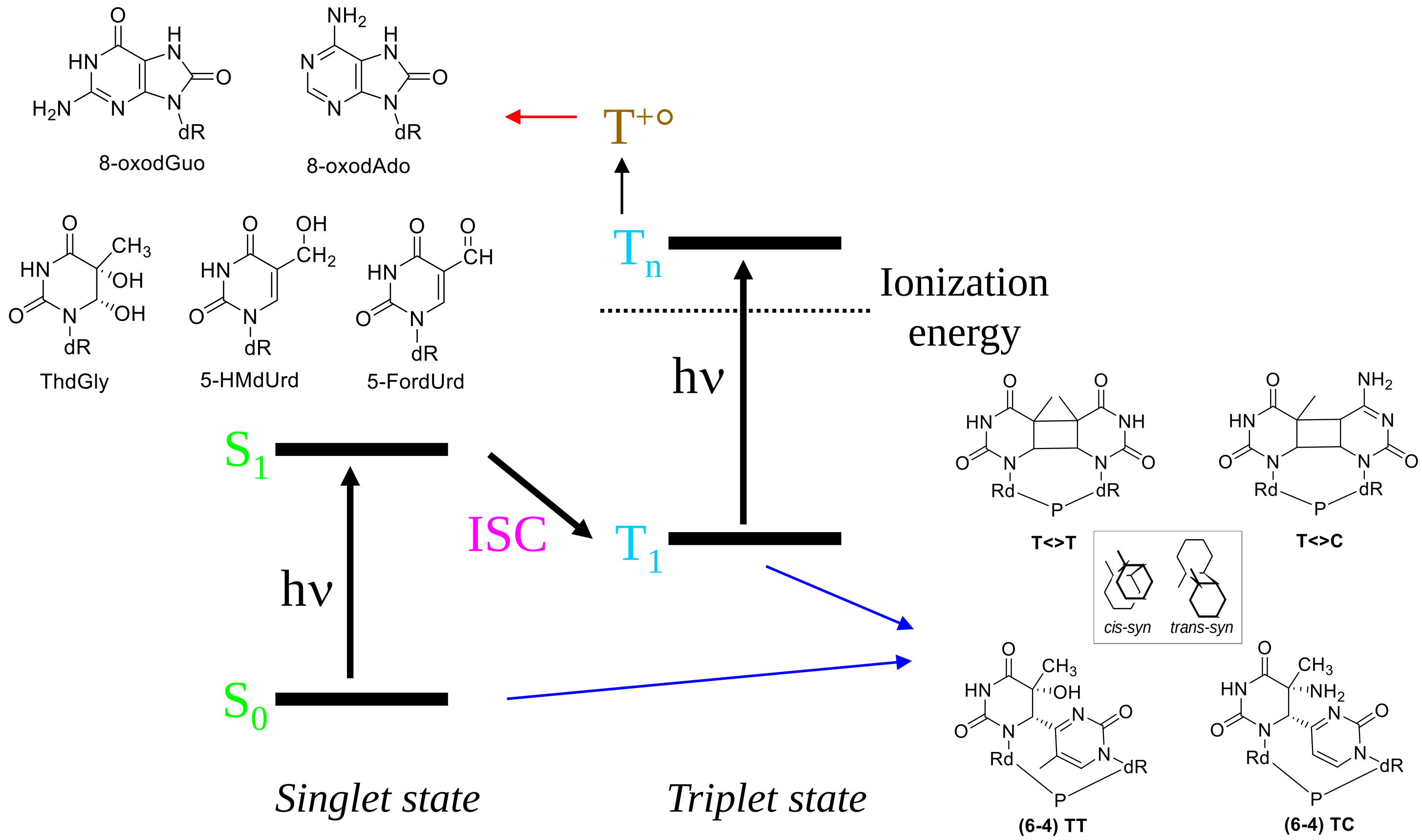
Main Chemical Reactions of the Guanine Radical Cation



Kasai et al, JACS, 1992
Cadet et al, JACS 1994
Gasparutto et al, JACS 1998
Ravanat et al, JACS 2003

Biphotonic Products can be Observed with Intensive Irradiation (laser)

Biphotonic products:
oxidized nucleosides



Monophotonic products:
pyrimidine dimers

Photochemical Processes

Examples:

a) Aromatic substitution

b) Intramolecular substitution

c) Fragmentation, intramolecular hydrogen-abstraction, cyclization

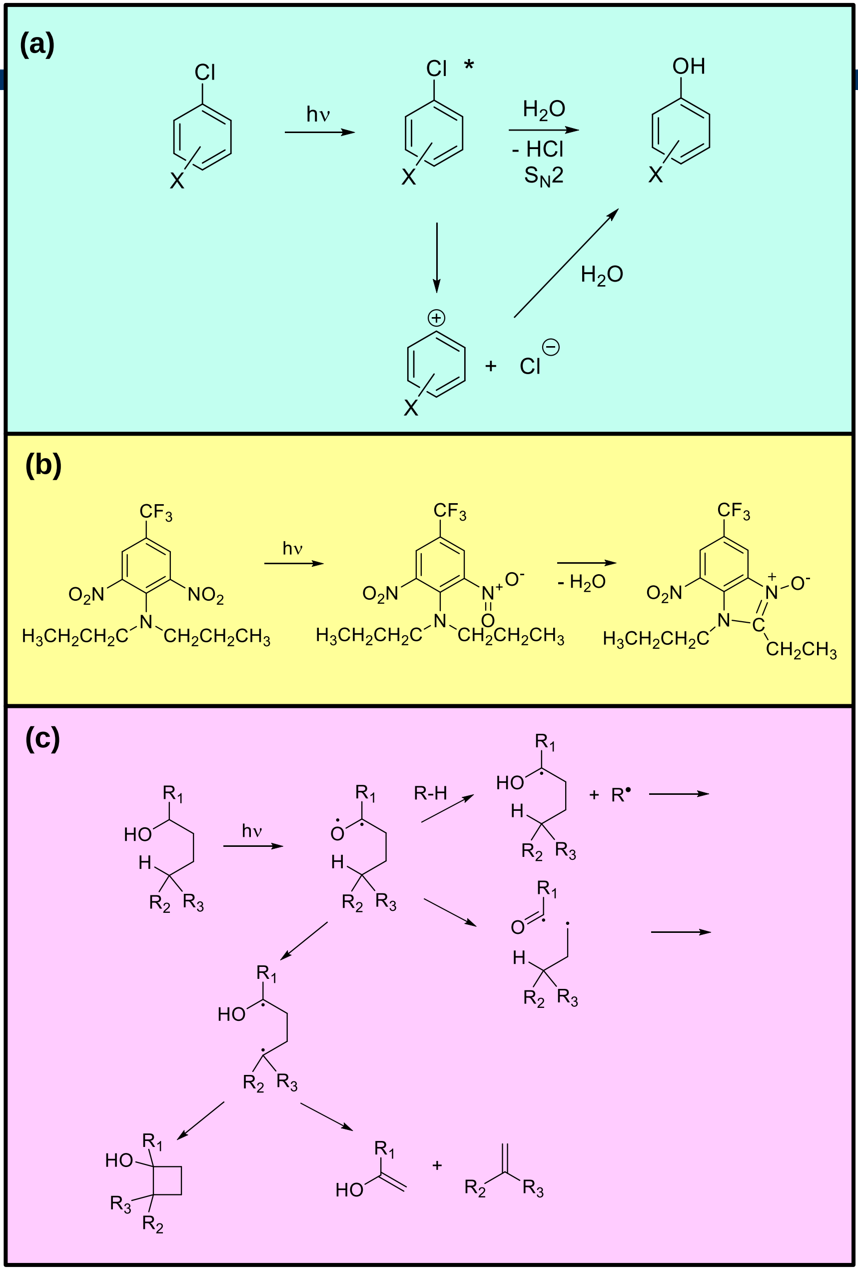


Photo-oxidation of Polymers

polyolefines (PE, PP) = photo-oxidation is the dominating mechanism.

These polymers **do not have an inherent absorption** at wavelengths present in terrestrial sunlight (>290-400 nm)

photolysis can not play an important role.

Nevertheless, irradiation of these polymers with terrestrial wavelengths results in **accelerated degradation – especially for PP**

This can be ascribed to **impurities** that are formed during storage and processing.

Due to photolytic reactions of these absorbing species, **radicals are formed** that initiate the photo-oxidation reaction.

Impurities Responsible for the Initiation

Hydroperoxide >> carbonyls > unsaturations

- complex [PH...O_2], atmospheric impurities (SO_2, NO), aromatic hydrocarbons, singlet oxygen

- Main steps of photo-oxidation
  - Initiation
  - Propagation
  - Branching
  - Termination

Photo-oxidation of Polymers

In contrast to polyolefins, the majority of engineering plastics

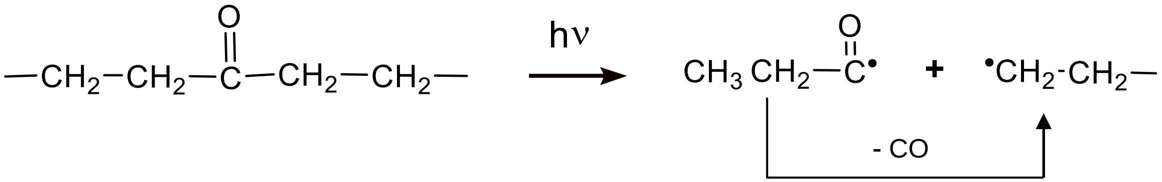
e.g. aromatic polyesters, polyamids, polyuretanes, polycarbonates, polyketones etc.) do have absorptions at wavelengths being present in terrestrial sunlight, so that for these polymers photolysis can play an important role too.

For these polymers in principle there are three mechanisms that can describe their light-induced degradation:

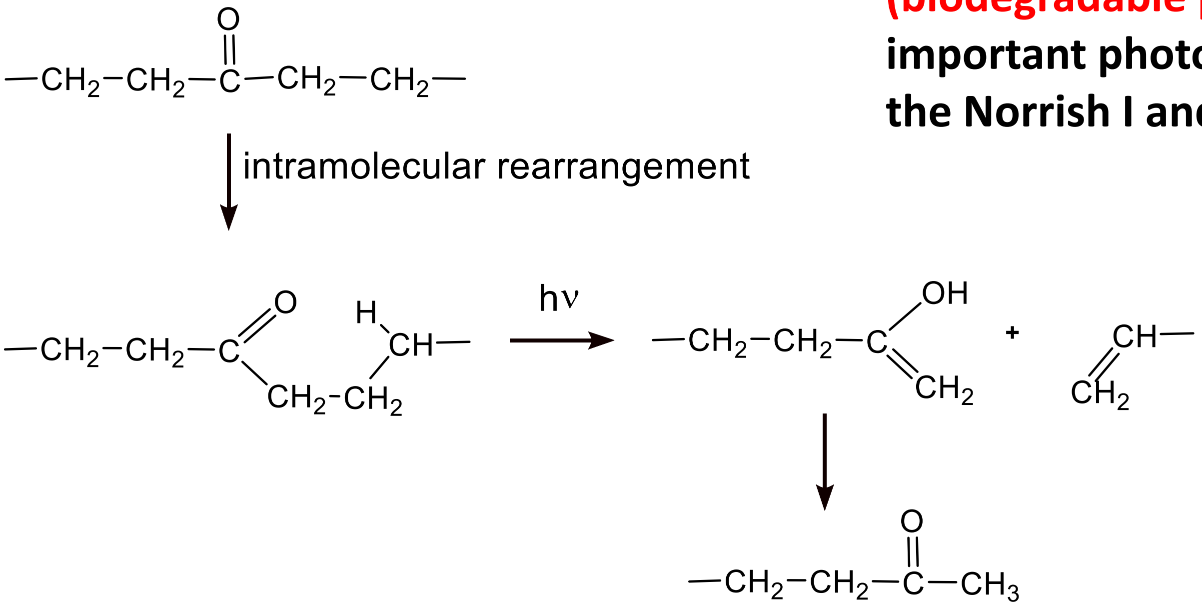
- **Photolysis** - absorption as a result of the inherent polymeric structure results in chemistry causing changes in the molecular structure;
- **Photo-oxidation initiated by photolysis** reactions of the polymer itself;
- **Photo-oxidation initiated by impurities** not part of the inherent polymer structure.

Photolysis: Norrish I, Norrish II of Carbonyl Polymers

Norrish I reaction

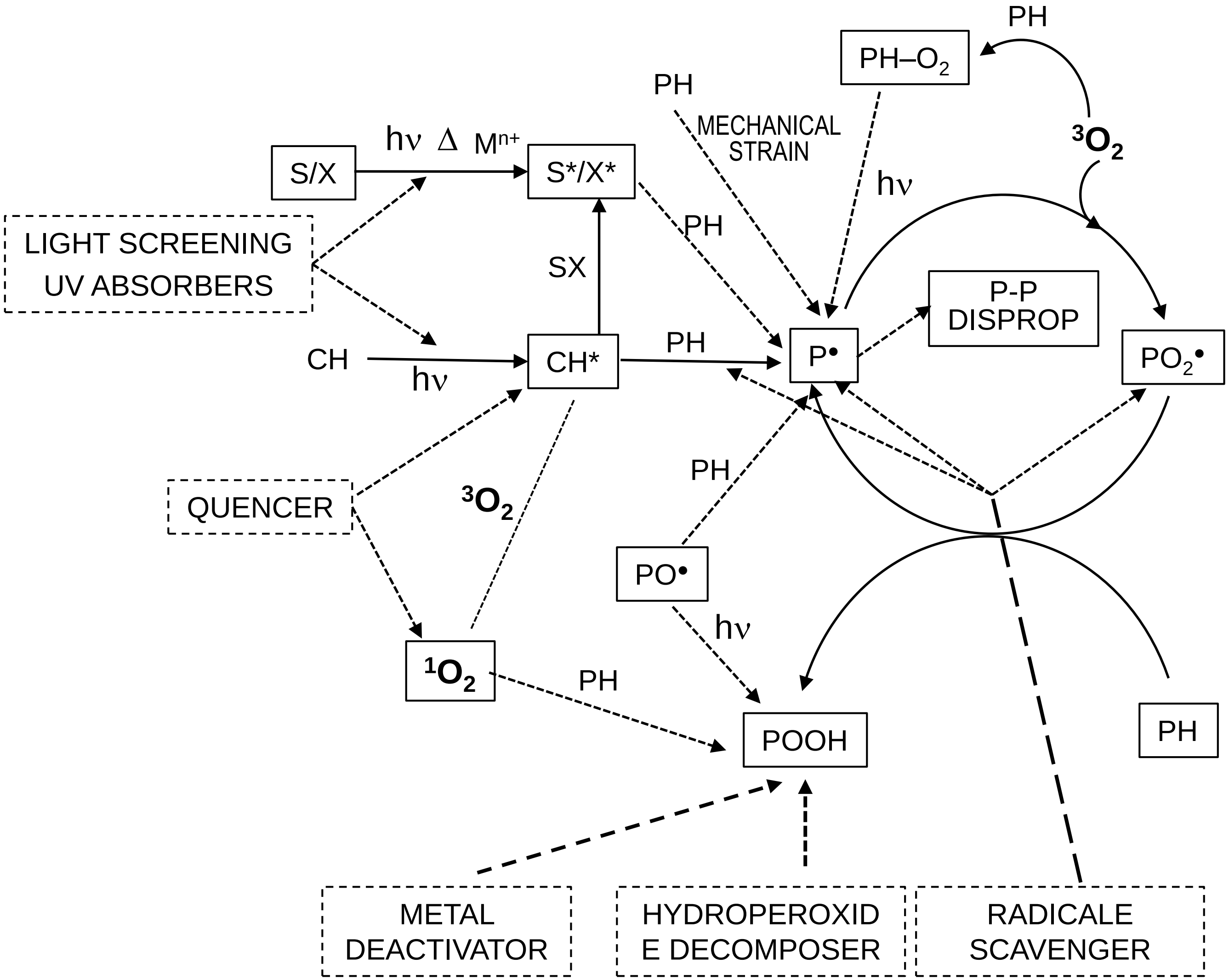


Norrish II reaction



For polyamides and polyesters (biodegradable polymers) the most important photolytic reactions are the Norrish I and II reactions.

General Scheme for Degradation and Stabilization of Polymers



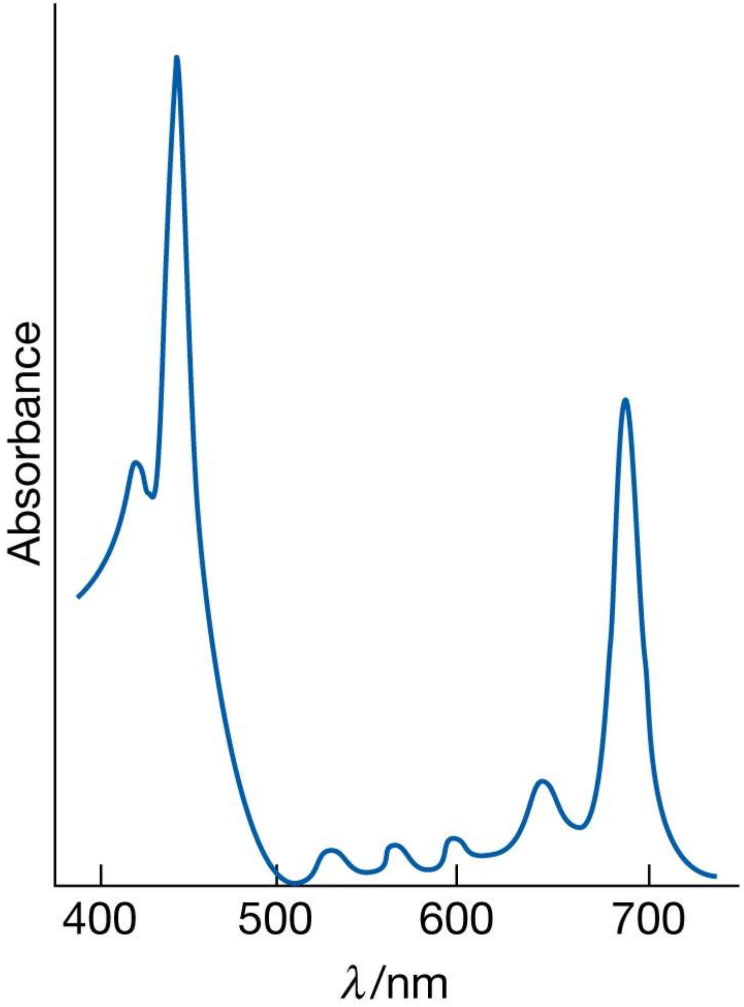
Photosynthesis

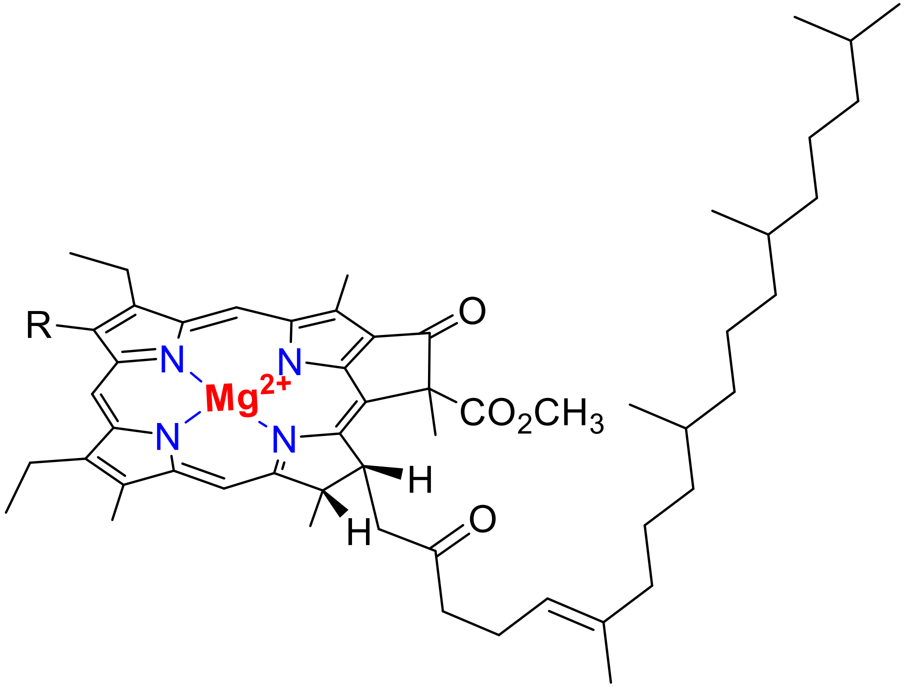
- Two parallel photosystems in plants PSI and PSII – chlorophyll protein complexes
- Light absorption by harvesting chlorophyll molecules followed by fast energy and electron transfer processes
- Electrons funnelled into reaction centre to cause net reduction of H_2O to O_2 and conversion of NADP to NADPH, plus fixation of CO_2.

$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$$

saccharides and *polysaccharides*

Absorption Spectrum of Chlorophyll in Solution





1 Chlorophylls a (R = CH_3) and b (R = CHO)

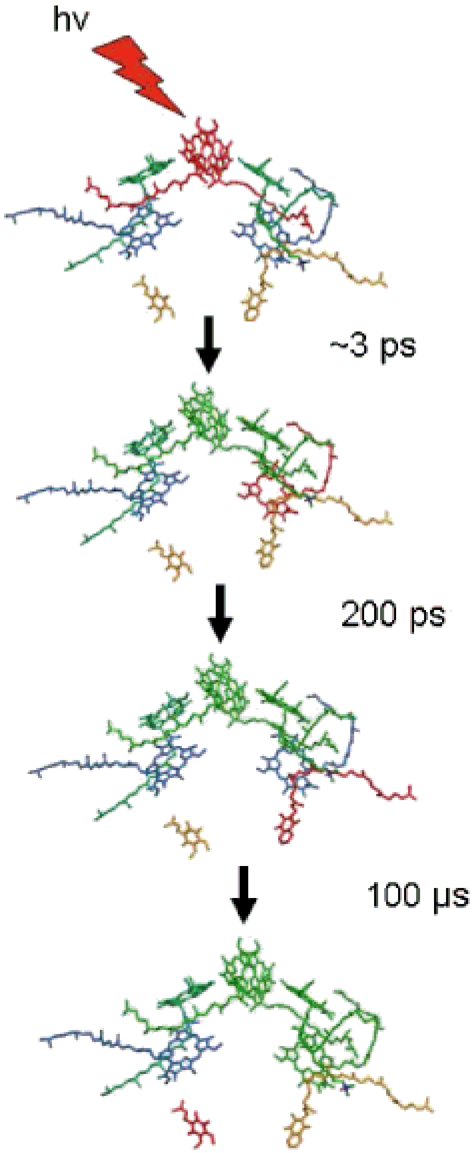
Photosynthetic Bacteria

Photosynthetic bacteria	3×10^9 years
Higher plants	0.5×10^9 years

Rhodobacter sphaeroides highly studied model system: Contains only one photosystem, and bacteriochlorophyll instead of chlorophyll as active pigment

Photosynthesis in Bacteria

- Step 1a: Light harvesting (absorption) by chlorophyll and auxiliary pigments.
- Step 1b: Rapid multistep Forster energy transfer to reaction centre, “special pair” of chlorophyll a.
- Step 2: Rapid (≈ ps) electron transfer to pheophytin
- Step 3: Charge separation by electron transfer via quinones and further electron transfer
- Steps 4 - x: Reduction processes at reaction centre
- Studies of these processes by ps or fs flash photolysis.



Electron Transfer in Photosynthesis

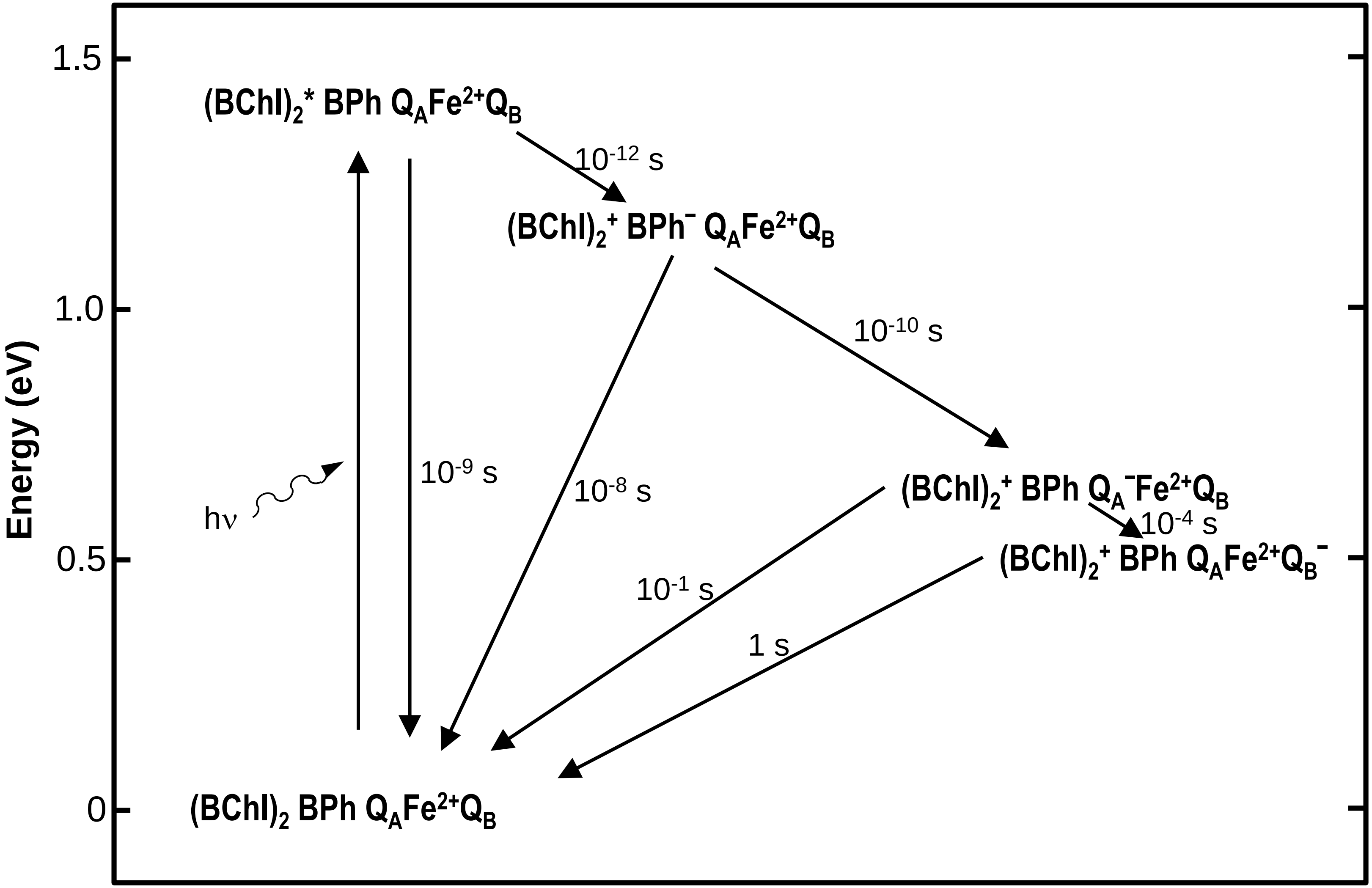


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Photo Reactions:
Photosensitization

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”

Indirect Photolysis

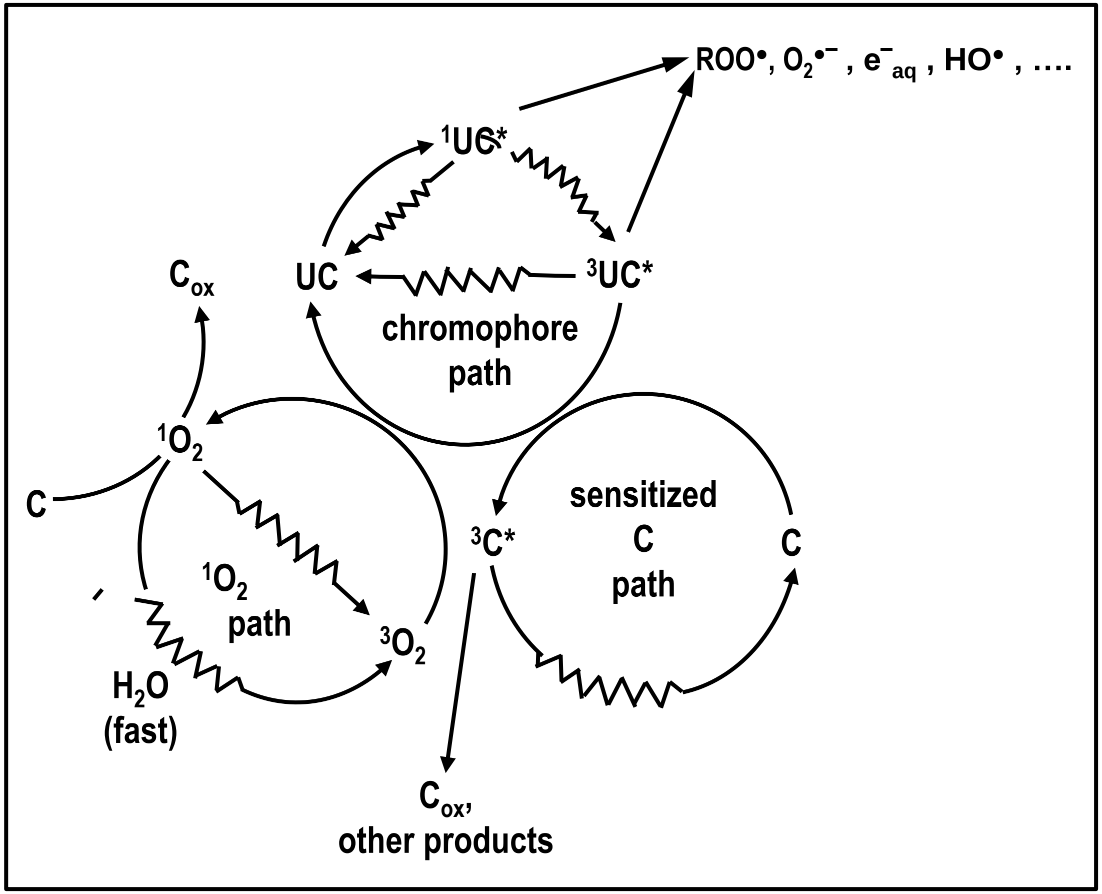


Figure 13.12 – Pathways for indirect photolysis of organic chemical (C). UC refers to unknown chromophores. Wavy arrows symbolize radiationless transition from Zafiriou et al. 1984)

Important reactants (electrophiles):

- ✓ Singlet oxygen ($^1O_2$)
- ✓ Peroxy Radicals ($ROO^\bullet$)
- ✓ Hydroxyl radicals

Photosensitization

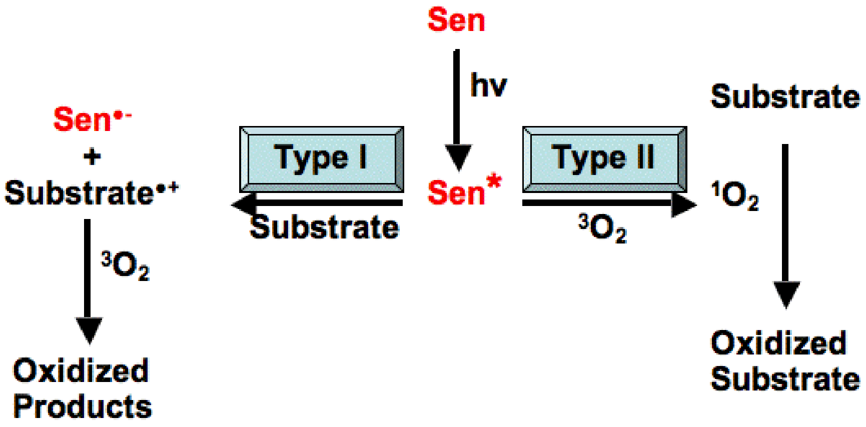
Photosensitization is a reaction to light that is mediated by a light-absorbing molecule, which is not the ultimate target. Photosensitization can involve reactions within living cells or tissues, or they can occur in pure chemical systems. In photobiology, we are concerned with the reactions in living systems.

In some cases, the molecule that absorbs a photon is altered chemically, but does not change any other molecule in the system. In other cases, the molecule that absorbs the photon ultimately alters another molecule in the system. In the latter process (photosensitization), the molecule that absorbs the photon is called the photosensitizer (or simply sensitizer), and the altered molecule is the acceptor or substrate. Both the photosensitizer and light are required for photosensitization.

Photosensitizer **AND** **Light** → **Change in Organism**

Type I and II Sensitized Reactions

In photosensitized reactions, the absorbed photon excites the sensitizer (Sen) to one or more energy-rich state(s) (Sen*). The excited Sen* undergoes internal reactions that ultimately result in the chemical alteration of the substrate. This can occur in one of two types of reactions:



In the Type I reaction, the excited sensitizer reacts directly with the substrate, in a one-electron transfer reaction, to produce a radical or radical ion in both the sensitizer and the substrate (commonly resulting in a substrate radical cation (Substrate$^{\cdot+}$), and a sensitizer radical anion (Sen$^{\cdot-}$). In the presence of O_2, these radicals react further to produce oxygenated products. In the Type II reaction, the excited sensitizer transfers its excess energy to ground-state of O_2 ($^3O_2$), producing excited state singlet oxygen ($^1O_2$), and regenerating the ground-state sensitizer. Singlet oxygen then reacts with the substrate to generate oxidized products.

Efficient Photosensitizers and Photodynamic Action

Photosensitizers are molecules in which internal conversion is not efficient. Rather they transfer an electron to or from another molecule, or they transfer their energy of excitation to other molecules, often to molecular oxygen. In most cases, the reason that some molecules are so effective at electron transfer and/or energy transfer is that they very efficiently populate their excited triplet states. The relatively longer lifetime of the triplet state allows more time for energy and/or electron transfer to occur. So, most highly effective photosensitizers are characterized by high quantum yields for the production of their excited triplet state.

The term photodynamic action was coined near the turn of the 20th century to refer to a light-driven reaction in which a photosensitizer molecule reacts in an oxygen-dependent manner with a substrate, to produce a change in the substrate. While it is often used to refer to Type II reactions, its original definition can also include Type I reactions that involve oxygen. Note that oxygen is an important reactant in most photosensitization reactions, whether it is part of the initial reaction with the excited photosensitizer (Type II), or reacts with later products to "fix" the initial radicals as oxidized products (Type I).

Importance of Photosensitization

There are many ways in which photosensitization reactions impact our lives. For example, they are used in synthetic chemistry to produce products that would be much more difficult or expensive to produce by other means.

Examples of the biological relevance of photosensitization reactions are mainly related to a differential photosensitivity of targets. In addition, the requirement for both photosensitizer and light to produce an effect allows photosensitization reactions to be better controlled than conventional chemical reactions.

a) Photosensitization of viruses in blood banks.

b) Photosensitization of Cells in Photodynamic Therapy.

c) Photosensitization of plants and animals by photodynamic pesticides.

d) Photosensitization of plants and animals by naturally occurring photosensitizers.