Photochemistry

Photochemical principles; Rates of intramolecular processes and Intermolecular processes

Energy transfer

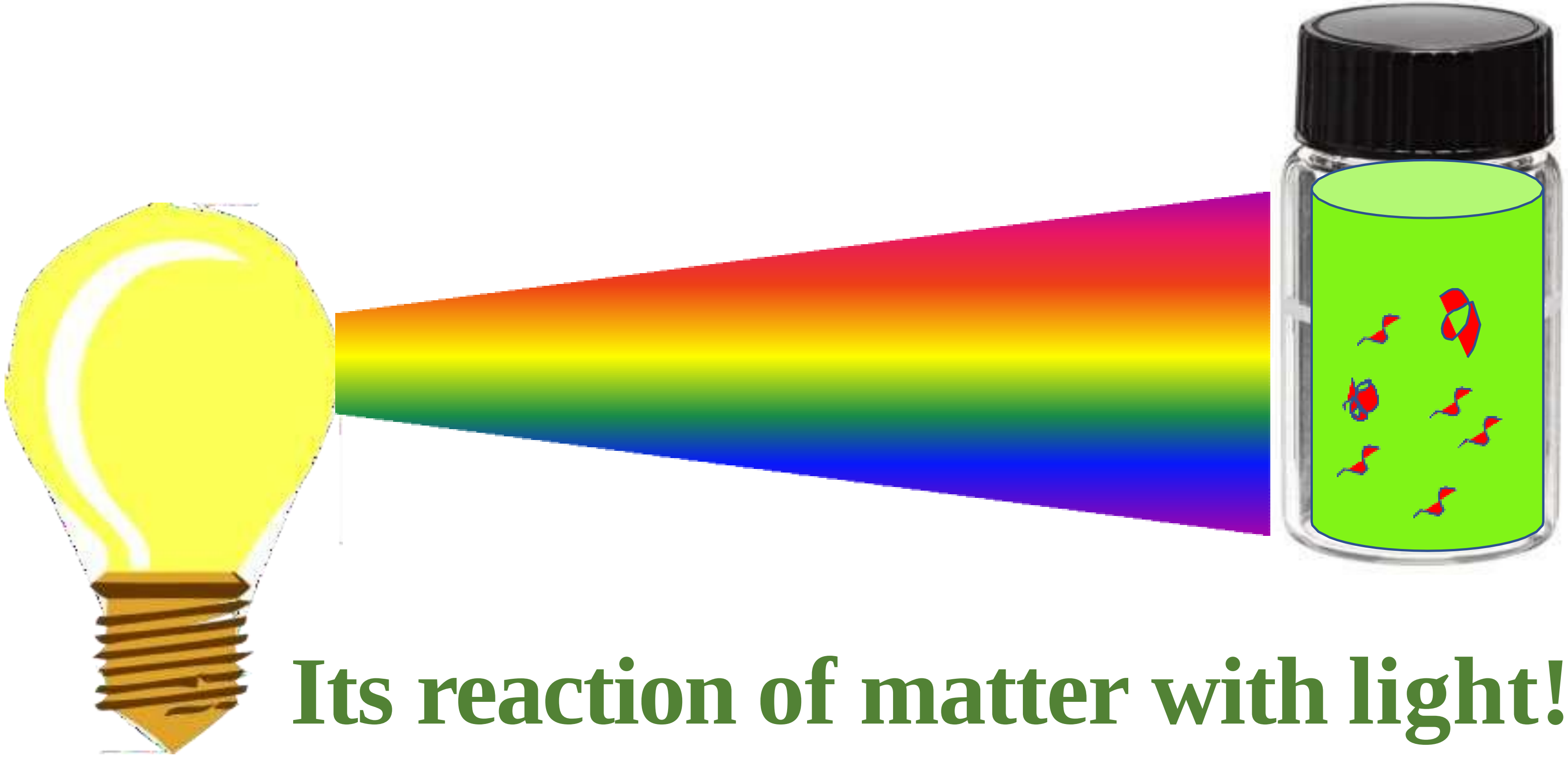
Photochemical reactions and their quantum yields

Photochemistry in nature

Special topics in photochemistry

What is Photochemistry?

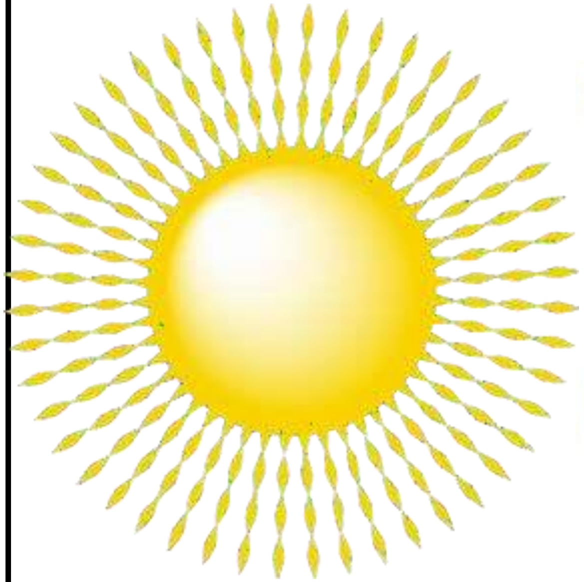
Mr. Photo

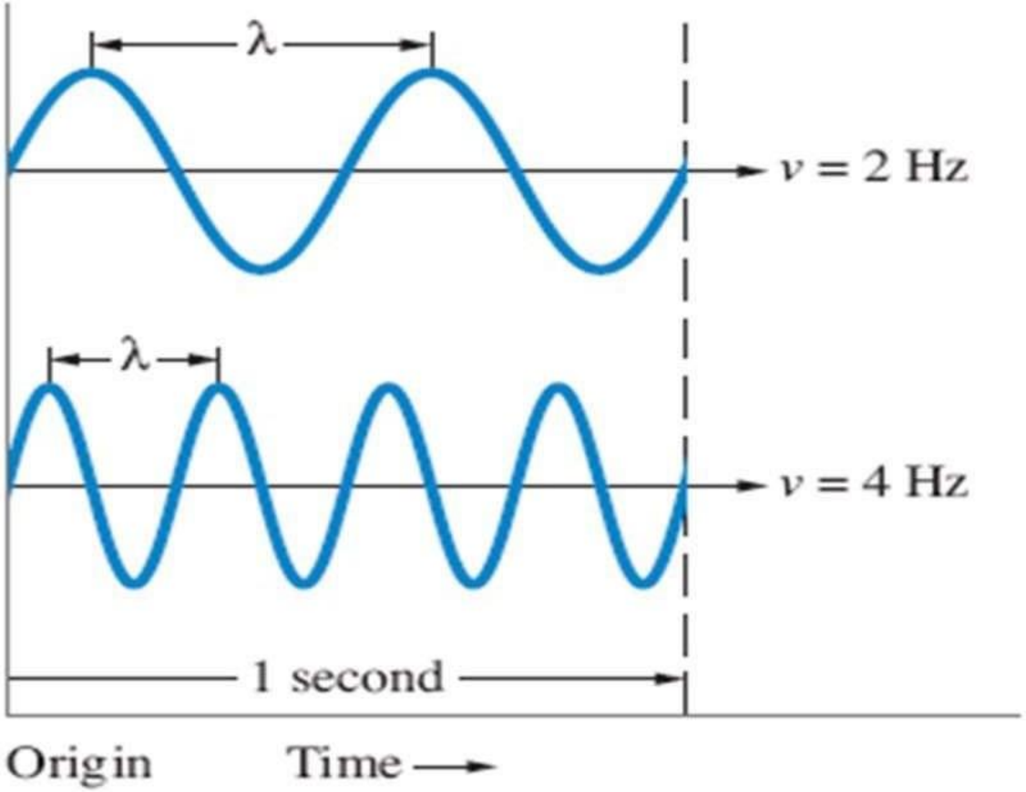


Its reaction of matter with light!

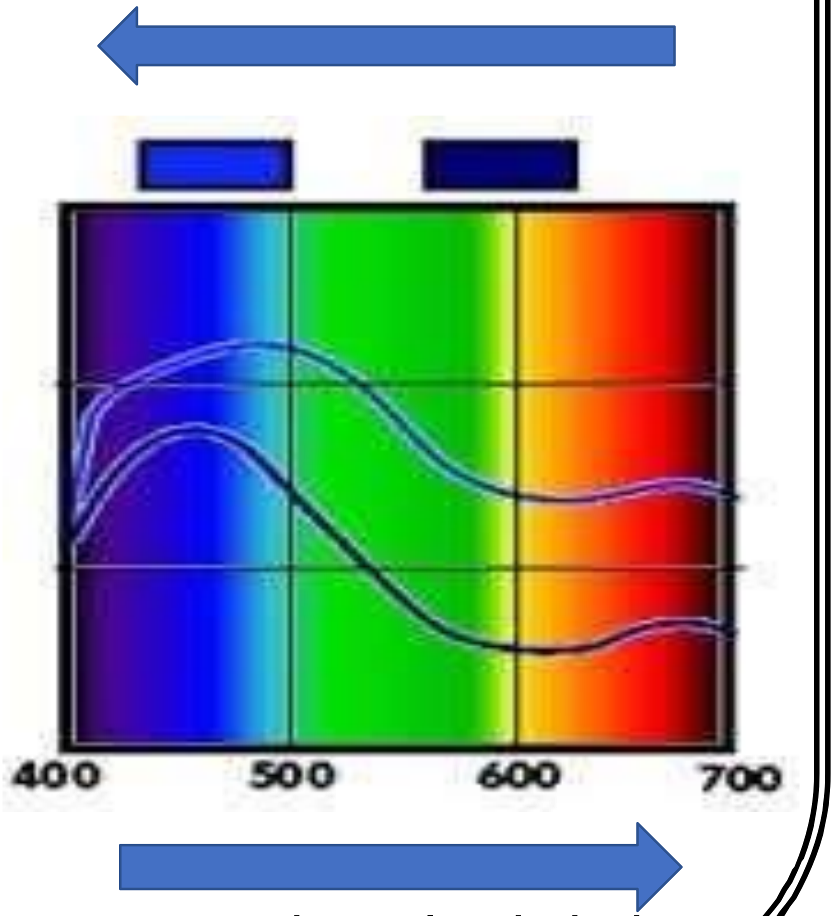
CHARACTERISTICS OF LIGHT

- **Light = band of waves of different wavelengths**



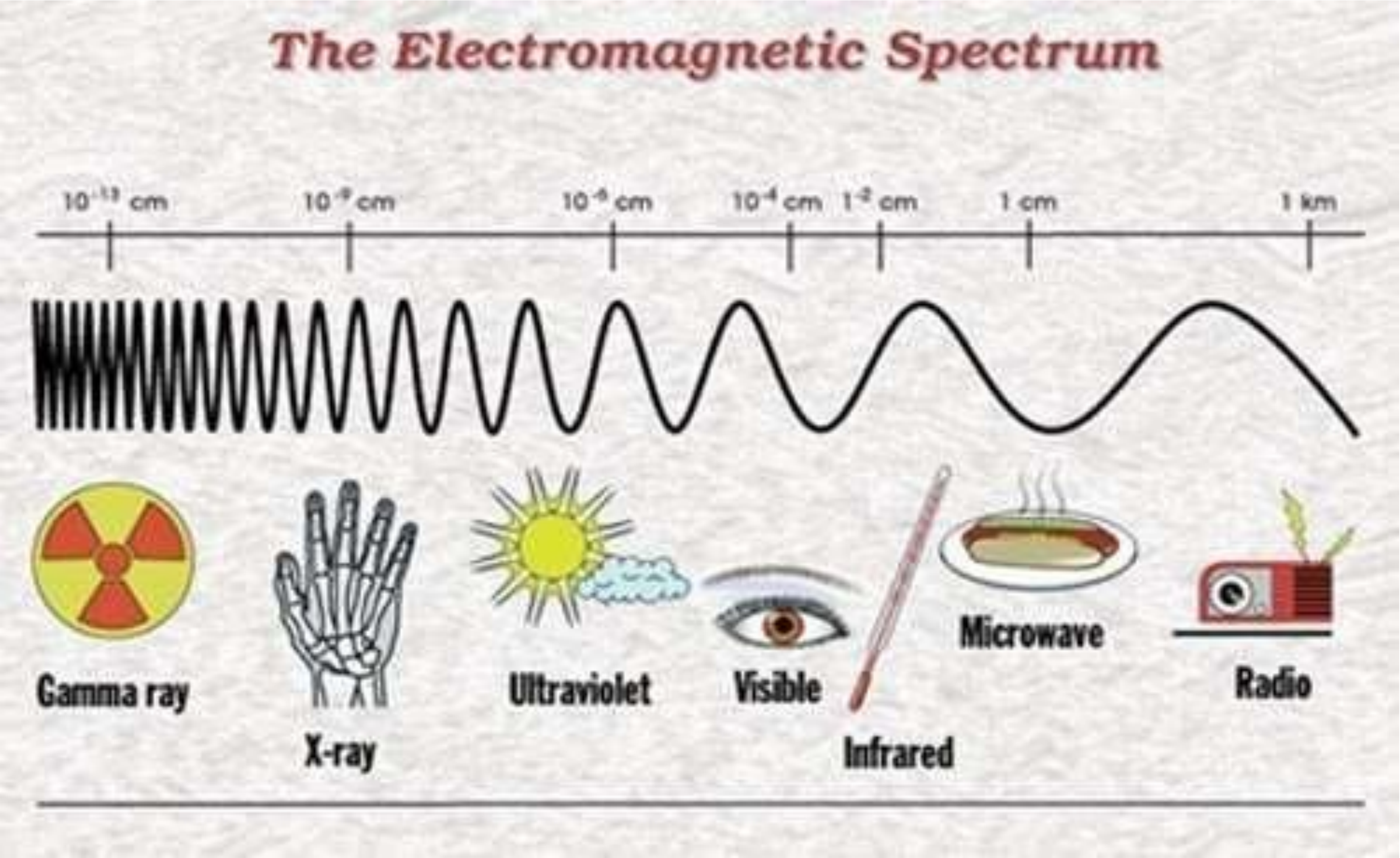


Increase in frequency (energy)



Increase in wavelengths (nm)

(Light) Electromagnetic spectrum important for photochemistry:



- Wavelength (λ): Distance between successive crests or troughs
- Frequency (ν): Number of crests or troughs that pass a point per second

- Speed of light (c) $c = \nu \lambda$
- Solar energy (E_s): ($E_s = h\nu$) It's the energy come from the sun or other radiant source.

- The dual nature of light: It means that, in some experiments, light behaves as a wave, In other experiments, light behaves as a particle.

PARTICLE CHARACTERISTICS OF LIGHT:

- Light = flux of discrete units (i.e quanta) called photons.

Fireworks:

ABSORBANCE, COLOUR ANDTRANSPARENCY OF MATERIALS:

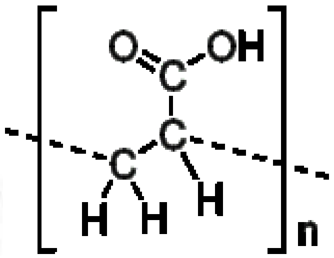
Transparent materials absorb no light in the visible wavelength range, and hence have no energy states separated by between 1.65 and 3.10eV.

Examples:

SiO_2 (glass, quartz);

C(Diamond);

Water soluble polymers like: Poly(acrylic acid) (PAA)



ABSORBANCE, COLOUR ANDTRANSPARENCY OF MATERIALS:

Opaque materials: are absorb light in all the visible wavelength range, and hence have many energy states separated by between 1.65 and 3.10eV.

Examples:

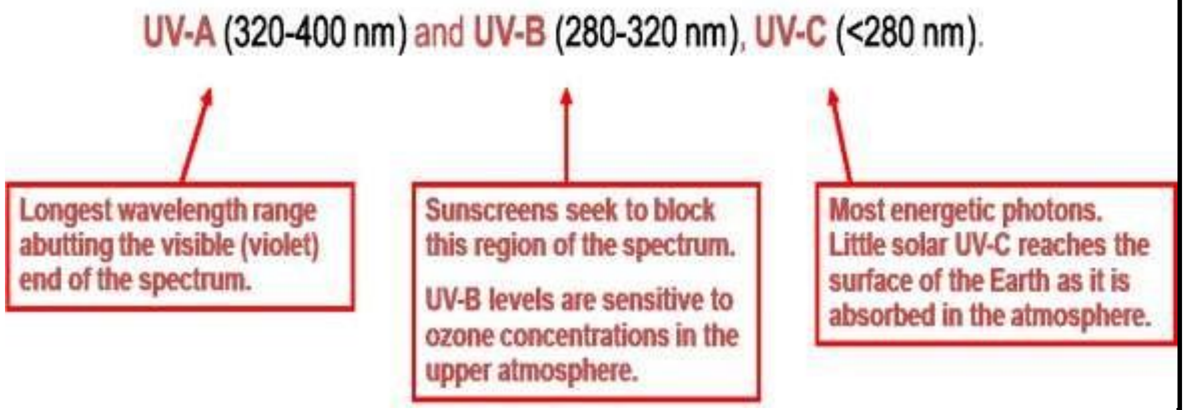
- C(graphite) also absorbs light at all wavelengths, but is black and not reflective like ametal.
- Some metals (Cu, Fe…)

are coloured as well as reflective.

- Dyes and many other materials may be coloured because they absorb some of the wavelengths in the visible range.

UV Absorbance –Sunscreens:

- Absorbance in the ultraviolet (UV) range in important for transparent materials. UV is higher energy light, and UV absorbance can lead to photochemical reactions and the formation of highly reactive free radicals. As with ionizing radiation these can lead to cell damage and (skin) cancer.



UV-A (320-400 nm) and UV-B (280-320 nm), UV-C (<280 nm).

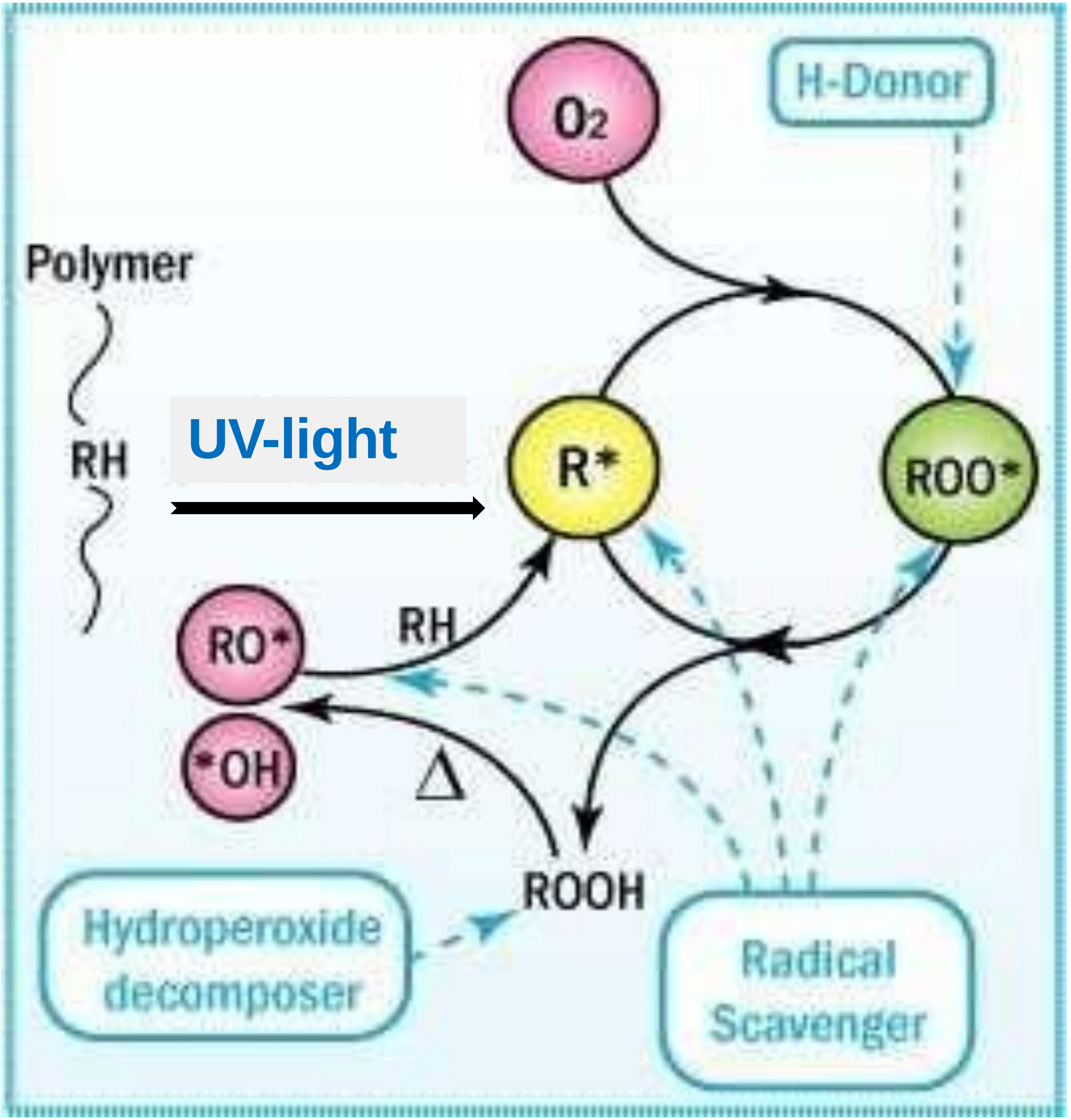
Longest wavelength range abutting the visible (violet) end of the spectrum.

Sunscreens seek to block this region of the spectrum.

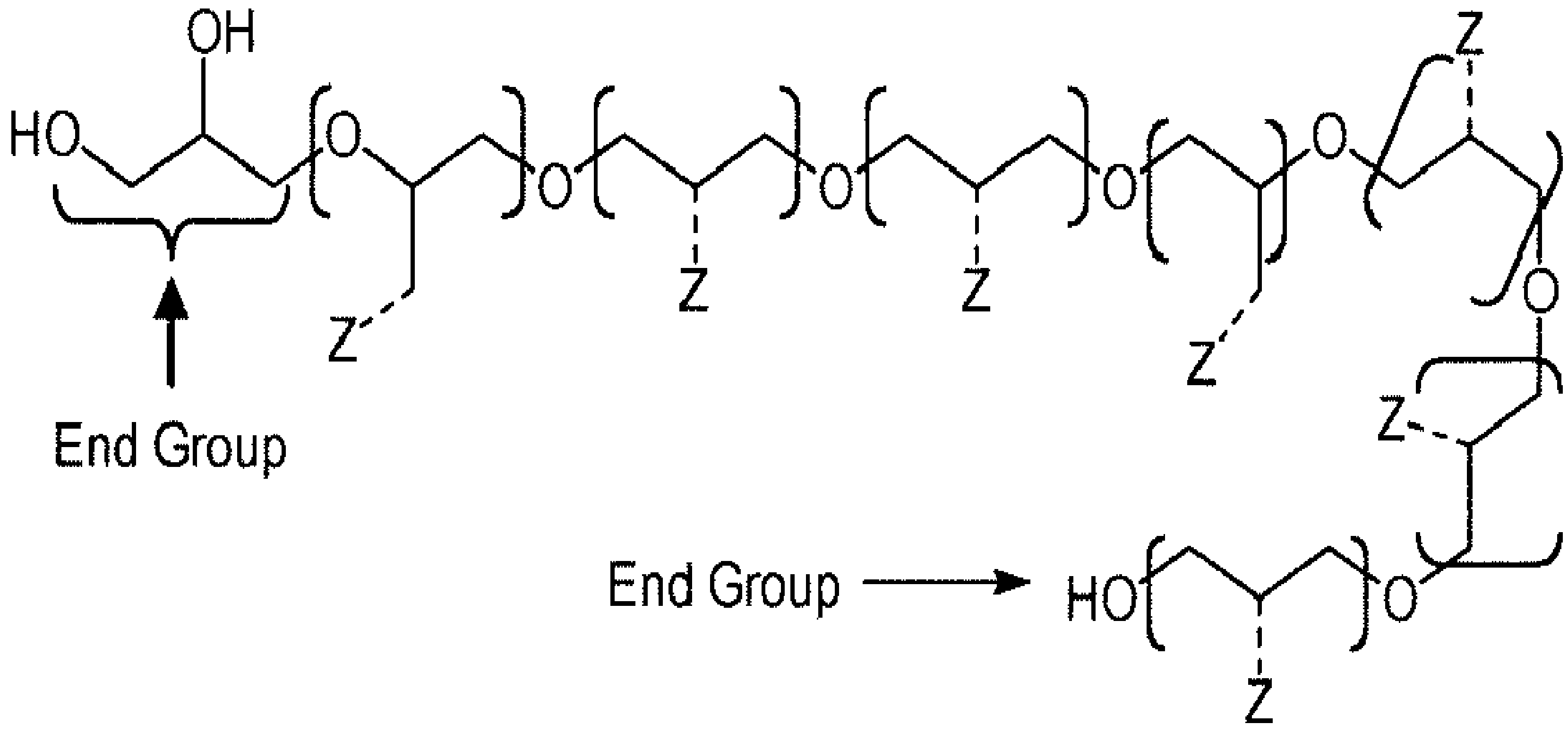
UV-B levels are sensitive to ozone concentrations in the upper atmosphere.

Most energetic photons. Little solar UV-C reaches the surface of the Earth as it is absorbed in the atmosphere.

Mechanism of UV-degradation of polymer chain In presence of O_2:

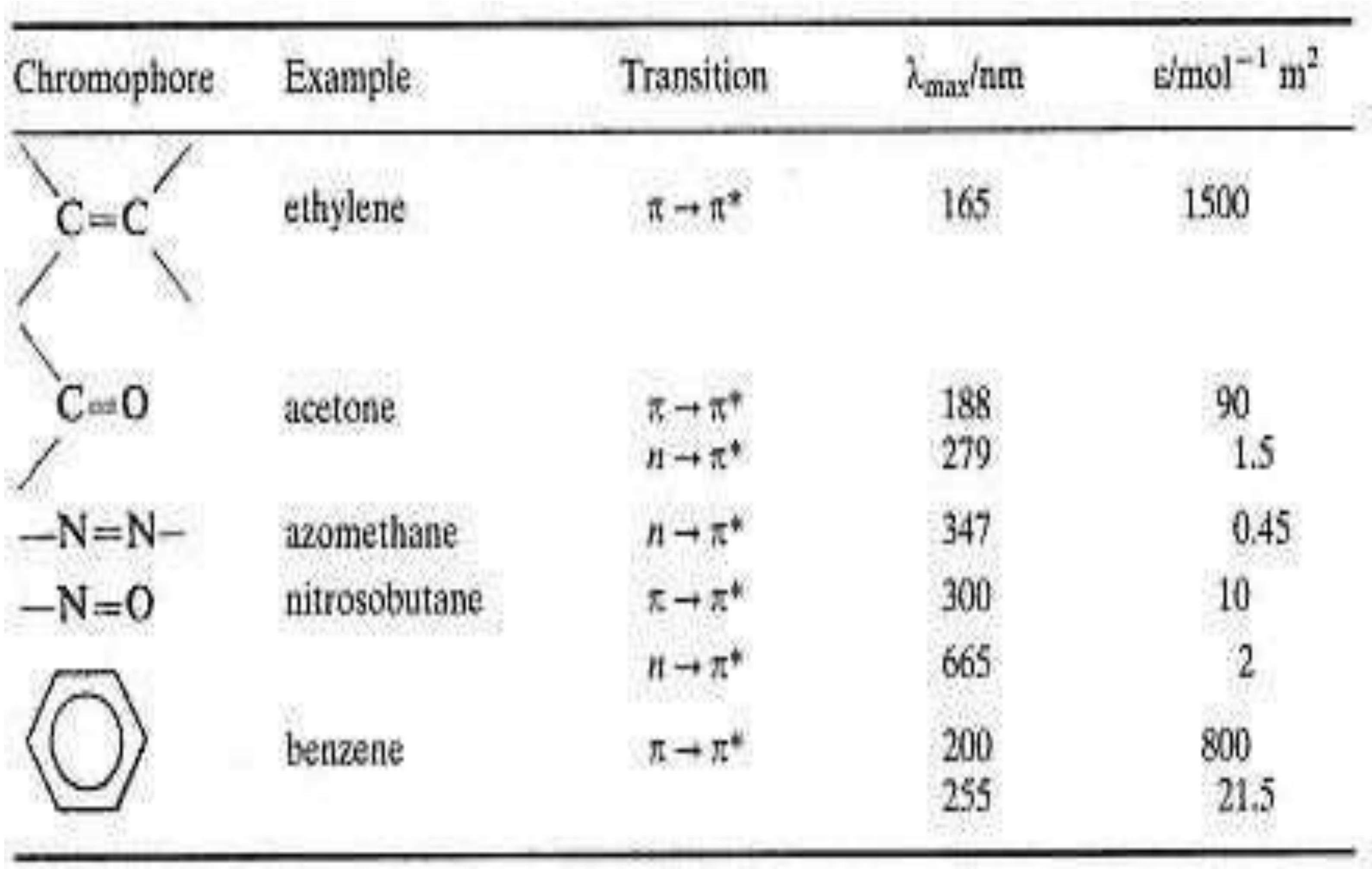


- Sunscreens contain a mixture of compounds, like polymers, that absorb UV light from the solar spectrum:



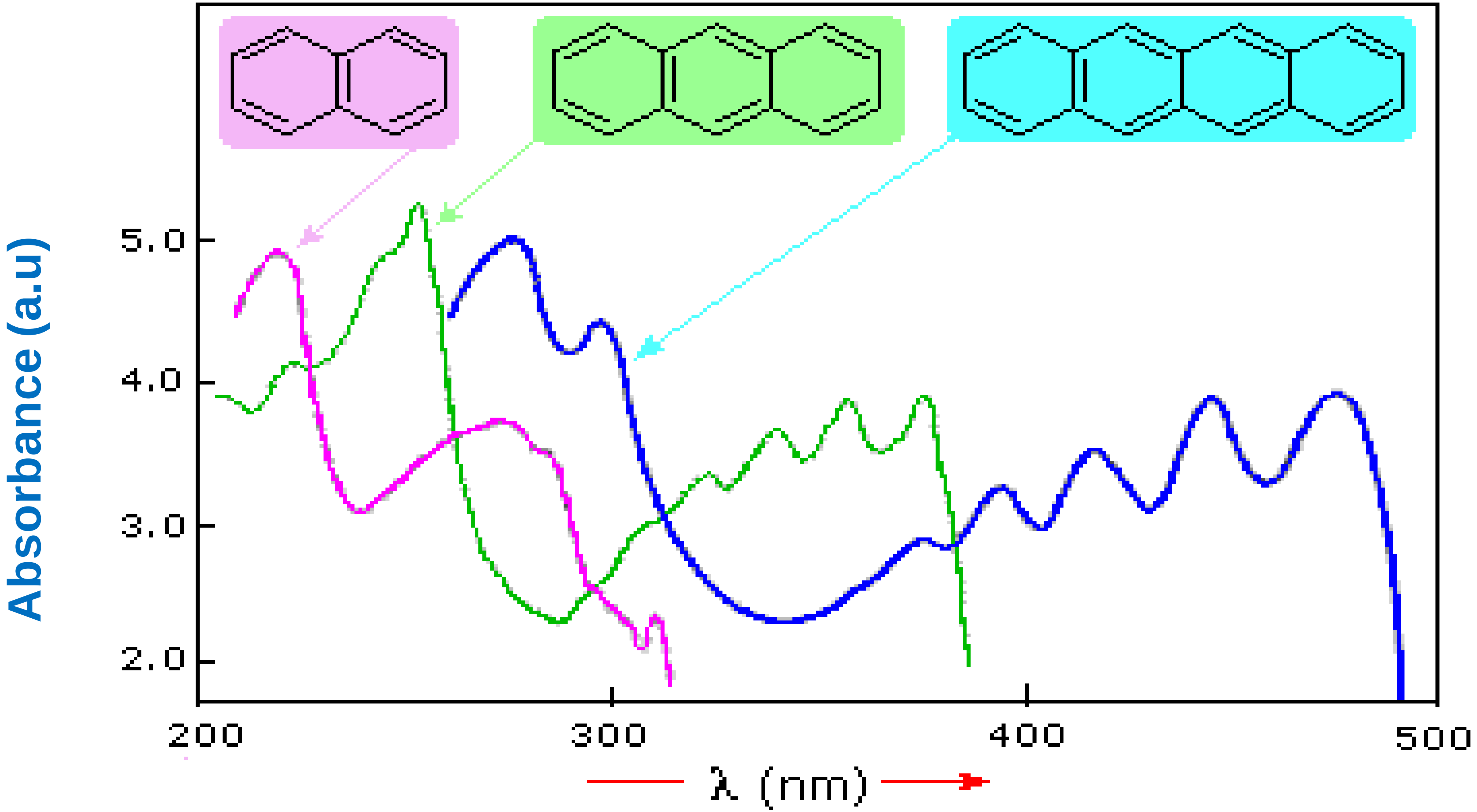
FORMULA I. UV-ABSORBING POLYGLYCEROL

- The " Z" in Structure I is selected from a UV-chromophore:



Chromophore	Example	Transition	λ_{max}/nm	ε/mol^{-1} m^2
C=C	ethylene	$\pi \rightarrow \pi^*$	165	1500
C=O	acetone	$\pi \rightarrow \pi^*$	188	90
		$n \rightarrow \pi^*$	279	1.5
—N=N—	azomethane	$n \rightarrow \pi^*$	347	0.45
—N=O	nitrosobutane	$\pi \rightarrow \pi^*$	300	10
		$n \rightarrow \pi^*$	665	2
	benzene	$\pi \rightarrow \pi^*$	200	800
			255	21.5

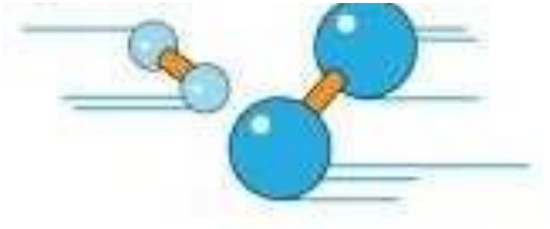
Relation between wavelength and conjugation



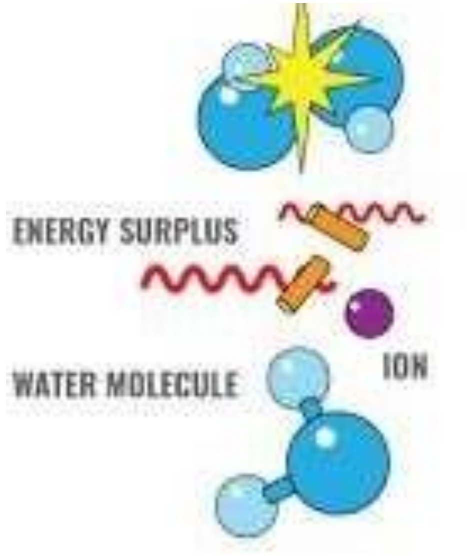
- **Ordinary reaction (**thermal or dark reaction**):**
- Its occurs by absorption of heat energy from outside in absence of light.

Steps of Ordinary reactions

1. The reacting molecules are energised

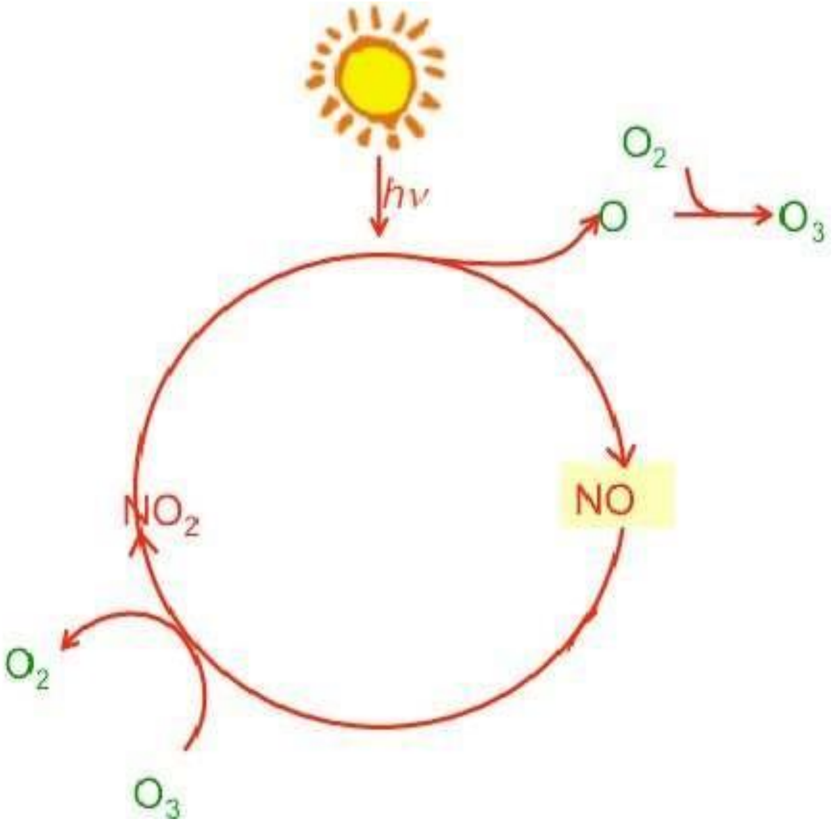


2. Molecular collision is occurred



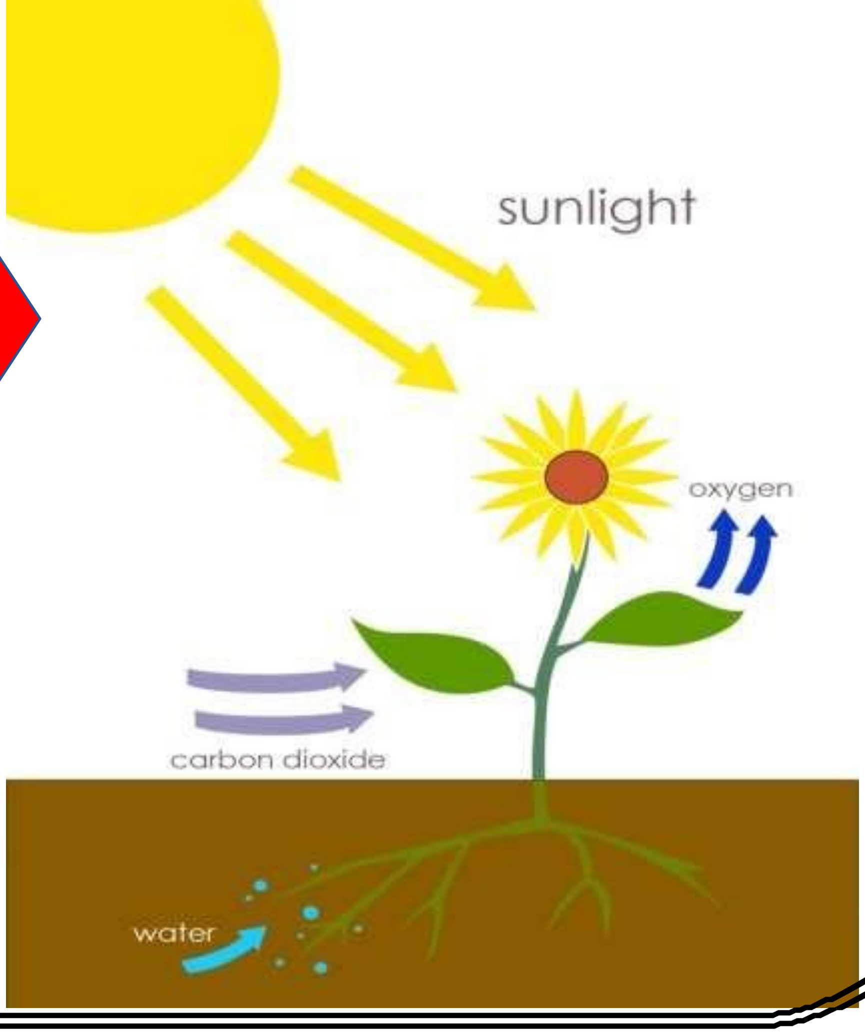
3. Product is formed

- **Photochemical reaction**:
- Its a reaction which takes place by absorption of the visible and ultraviolet radiations (200-800 nm)
- Photochemical reaction leads to the heating of the atmosphere during the daytime by absorption of ultraviolet radiation.



- Mechanism of photochemical reactions occurring during atmospheric: Photochemical change occurs only by absorption of photons.

- Photochemical reaction includes the absorption of visible radiation during photosynthesis.
- Without photochemical processes, the Earth would be simply a warm, sterile, rock.



Schematic of photosynthesis in plants. The carbohydrates produced are stored in or used by the plant.

$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

Overall equation for the type of photosynthesis that occurs in plants

- **Photochemistry:**
- **Its the branch of chemistry which deals with the study of photochemical reactions.**
    - **Demonstration of a Photochemical reaction**

$$H_2 + Cl_2 \xrightarrow{\text{dark}} \text{No reaction}$$

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$$

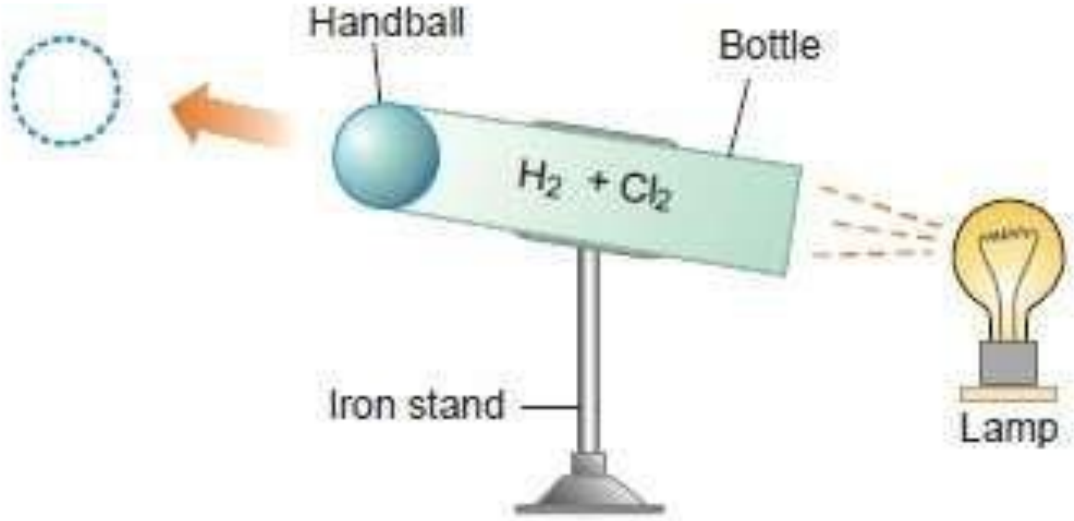
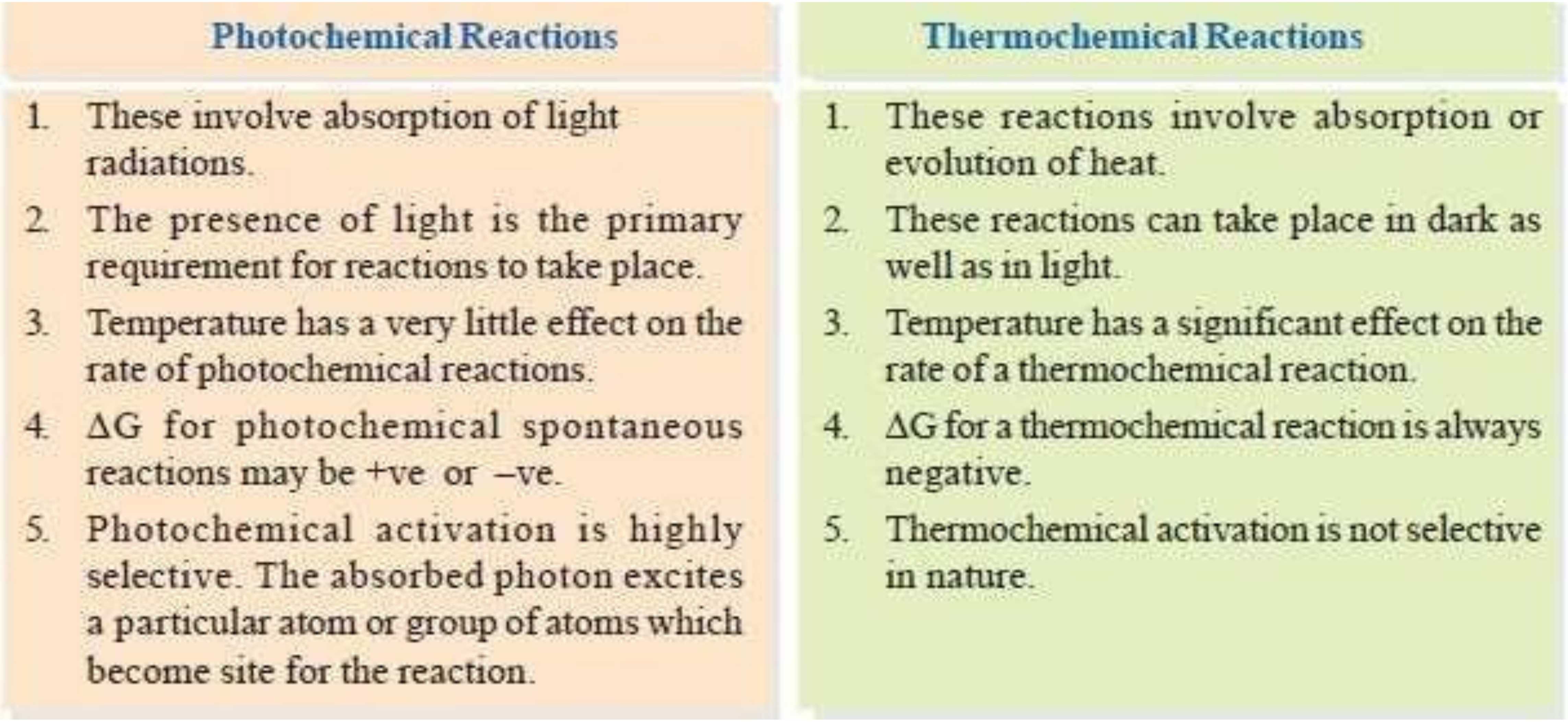


Figure 30.1
The 'HCl-cannon' experiment.

○ Difference between photochemical and thermochemical reactions



Photochemical Reactions	Thermochemical Reactions
1. These involve absorption of light radiations.	1. These reactions involve absorption or evolution of heat.
2. The presence of light is the primary requirement for reactions to take place.	2. These reactions can take place in dark as well as in light.
3. Temperature has a very little effect on the rate of photochemical reactions.	3. Temperature has a significant effect on the rate of a thermochemical reaction.
4. ΔG for photochemical spontaneous reactions may be +ve or –ve.	4. ΔG for a thermochemical reaction is always negative.
5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	5. Thermochemical activation is not selective in nature.

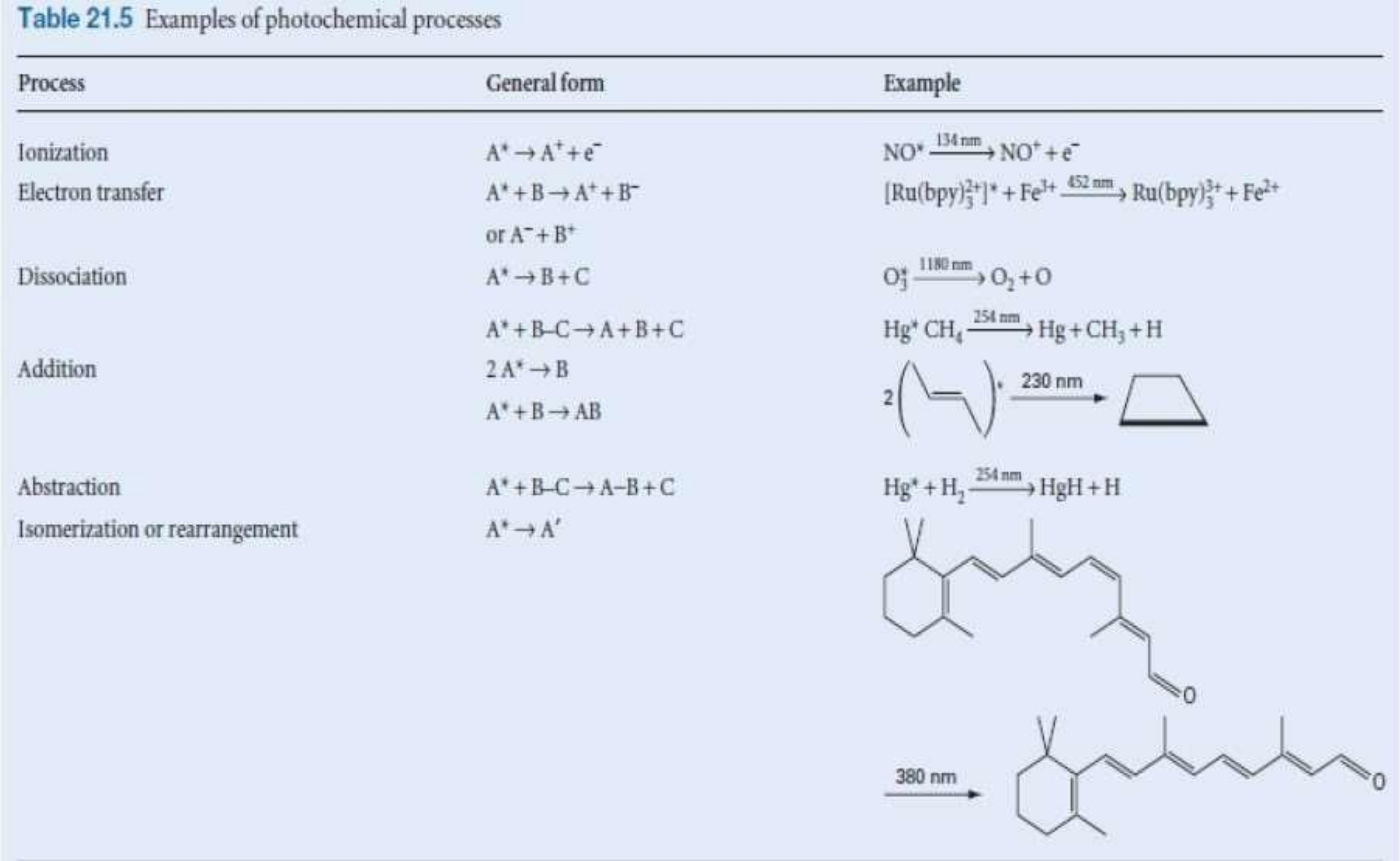


Table 21.5 Examples of photochemical processes

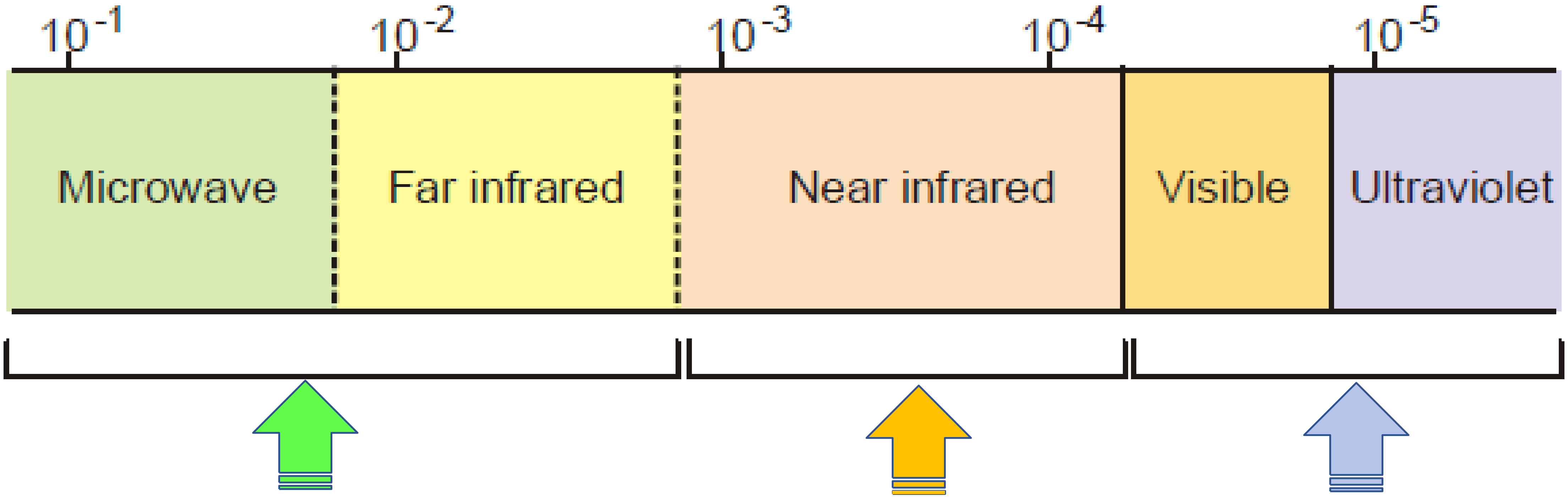
Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \xrightarrow{134\text{ nm}} NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$[Ru(bpy)_3^{2+}]^* + Fe^{3+} \xrightarrow{452\text{ nm}} Ru(bpy)_3^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow B + C$	$O_3^* \xrightarrow{1180\text{ nm}} O_2 + O$
	$A^* + B\text{–}C \rightarrow A + B + C$	$Hg^*\ CH_4 \xrightarrow{254\text{ nm}} Hg + CH_3 + H$
Addition	$2\,A^* \rightarrow B$ $A^* + B \rightarrow AB$	2 ( )* $\xrightarrow{230\text{ nm}}$
Abstraction	$A^* + B\text{–}C \rightarrow A\text{–}B + C$	$Hg^* + H_2 \xrightarrow{254\text{ nm}} HgH + H$
Isomerization or rearrangement	$A^* \rightarrow A'$	$\xrightarrow{380\text{ nm}}$

ENERGY TRANSITIONS:

- Molecules absorb radiation by increasing internal energy:

Internal energy ≡ electronic, vibrational, & rotational states

- **Energy requirements:**



(3). Rotational transitions

≡ Far-IR-Mic (> 2000 nm)

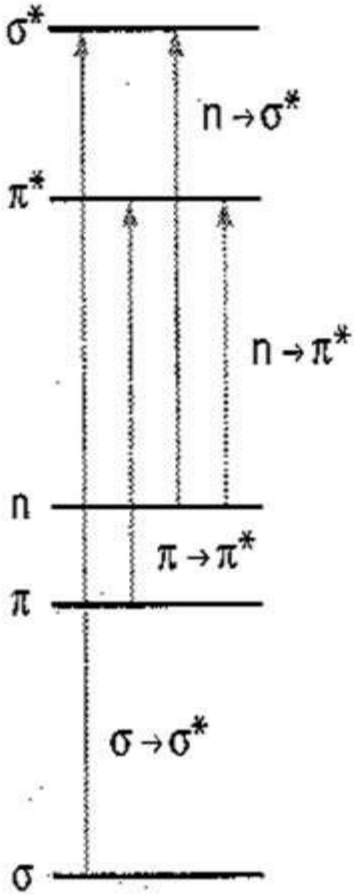
(2). Vibrational transitions

≡ Near-IR (700-2000 nm)

(1). Electronic transitions

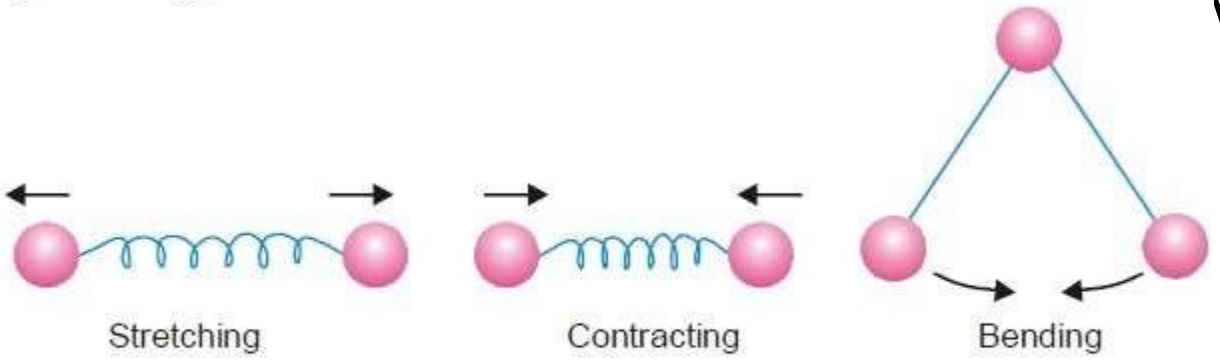
≡ UV-vis (400-700 nm)

Typical electronic transitions:

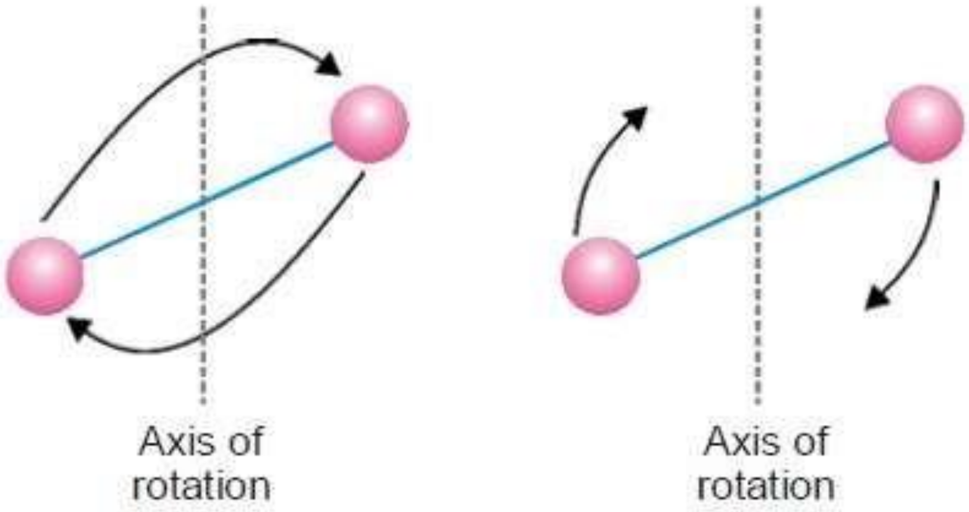


n → π*	carbonyls, nitro-, azo- and imino-group containing compounds
π → π*	alkenes, alkynes, aromatics
n → σ*	amines, alcohols, haloalkanes
σ → σ*	alkanes

Typical Molecular vibrations



Typical Molecular rotations

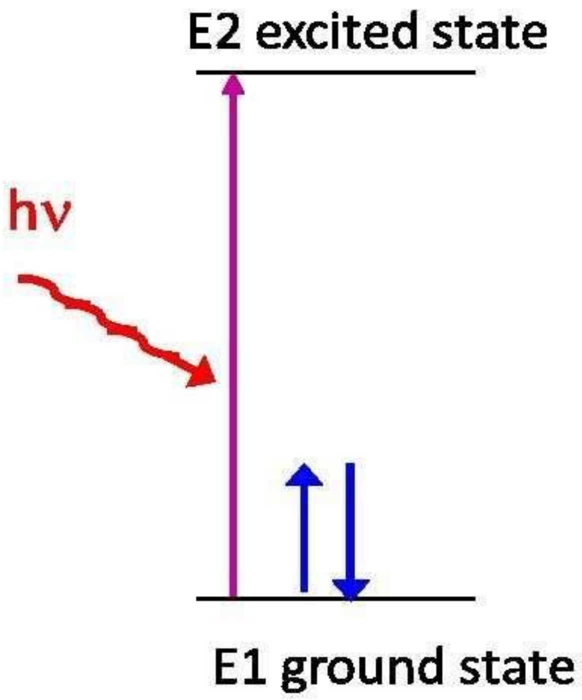


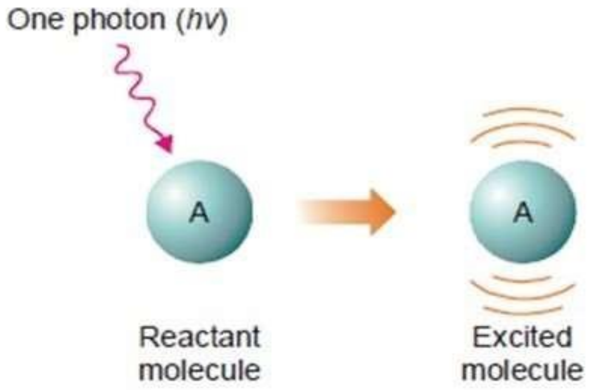
What Happens When Radiation Hits a Molecule?

We learned in radiative transfer that two possible outcomes are:

1. scattering (no chemical interaction)

2. absorption:



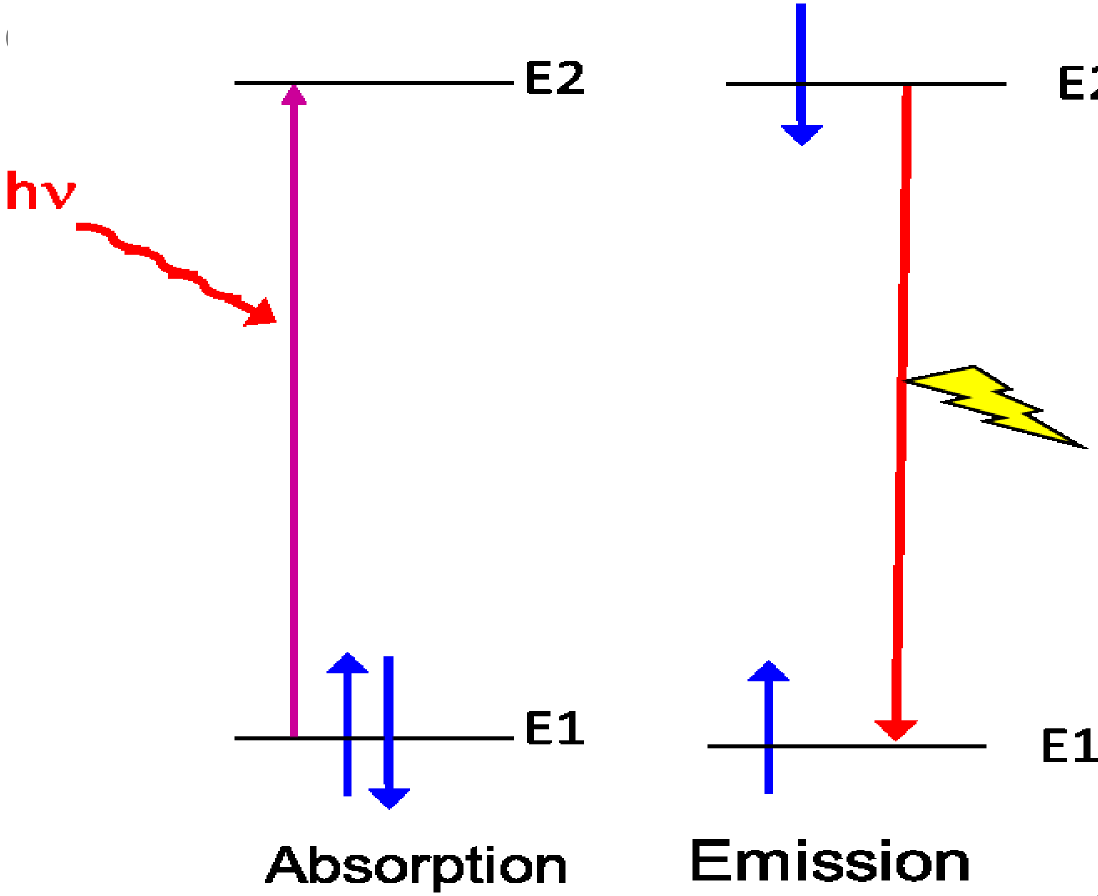


Absorption and Emission:

- An electronic transition occurs when an electron changes from state to another.
- The orbital it is *leaving* must be partly filled (it contains at least one electron), and the orbital it is *entering* must be partly unfilled (it contains less than two electrons).

Absorption or Absorbance: An electron absorbs the energy of a photon, and jumps from a lower into a higher energy orbital.

Emission: An electron jumps from a higher into a lower orbital, and releases (emits) a photon of energy e



Light absorption

- When light is passed through a medium, a part of it is absorbed. This absorbed portion of light which causes photochemical reactions.

- Let a beam of monochromatic light pass through a thickness dx of the medium. The intensity of radiation reduces from I to I-dI.

- The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time.

- Let us denote the number of incident photons by N and the number absorbed in thickness dx by dN.

- The fraction of photons absorbed is then dN/N which is proportional to thickness dx. That is,

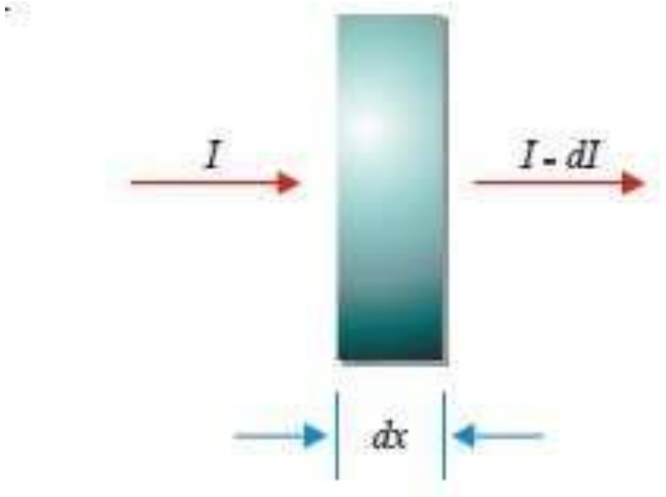


Figure 30.2
As a beam of intensity I passes through a medium of thickness dx, the intensity of the beam is reduced to $I - dI$.

$$\frac{dN}{N} \propto dx$$

$$\frac{dN}{N} = b\ dx = -\frac{dI}{I}$$

- where **b** is proportionality constant called **absorption coefficient**.
- Let us set **$I = I_0$** at **$x = 0$** and integrate. This gives

$$\ln\left(\frac{I}{I_0}\right) = -bx \qquad ...(1)$$

- **Lambert** first derived equation (1) and it is known as **Lambert Law**. Beer extended this relation to solutions of compounds in transparent solvents. The equation (1) then takes the form (2).

$$\ln\left(\frac{I}{I_0}\right) = -\in C\,x \qquad ..(2)$$

Lambert-Beer Law. This law forms the basis of spectrophotometric methods of chemical analysis.

- where **C** = molar concentration; **∈** is a constant characteristic of the solute called the **molar absorption coefficient**.

The attenuation of a beam by absorbance is typically represented in two ways:

1. Fraction or Percent Transmission (%T)
2. Absorbance (A)

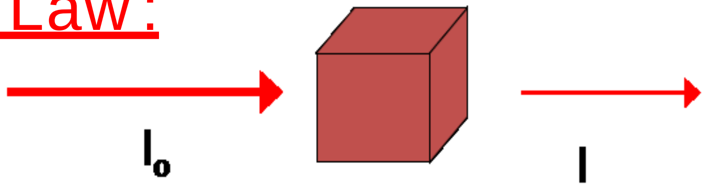
Absorbance $A = \ln (I_o/I)$

$A = \log_{10} (I_o/I)$

Absorbance, *A*, is a *logarithmic* scale that increases as the transmission decreases.

where *I* denotes intensity, and I_0 is the intensity of a reference beam (no sample present).

Beer-Lambert Law:



$$A = \varepsilon\, b\, c$$

ε = molar absorption coefficient

c = concentration of the absorbing species (mol/L)

b = path length of the light-absorbing sample (cm)

b = x

$$A = \sigma b c$$

σ= absorption cross-section (per molecule) cm^2/molecule ($\sigma = \varepsilon \times 3.8 \times 10^{-21}$)

c = concentration (molecules cm^{-3})

Transmission, T, is simply defined as the fraction of light that reaches a detector after passing through a sample

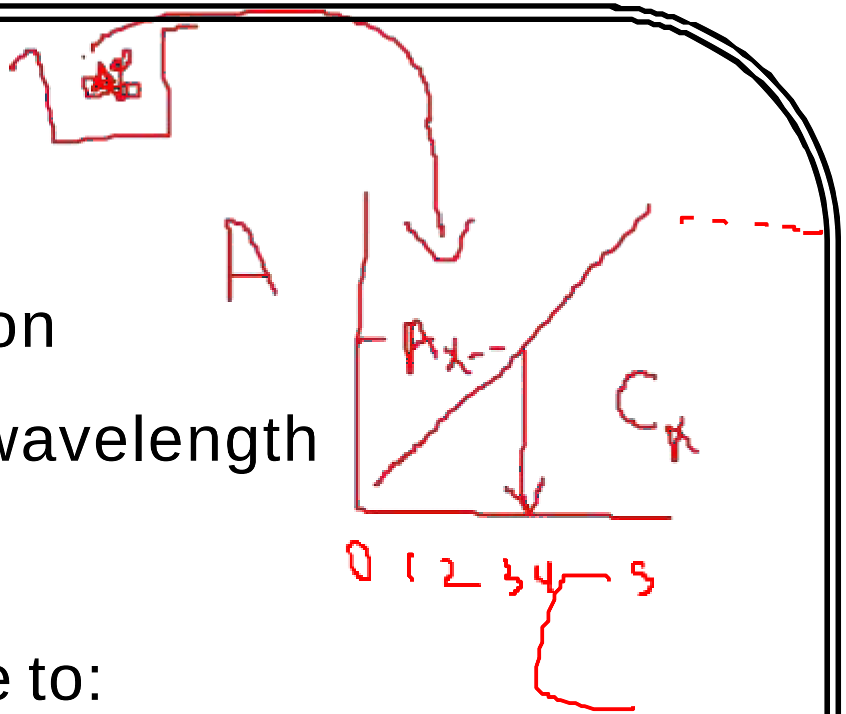
$$T = \frac{I}{I_0} \qquad \%T = 100\frac{I}{I_0}$$

Example: ***What is the absorbance of a sample with a 1.0% transmission?***

$\%T = 1.0 \Rightarrow I/I_0 = 0.010$ or $I_0/I = 100$

$A = \log_{10}(100) = \underline{2.0}$

ABSORBANCE SPECTROMETRY



- Determines concentration of a substance in solution
- Measures light absorbed by solution at a specific wavelength

- Visible region: low energy electronic transition due to:

a. Compounds containing transition metals

b. Large aromatic structures & conjugated double bond systems

- UV region (200-400 nm):

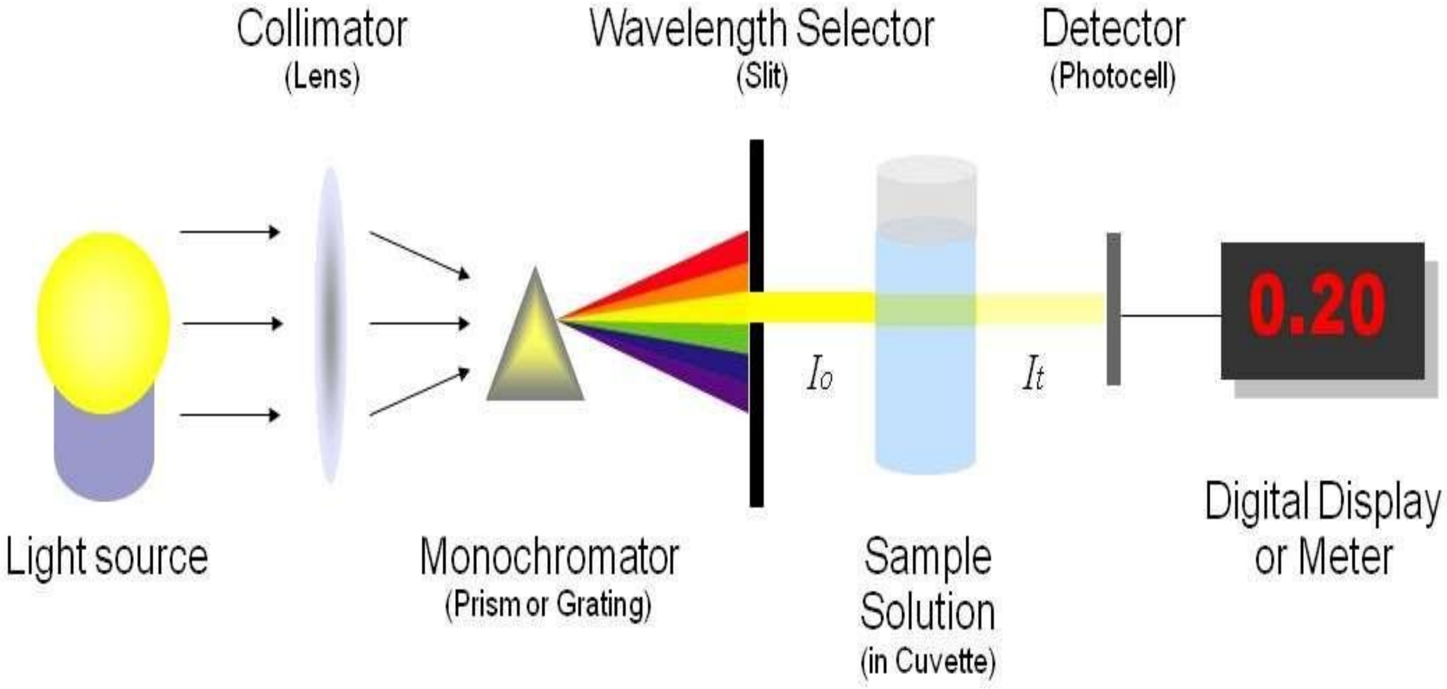
c. Small conjugated ring systems

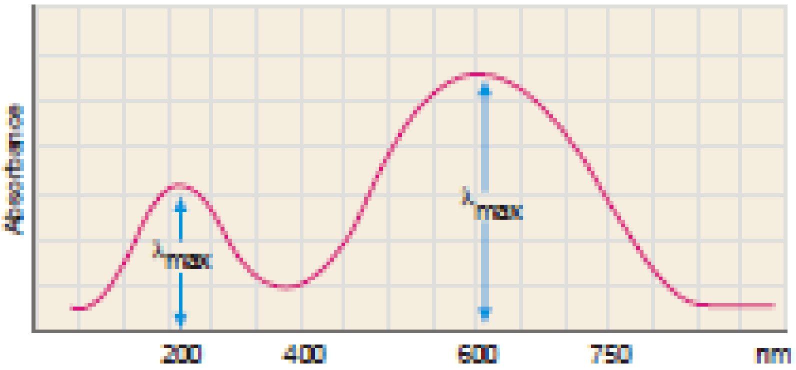
d. Carbonyl compounds

Determination of absorbed intensity

- **A photochemical reaction occurs by the absorption of photons of light by the molecules.**
- **Therefore, it is essential to determine the absorbed intensity of light for a study of the rate of reaction.**

Schematic diagram of the spectrophotometer used for measurement of light intensity





A sample UV-Vis spectrum.

○ Steps of absorbance measurements

1. Light beam from a suitable source (tungsten filament or mercury vapour lamp) is rendered parallel by the lens.

2.The beam then passes through a ‘filter’ or monochrometer which yields light of one wavelength only. The monochromatic light enters the reaction cell made of quartz.

3.The part of light that is not absorbed strikes the detector. Thus the intensity of light is measured first with the empty cell and then the cell filled with the reactionsample.

4.The first reading gives the incident intensity, I_0, and the second gives the transmitted intensity, I. The difference, $I_0 – I = I_a$, is the absorbed intensity.

- The detector generally used for the measurement of intensity of transmitted light is :

(a) a thermopile **(b) photoelectric cell** **(c) achemical actinometer.**

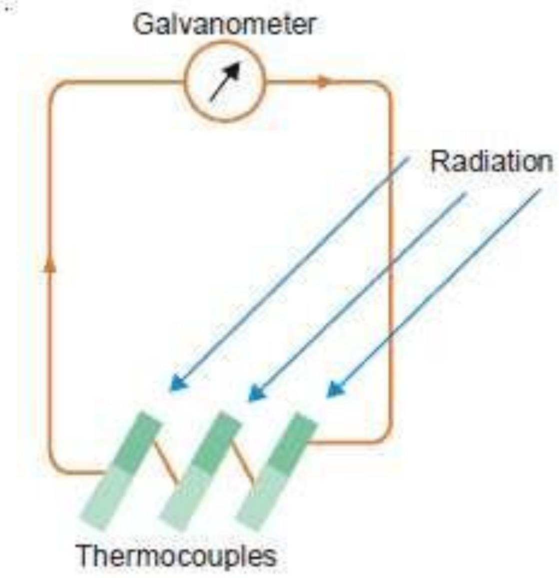


Figure 30.4
A thermopile.

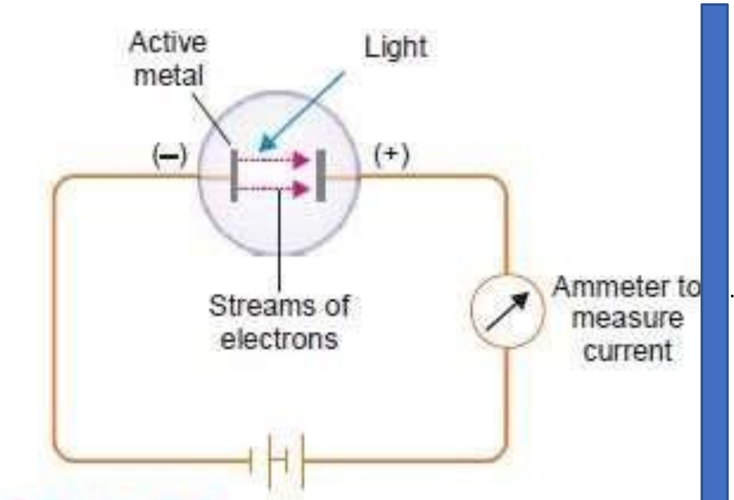
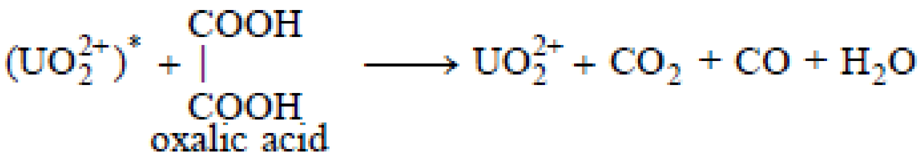


Figure 30.5
A photoelectric cell (illustration).

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$



$$(UO_2^{2+})^* + \begin{matrix}COOH\\ |\\ COOH\end{matrix} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

oxalic acid

LAWS OF PHOTOCHEMISTRY

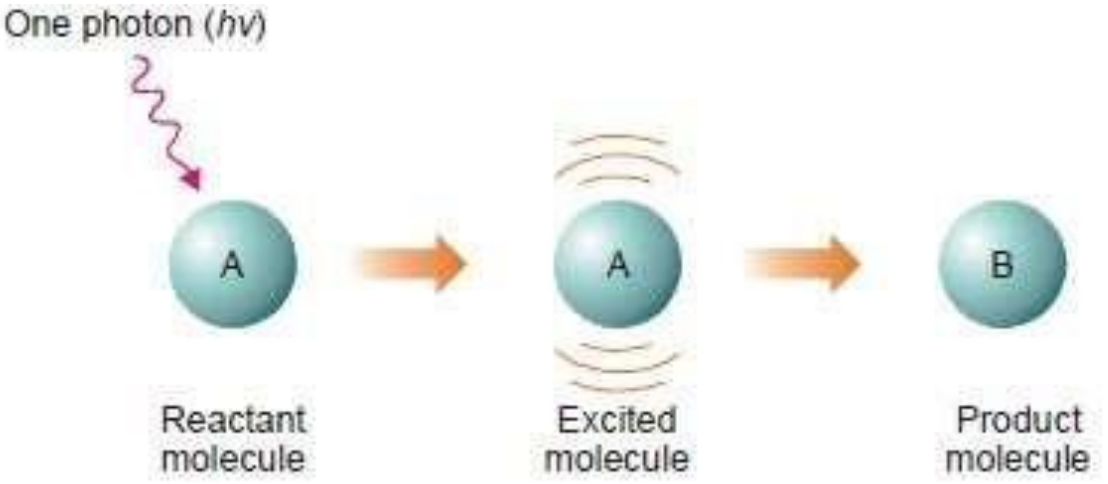
1) Grothus–Draper Law (qualitative aspect)

It is only the absorbed light radiations that are effective in producing a chemical reaction.

2) Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of Quantum theory of light.

Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule.



- **In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.**

$$\begin{array}{lrcl} & A + h\nu & \longrightarrow & A^* \\ & A^* & \longrightarrow & B \\ \hline \text{overall} & A + h\nu & \longrightarrow & B \end{array}$$

- **In practice, we use molar quantities. That is, one mole of A absorbs one mole of photons or one einstein of energy, E. The value of E can be calculated by using the expression given below:**

$$E = \frac{2.859}{\lambda} \times 10^5 \ \ \text{kcal mol}^{-1}$$

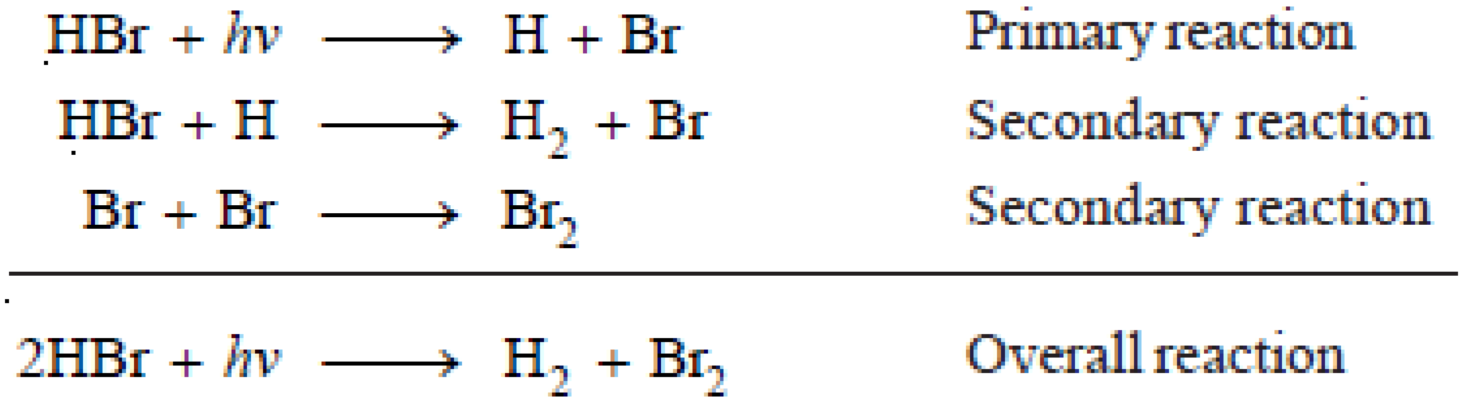
○ Primary and Secondary reactions:

The overall photochemical reactionmay consist of :

(a) a primary reaction: proceeds by absorption of radiation.

(b)secondary reaction: is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows :



$$HBr + h\nu \longrightarrow H + Br \qquad \text{Primary reaction}$$

$$HBr + H \longrightarrow H_2 + Br \qquad \text{Secondary reaction}$$

$$Br + Br \longrightarrow Br_2 \qquad \text{Secondary reaction}$$

$$2HBr + h\nu \longrightarrow H_2 + Br_2 \qquad \text{Overall reaction}$$

- **Evidently, the primary reaction only obeys the law of photochemical equivalence strictly. The secondary reactions have no concern with the law.**

○ Quantum yield (or Quantum efficiency) (ɸ)

$$\phi = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed}}$$

- ○ For a reaction that obeys strictly the Einstein law, one molecule decomposes per photon, the quantum yield $\varphi = 1$.

- ○ When two or more molecules are decomposed per photon, $\varphi > 1$ and the reaction has a high quantum yield.

- ○ If the number of molecules decomposed is less than one per photon, $\varphi < 1$ the reaction has a low quantum yield.

○ Causes of high quantum yield

The chief reasons for high quantum yield are :

(1) Reactions subsequent to the Primary reaction:

$$\mathrm{HI} + h\nu \longrightarrow \mathrm{H} + \mathrm{I} \qquad ...(1) \qquad \text{Primary}$$

$$\left.\begin{array}{ll} \mathrm{H} + \mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I} & ...(2) \\ \mathrm{I} + \mathrm{I} \longrightarrow \mathrm{I_2} & ...(3) \end{array}\right\} \quad \text{Secondary}$$

$$2\mathrm{HI} + h\nu \longrightarrow \mathrm{H_2} + \mathrm{I_2} \qquad \text{Overall reaction}$$

(2) A reaction chain forms many molecules per photon:

✓ **A reaction chain steps:**

1) **Initiation……………….>** $\mathrm{Cl_2} + h\nu \longrightarrow 2\mathrm{Cl} \qquad ...(1) \qquad \text{Primary reaction}$

2) **Self-propagating……>**

$$\left.\begin{array}{ll} \mathrm{Cl} + \mathrm{H_2} \longrightarrow \mathrm{HCl} + \mathrm{H} & ...(2) \\ \mathrm{H} + \mathrm{Cl_2} \longrightarrow \mathrm{HCl} + \mathrm{Cl} & ...(3) \end{array}\right\} \quad \text{Secondary reactions}$$

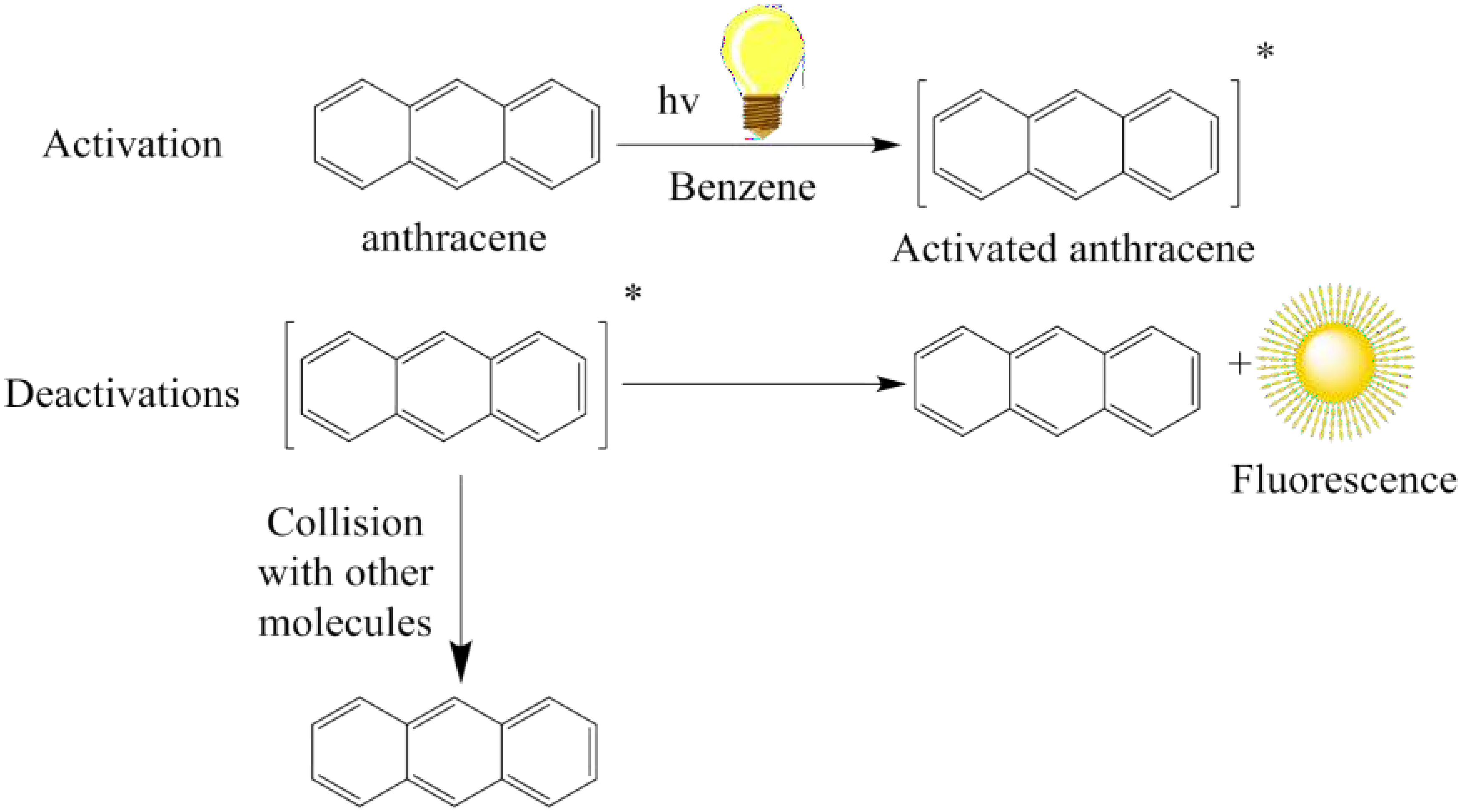
The number of HCl molecules formed for a photon of light is very high. The quantum yield of the reaction varies from 10^4 to 10^6

3) **Termination………..>** $2\mathrm{Cl} \xrightarrow{\text{walls}} \mathrm{Cl_2}$

Introductory Photochemistry, A. Cox and t. Camp, McGraw Hill

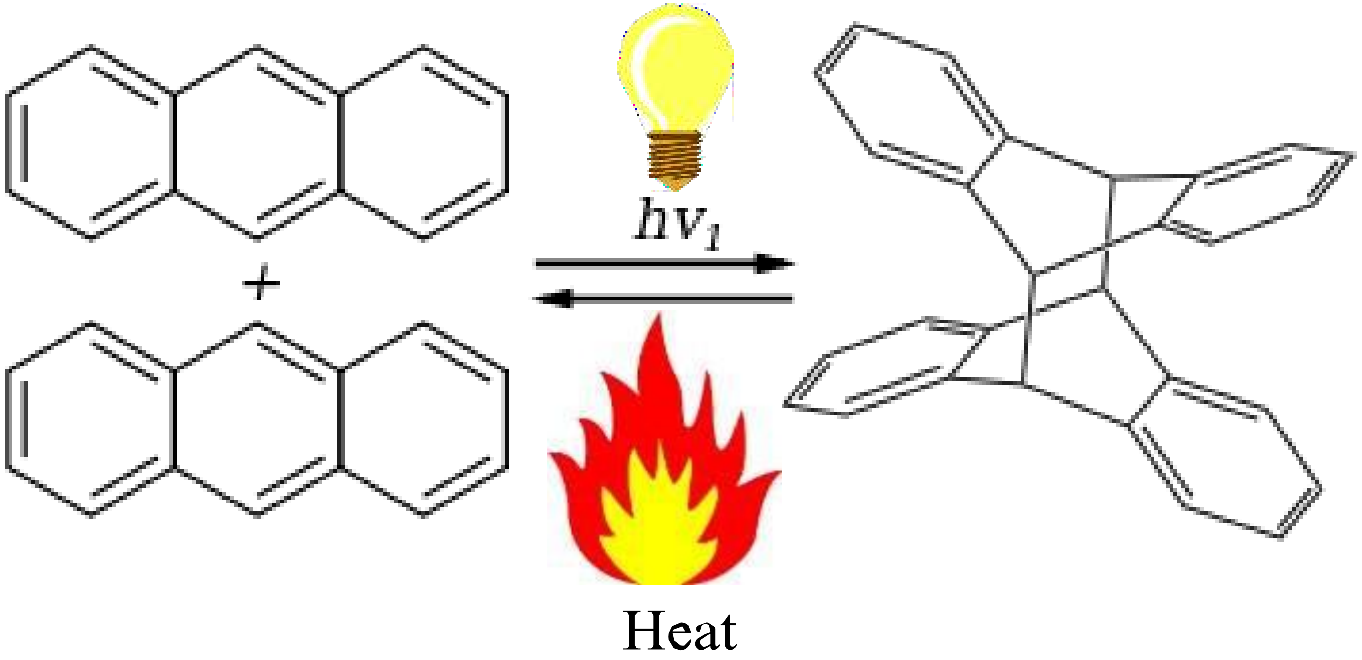
○ Causes of low quantum yield

(1) Deactivation of reacting molecules:



(2) Occurrence of reverse of primary reaction:

Dimerization of Anthracene:



- The quantum yield should be 2 but it is actually found to be 0.5. The low quantum yield is explained as the reaction is accompanied by fluorescence which deactivates the excited anthracene molecules. Furthermore, the above reaction is reversible.

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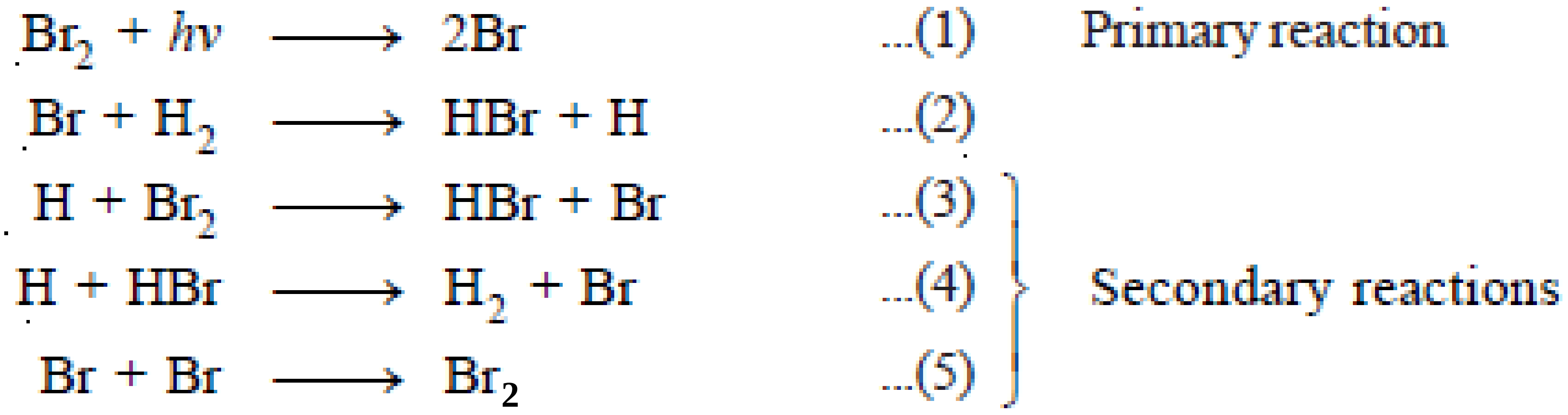
(3) Recombination of dissociated fragments:

Combination of H_2 andBr_2.



$$Br_2 + h\nu \longrightarrow 2Br \quad ...(1)$$

Primary reaction

$$Br + H_2 \longrightarrow HBr + H \quad ...(2)$$

$$\left.\begin{array}{ll} H + Br_2 \longrightarrow HBr + Br & ...(3) \\ H + HBr \longrightarrow H_2 + Br & ...(4) \\ Br + Br \longrightarrow Br_2 & ...(5) \end{array}\right\}$$

Secondary reactions

- The reaction (2) is extremely slow. The reactions (3), (4) and (5), depend directly or indirectly on (2) and so are very slow. Therefore most of the Br atoms produced in the primary process recombine to give back Br_2 molecules.

- Thus the HBr molecules obtained per quantum is extremely small. The quantum yield of the reaction is found to be 0.01 at ordinary temperature.

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CALCULATION OF QUANTUM YIELD

By definition, the quantum yield, ϕ, of a photochemical reaction is expressed as :

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

or

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

Thus we can calculate quantum yield from :

(a) The amount of the reactant decomposed in a given time and
(b) The amount of radiation energy absorbed in the same time

- **The radiation energy is absorbed by a chemical system as photons. Therefore we should know the energy associated with a photon or a mole of photons.**

PHOTOSENSITIZED REACTIONS

- **In many photochemical reactions the reactant molecule does not absorb the radiation required for the reaction. Hence the reaction is not possible.**
- **In such cases the reaction may still occur if a foreign species such as mercury vapour is present.**
  - **A species which can both absorb and transfer radiant energy for activation of the reactant molecule, is called a photosensitizer. The reaction so caused is called a photosensitized reaction.**

Reaction between H_2 and CO:

$Hg + h\nu \longrightarrow Hg^*$ Primary absorption

$Hg^* + H_2 \longrightarrow 2H^* + Hg$ Energy transfer

$H + CO \longrightarrow HCO$

$$\left.\begin{array}{l} HCO + H_2 \longrightarrow HCHO + H \\ 2HCO \longrightarrow HCHO + CO \end{array}\right\}\ \text{Reaction}$$

$$\mathbf{Hg + h\nu \dashrightarrow Hg^*}$$

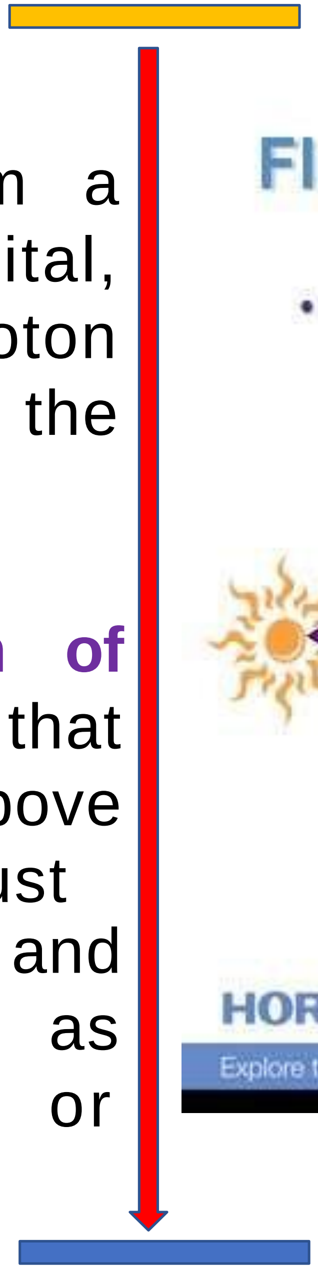
$$\mathbf{Hg^* + A \dashrightarrow A^* + Hg}$$

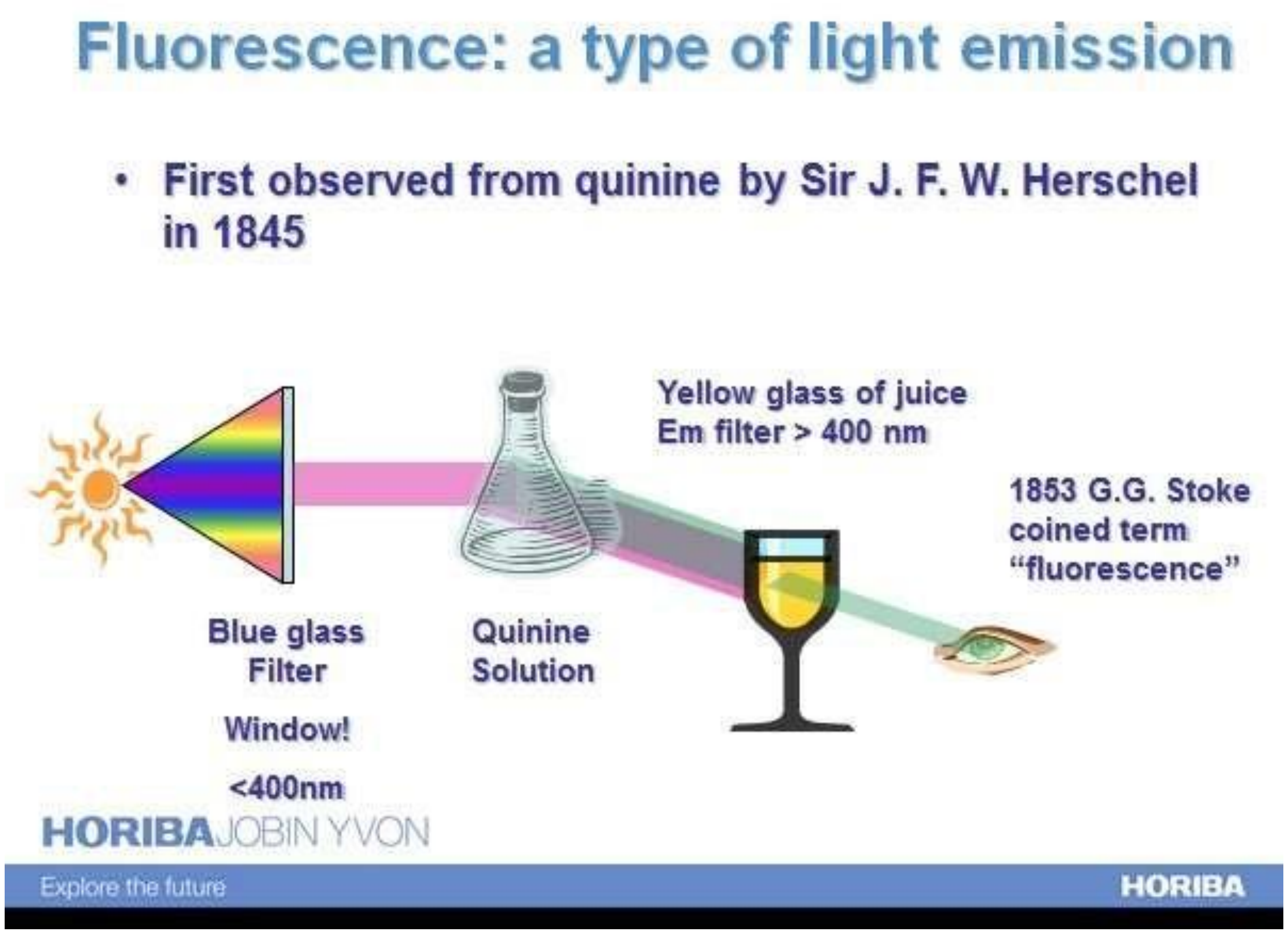
Some glyoxal, CHO-CHO, is also formed by dimerization of formyl radicals, HCO.

EMISSION:

- An electron jumps from a higher into a lower orbital, and releases (emits) a photon of energy equal to the difference ($\Delta E = h\nu$).

- **Luminescence (emission of light)** works on the basis that if a molecule is excited above its ground state, then it must de-excite somehow and release excess energy as either non-radiative or radiative energy.





Fluorescence: a type of light emission

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

Yellow glass of juice
Em filter > 400 nm

1853 G.G. Stoke coined term “fluorescence”

Blue glass Filter

Window!

<400nm

Quinine Solution

HORIBA JOBIN YVON

Explore the future

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Jablonski diagram (JD)

☐ A good starting point for a discussion of luminescence (fluorescence or phosphorescence) principle is a simplified Jablonski diagram.

•The Jablonski diagram is employed to represent the energy levels of a molecule. As depicted in JD, S0, S1 and S2 represent ground, first and second singlet electronic states, respectively, whereas T1 and T2 describe first and second triplet electronic states, respectively.

•Each electronic energy level of a molecule also has numerous vibrational (v) and rotational (n) energy sublevels.

Figure 1.4. Professor Alexander Jablonski (1898–1980), circa 1935. Courtesy of his daughter, Professor Danuta Frackowiak.

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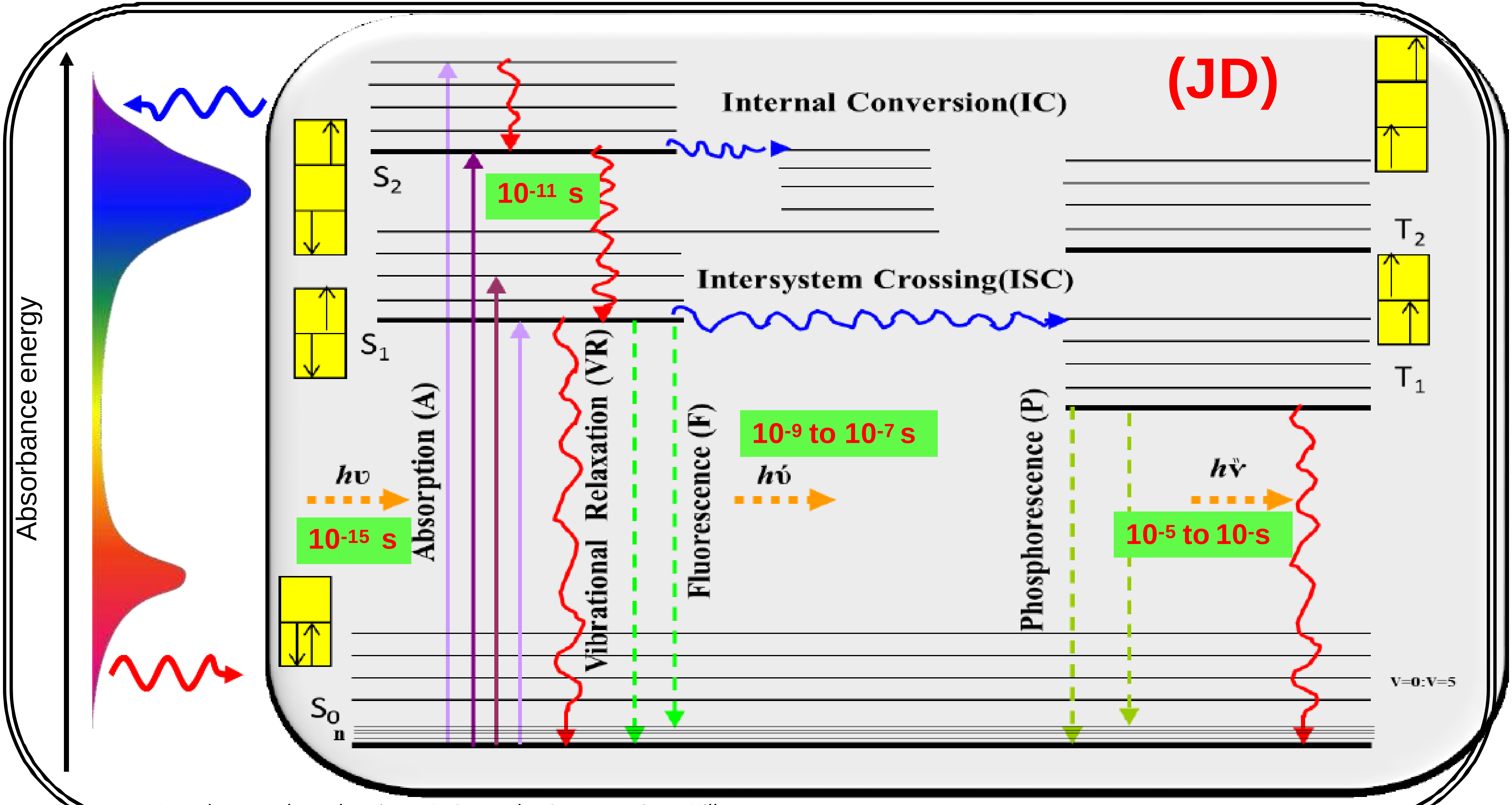

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PHOTOPHYSICAL PROCESSES:

- If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength. The three such photophysical processes which can occur are :

(1) Fluorescence (2) Phosphorescence (3) Chemiluminescence

- **Fluorescence**

✓ Process at which certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength.

✓ Substance that exhibits fluorescence is called fluorophore.

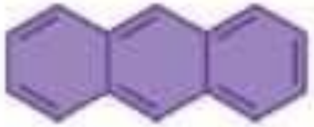
✓ Florescence stops as soon as the incident radiation is cut off.

Examples:

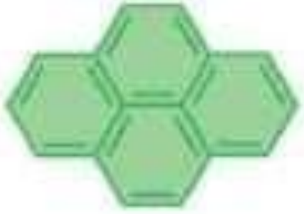
(a) a solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

(b) a solution of chlorophyll in ether shows blood red fluorescence.

Molecular formulas of common dyes of fluorescent probes (fluorophores)


Anthracene

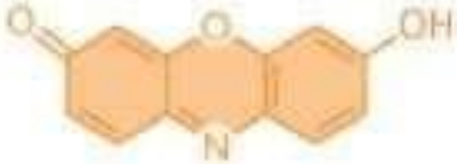
Naphthalimide


Pyrene

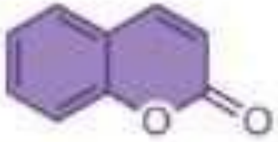
BODIPY

Fluorescein

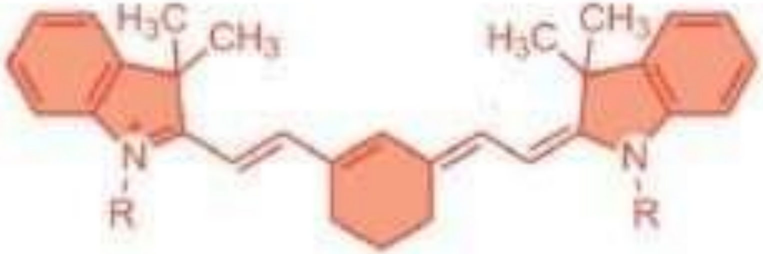
Rhodamine



Resorufin



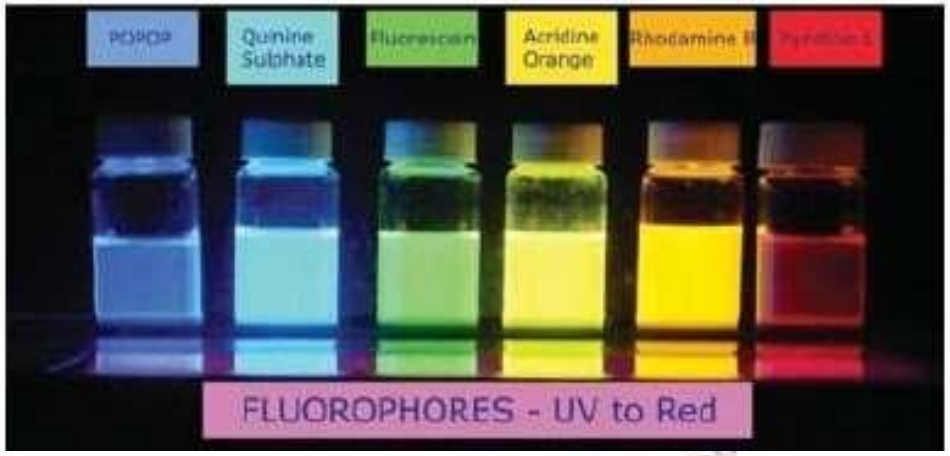
Coumarin



Cyanine

○ Fluorescence dependson:

1. pH
2. Solvent
3. Temperature
4. Salts
5. Concentration



Fluorescent minerals, shown under ultraviolet light:

Phosphorescence

- **When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence.**

- The substance which shows phosphorescence is called **phosphorescent substance.**

- Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by **solids**.

Examples:

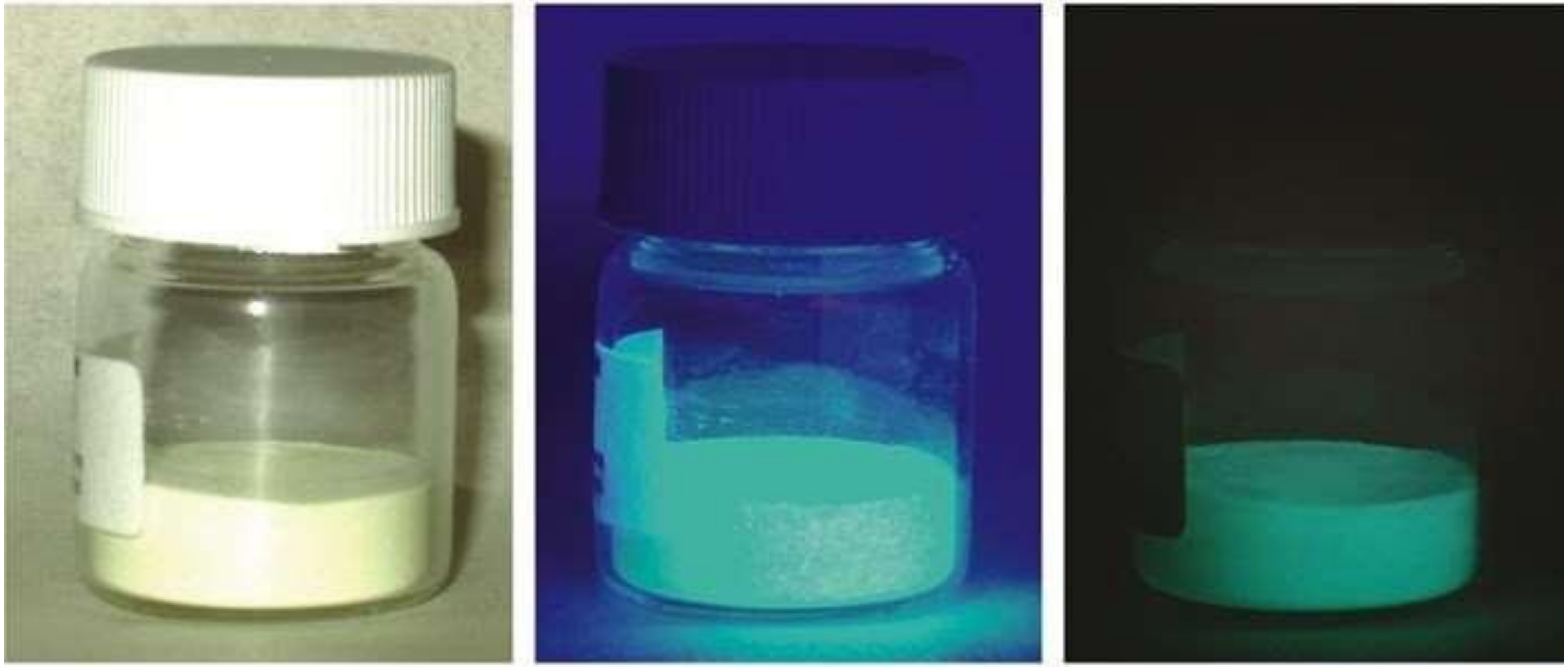
(a) Sulphates of calcium, barium and strontium exhibit phosphorescence.

(b)Fluorescein in boric acid shows phosphorescence in the blue region at 570nm wavelength.

- **Phosphorescence could be designated as delayed fluorescence.**

$$A + h\nu \dashrightarrow A^{*} \xrightarrow{\text{slow}} h\nu'$$

Phosphorescent powder under:



visible light, ultraviolet light, darkness

Chemiluminescence:

- **The emission of light as a result of chemical action is called chemiluminescence.** The reaction is referred to as **a chemiluminescent reaction.**

- **Chemiluminescent reaction** is the reverse of a photochemical reaction which proceeds by absorption of light.

- The light emitted in a chemiluminescent reaction is also called **'cold light'** because it is produced at ordinary temperature.

- In a chemiluminescent reaction, the energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.

Chemiluminescence of fireflies and luminol

Examples:

(a)The glow of fireflies due to the aerial oxidation of *luciferin* (a protein) in the presence of enzyme *luciferase.*

(b)The oxidation of 5-*aminophthalic* cyclic hydrazide (*luminol*) by hydrogen peroxide in alkaline solution, producing bright green light.

Photochemistry : It is the study of reactions that are brought about by the action of **visible or ultraviolet light.** e.g. photosynthesis of glucose in the plants by means of sunlight.

$$6\,CO_2 + 6\,H_2O \xrightarrow[\text{chlorophyll}]{\text{sun light}} C_6H_{12}O_6 + 6\,H_{2}0$$

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Chemical reactions accompanied with light are :

By the action of light

$$A \rightarrow B$$

(i) A new molecule is generated by chemical changes (light induced reactions)

(ii)In some reaction, during chemical reaction light is emitted (chemiluminescence)

Luminescence

- Chemiluminescence:

$$P_{4(g)} + O_{2(g)} + H_2O \longrightarrow \quad \longrightarrow \quad \longrightarrow \quad P_4H_{10} + h\nu$$

(green)

White phosphorus glows ignites in air to form phosphorus pentoxide.

-Bioluminescence :

(emission of light

by a living organism)

- mushrooms
- insects
- fishes

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Light : Electromagnetic field vibration spreading in quanta (photons).

Photon: The smallest amount of light carrying energy.

Energy of photons (A. Einstein)

$$E = h\nu = h\frac{c}{\lambda}$$

SO one particle of a chemical substance can absorb only one photon from a light beam: $\Delta E = h\nu$

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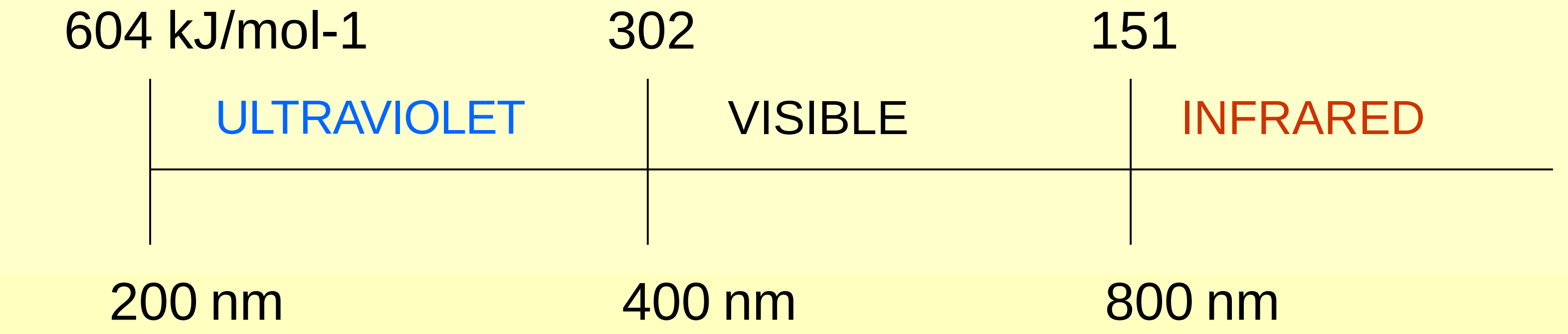
Chemical bond energies: from 100 – 1000 kJ/mol

Light energies:



604 kJ/mol-1 | 302 | 151

ULTRAVIOLET | VISIBLE | INFRARED

200 nm | 400 nm | 800 nm

So UV – and VIS region is expected to induce chemical reactions.

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1. Photochemical energy:

For any chemical transformation an activation energy, must be supplied to molecules.

Such energy can be provided by different way :

(i) Some molecules undergo **spontaneous transformations**.

(ii)In some cases, energy is supplied by **increasing the temperature** (**thermal condition**) as a result molecules present in the system have same amount of energy throughout the chemical transformation.

(iii) In another method, molecules present in the system involve the **absorption of electromagnetic radiation** in the visible or ultraviolet region (photochemical condition).

Such absorption of light excites an individual molecule from ground state to an excited electronic state without effecting the surrounding molecules.

- selective excitation
- chemistry of excited molecules differs from the chemistry of those in the ground state
- One can change the course of a reaction by activating the reactants by **light** rather than by heat.

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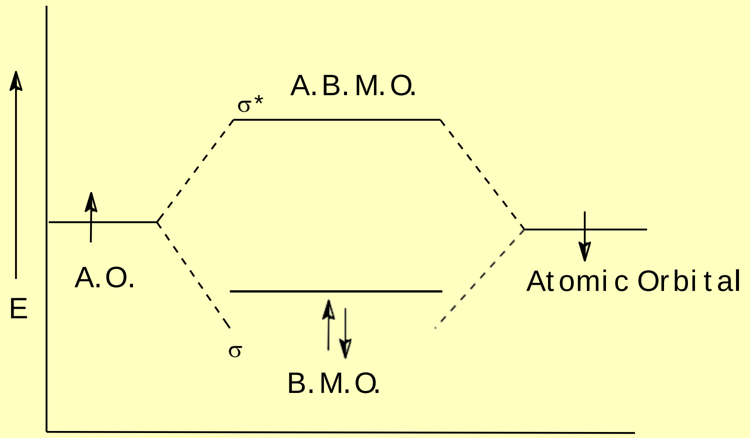
Infrared region is producing Vibrationally or rotationally excited molecules,

While light in the **visible and ultraviolet region** has sufficient energy to cover the range of chemical bond energies and is able to induce chemical changes by exciting molecules to higher electronic states.

2. Electronic excitation:



Promotion of an electron from the bonding orbital to the corresponding anti-bonding orbital take place .

o - σ^* ; π - π^* and n- π^*.

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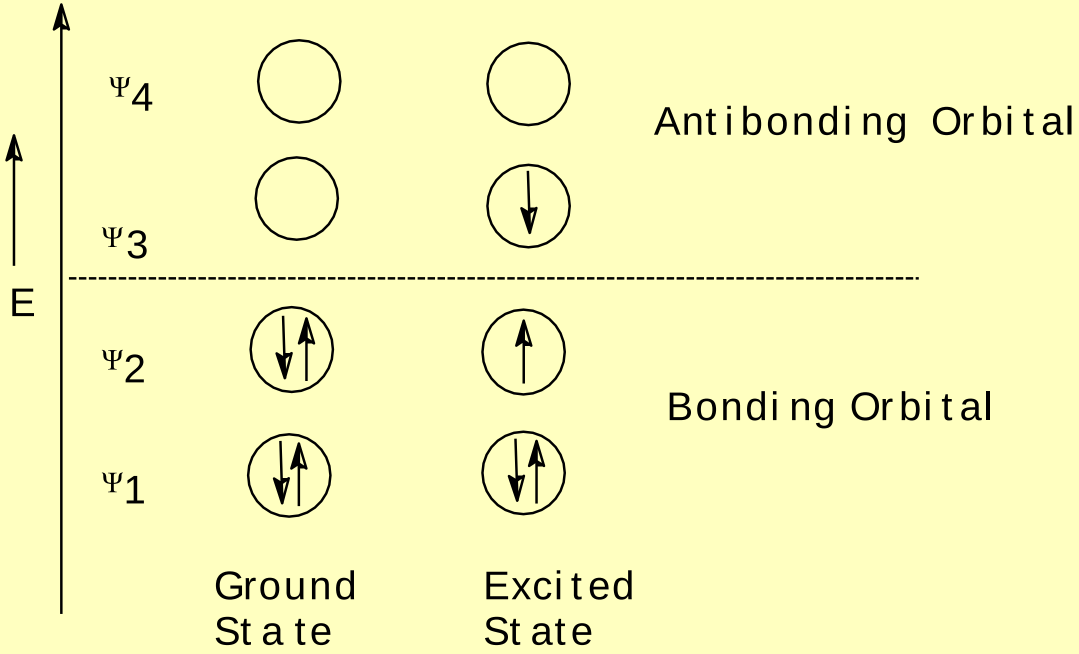
Molecular Orbital Diagram

$CH_2 = CH – CH = CH_2$



In butadiene π - π* transition occurs, from Ψ_2 to Ψ_3

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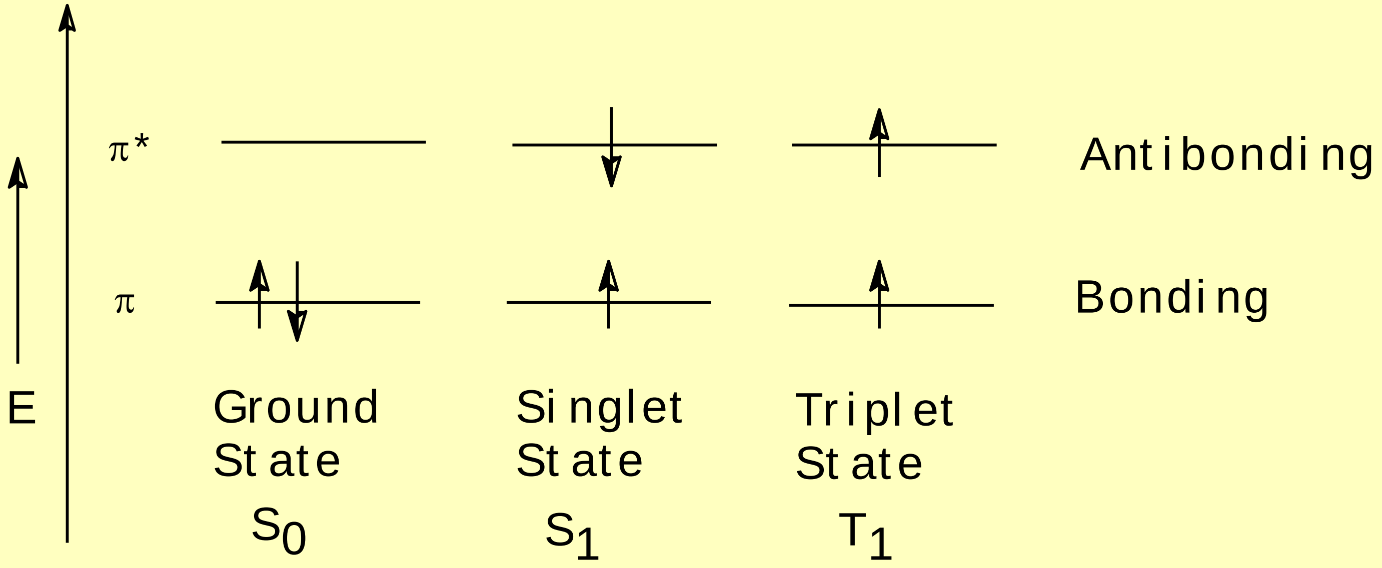
3. Excited States, Modes of Dissipation of Energy :

In an organic molecule, even number of electrons are paired in the ground state.

Now when absorption of light of the correct energy occurs, than one of the electron excited from ground state (π) to excited state(π^*) by retaining the spin, so the electron spins remain paired in the excited state. This state is called **excited singlet state (S_1).**

In some cases, spin inversion take places thus giving rise to a new excited state with two unpaired electrons. This state is called an **excited triplet state (T_1).**



A **triplet** state is **more stable** than the **singlet** state. Because in triplet state, electrons are unpaired - lesser inter electronic repulsion take place, while in singlet state electrons are paired, - causing inter electronic repulsion and is unstable.

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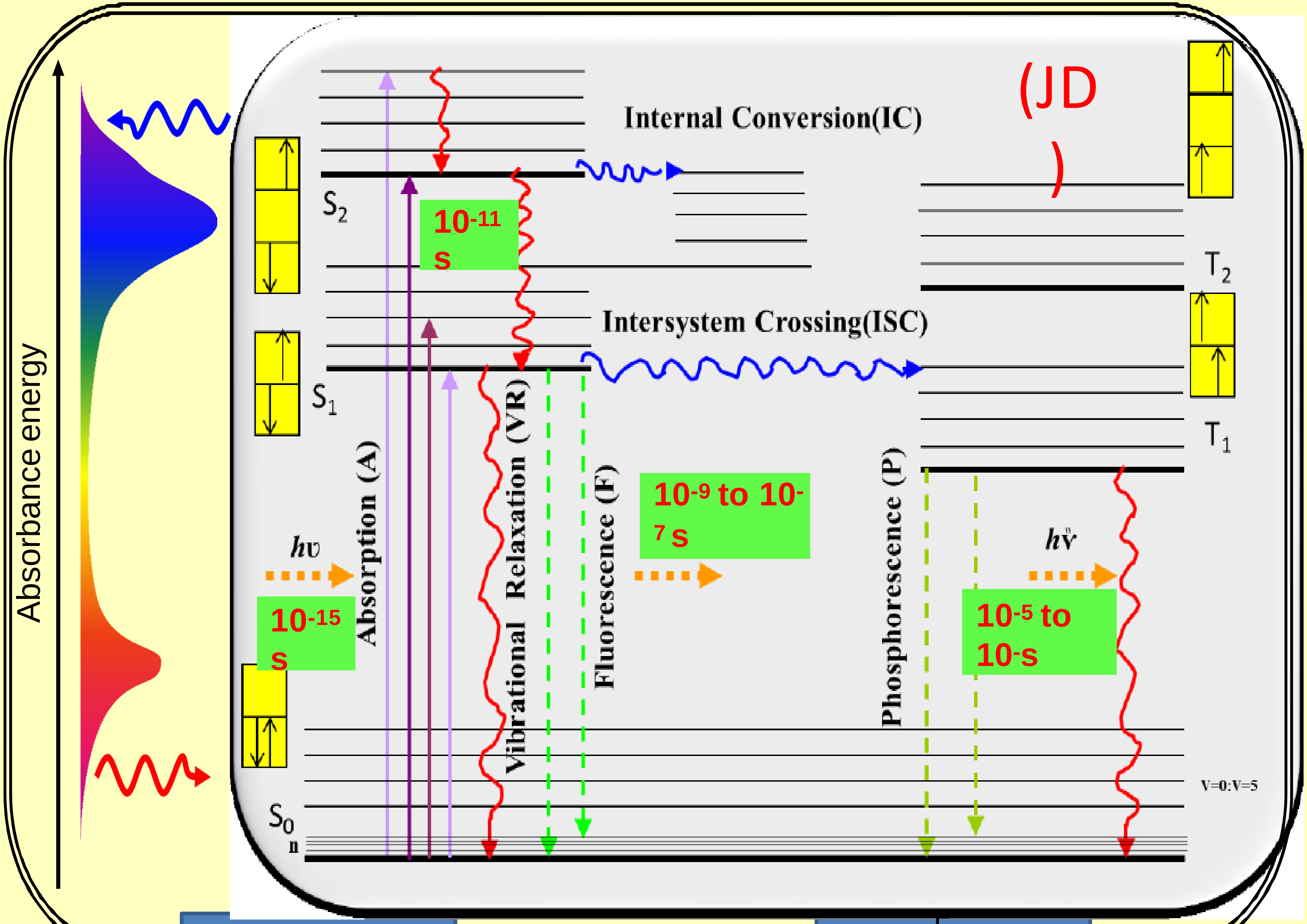
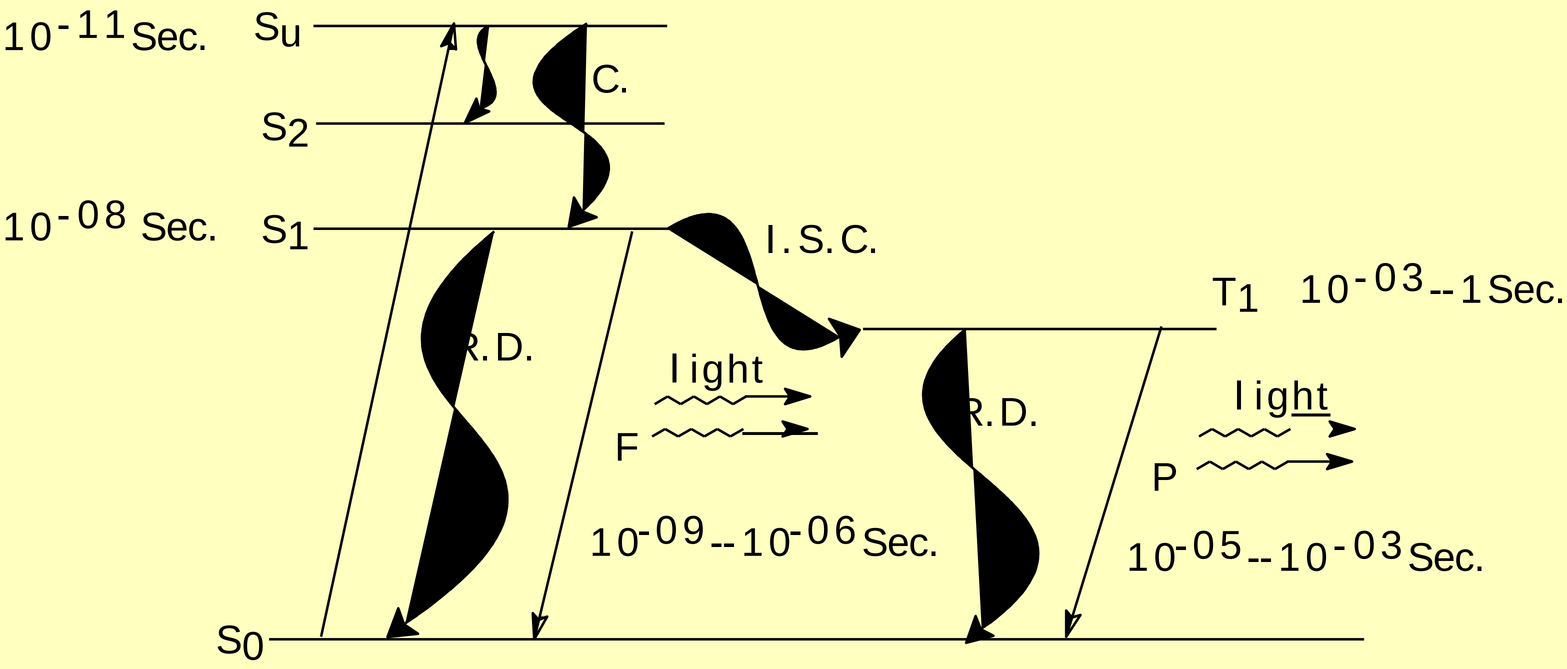

(JD
)
Absorbance energy
Internal Conversion(IC)
Intersystem Crossing(ISC)
S_2
S_1
S_0
n
T_2
T_1
10^{-11} s
10^{-9} to 10^{-7} s
10^{-15} s
10^{-5} to 10^{-}s
Absorption (A)
Vibrational Relaxation (VR)
Fluorescence (F)
Phosphorescence (P)
hυ
hὺ
V=0:V=5

Jablonski Diagram:



ISC = Intersystem crossing.
IC = Internal conversion.
F = Fluorescence.
P = Phosphorescence.
RD = Radiationless decay.

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When a molecule absorbs a photon of energy, electronic transition occurs (S_u or S_2 or S_1).

A molecule in S_1 state undergo one of the following four energy degrading (decay) processes to the ground state.

(i)The molecule can undergo chemical reaction or return to the ground state by emission of light by a process called **fluorescence** and generally occurs with in 10^{-9} to 10^{-6} sec.

(ii)It may return to ground state (S_0) by non radiative process in which excess energy of the excited state is shuffled into vibrational modes.

(iii) S_1 may undergo chemical reactions.

(iv) The molecule may undergo spin inversion to the triplet state (spin unpaired) by a process as "**intersystem crossing**", Which is a radiation less process.

Fluorescence : Emission of a photon from a singlet excited state to a singlet ground state, or between any two energy levels with the same spin, is called fluorescence. Fluorescence, decays rapidly after the excitation source is removed. Lifetime of the electron is only 10^{-5} to 10^{-8} s

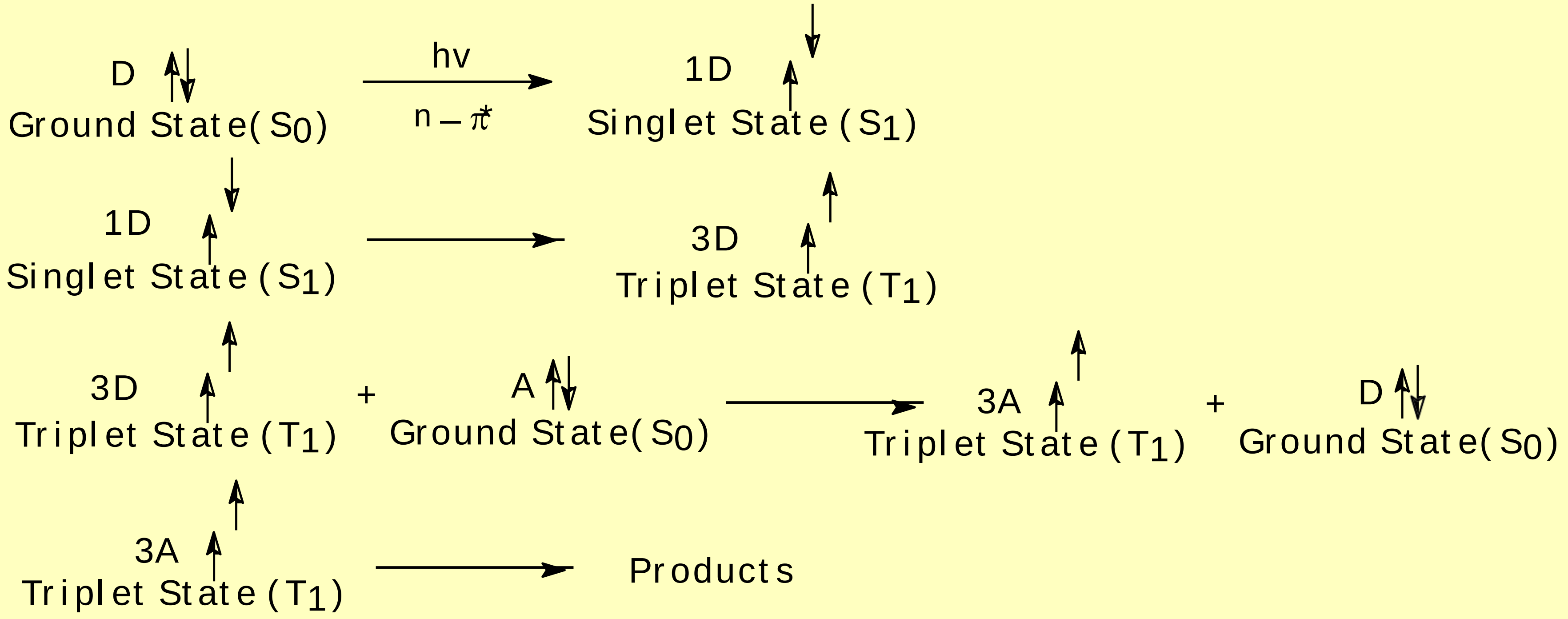
Phosphorescence : Emission between a triplet excited state and a singlet ground state is called phosphorescence. phosphorescence may continue for some time after removing the excitation source. Lifetime for phosphorescence ranges from 10^{-4} to 10^{4} s.

4. Energy Transfer and Photosensitization:

It is a one step radiationless transfer of excitation energy from an electronically excited molecule (donor) to the ground state of another molecule (acceptor).” As a result, the donor molecule returns to the ground state and the acceptor molecule gets excited.

For energy transfer the donor molecule should have at least 5 kcal/mole more energy than the acceptor molecule.

A typical mechanism for triplet energy (T_1) transfer is described below :



D Ground State(S_0) $\xrightarrow[n-\pi^*]{hv}$ 1D Singlet State (S_1)

1D Singlet State (S_1) $\longrightarrow$ 3D Triplet State (T_1)

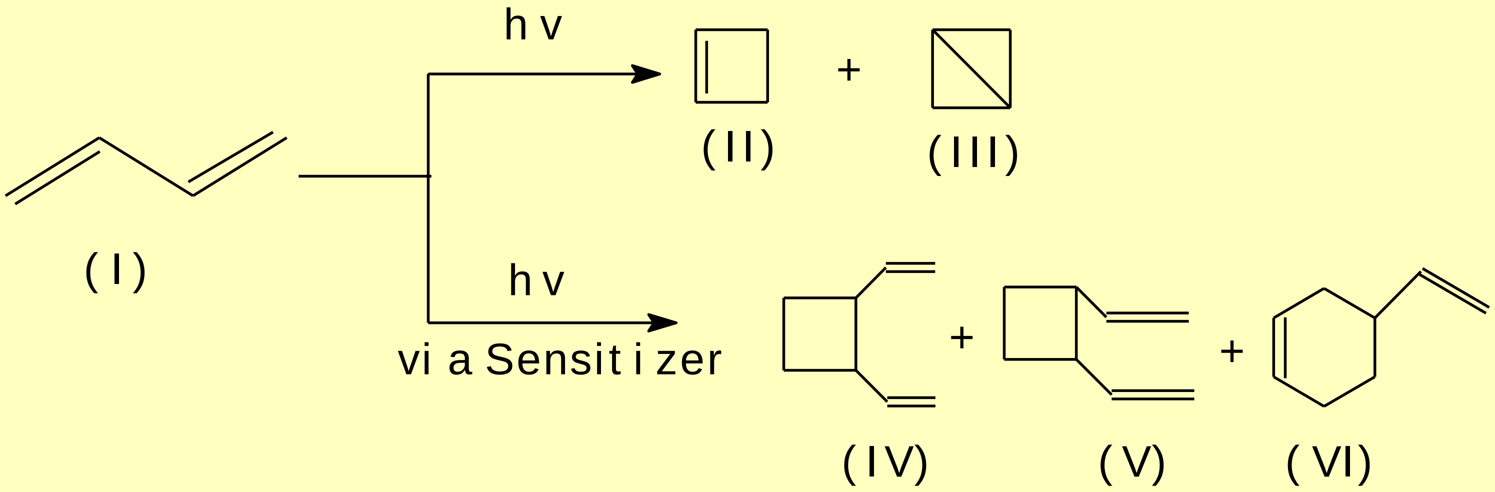
3D Triplet State (T_1) + A Ground State(S_0) $\longrightarrow$ 3A Triplet State (T_1) + D Ground State(S_0)

3A Triplet State (T_1) $\longrightarrow$ Products

Where D= Donor & A= Acceptor
1= Singlet & 3= Triplet

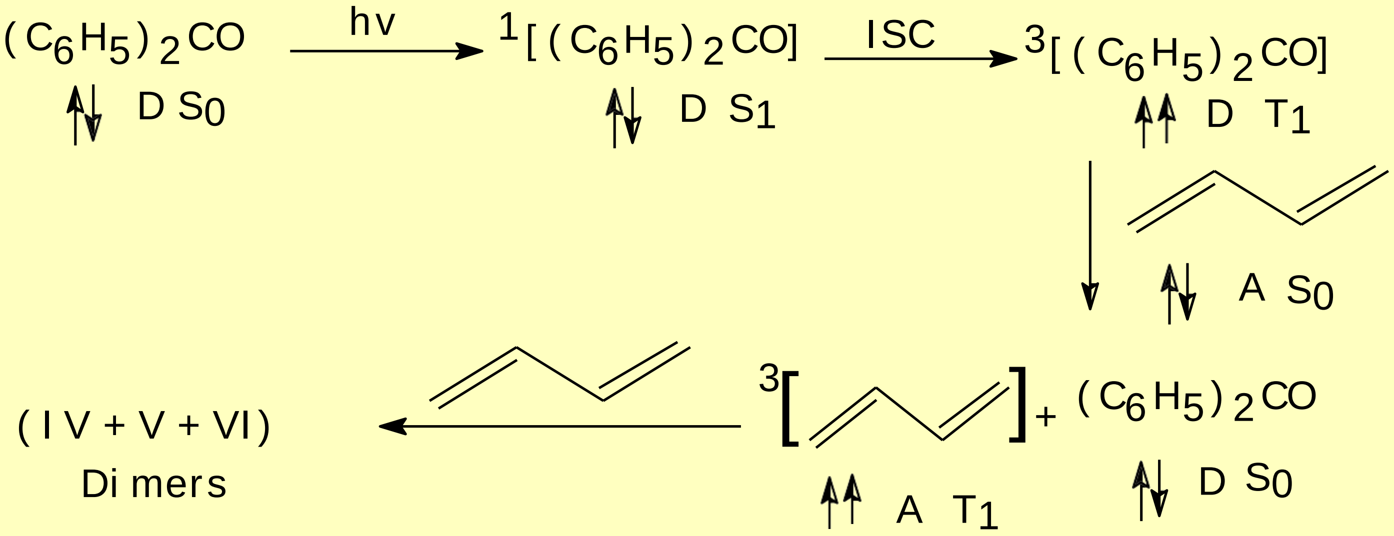
Energy transfer between butadiene as an acceptor and benzophenone as donor.

Butadiene (I) **(acceptor)** upon direct irradiation leads to produce product (II) and (III) via ring closure.



When butadiene is mixed with benzophenone **(donor)** and is irradiated at 366 nm, than butadiene undergoes photochemical change to yield dimmers (IV) (V) and (VI).

In this process light is absorbed by benzophenone **(donor)** but the reaction is taking place with butadiene **(acceptor)** . Here benzophenone **(donor)** is functioning as a photosensitizer, while **butadiene** is good **acceptor** as it has 9 kcal/mole less triplet energy than benzophenone.



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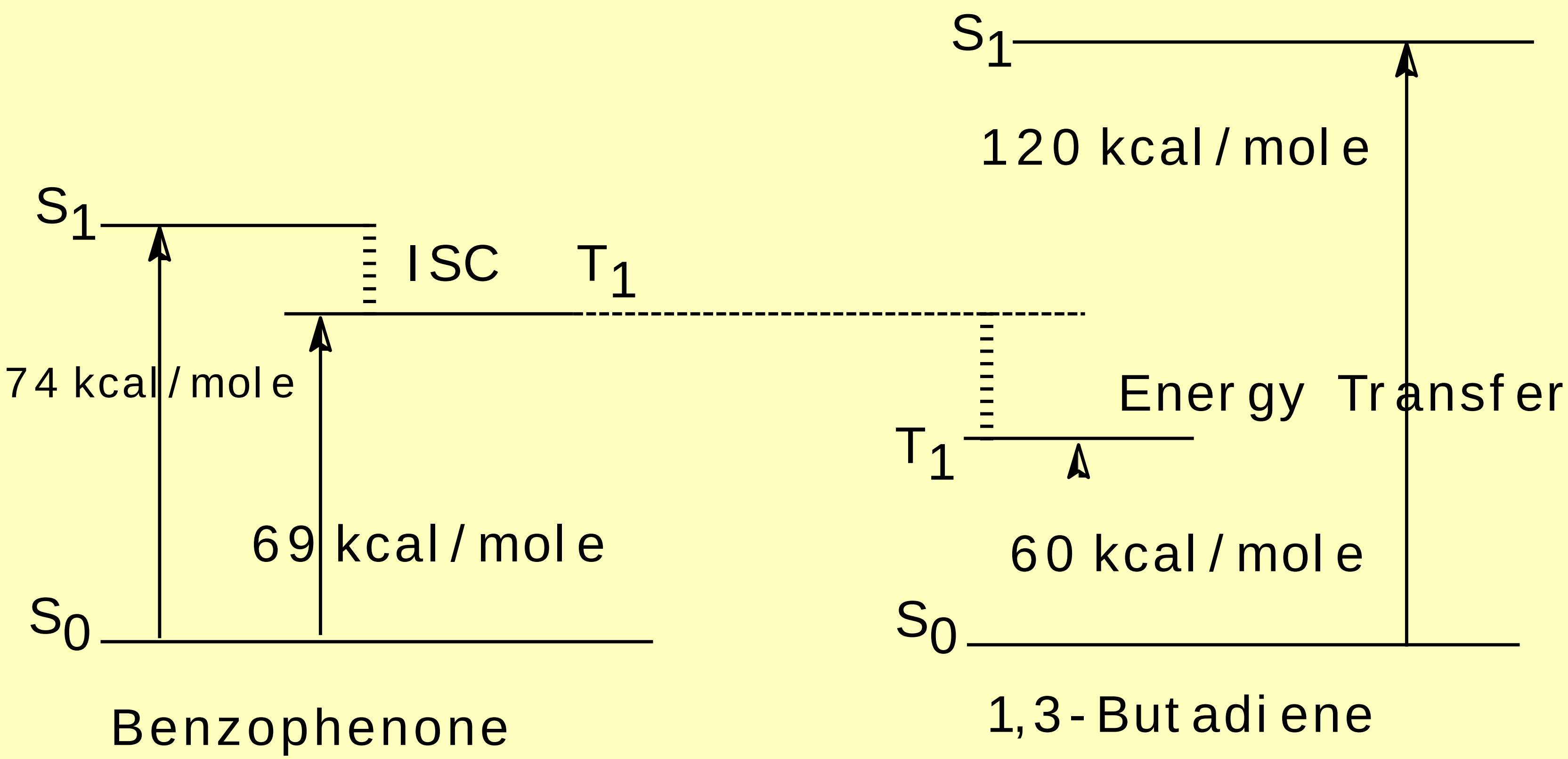

Benzophenone (69 Kcal/mole) **(donor)** triplet energy transfer to 1,3 - Butadiene (60 Kcal/mole) **(acceptor)** (Intermolecular energy transfer).

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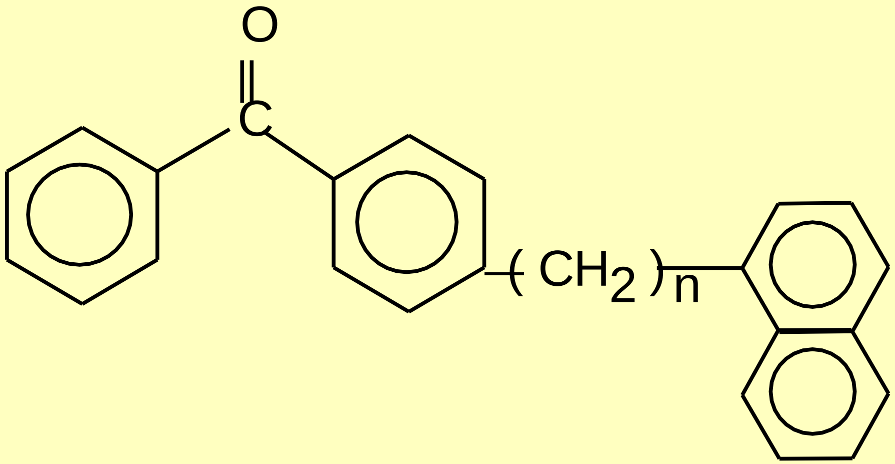
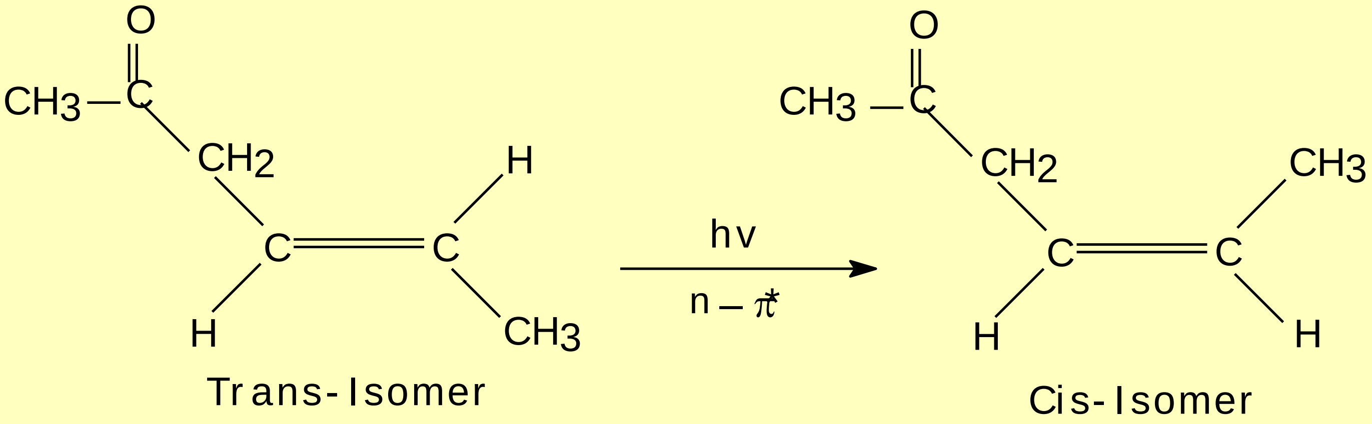
Intramolecular energy transfer in benzophenone (donor) and naphthalene.



Irradiation of these compounds with light of about 366 nm wavelength absorb by benzophenone showed that there is an efficient transfer of triplet excitation from the benzophenone moiety to the naphthalene moiety.

energy transfer in Cis – Trans Isomers of 4-hexen-2-one.

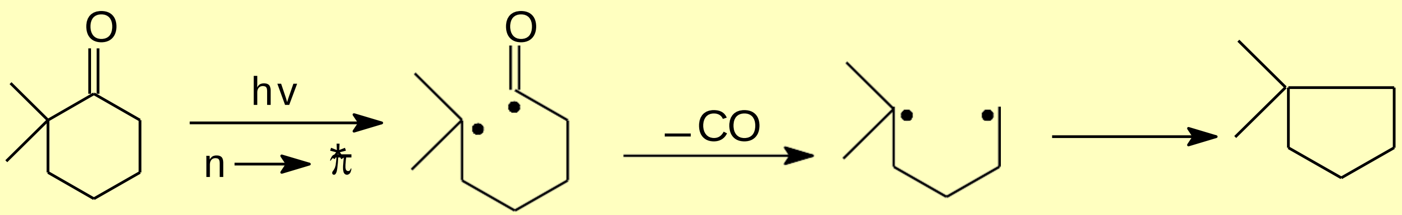


Cis - trans isomerization of 4-hexen-2-one shows intramolecular energy transfer when light is absorbed by the carbonyl group.

During this photoreaction energy transfer from the carbonyl group to the carbon-carbon double bond takes place.

Photochemical reaction of cyclic ketones.

The photochemical reaction of saturated cyclic ketones begin with the n - π* excitation of the carbonyl group followed by α – fission. The biradical may then undergo hydrogen transfer from the α–carbon atom to the carbonyl group yielding a **ketene** or it may give rise to an **unsaturated aldehyde** by hydrogen transfer to the carbonyl group.



2,2ǀ -dimethyl cyclohexanone converted to 1,1ǀ -dimethyl cyclopentane .

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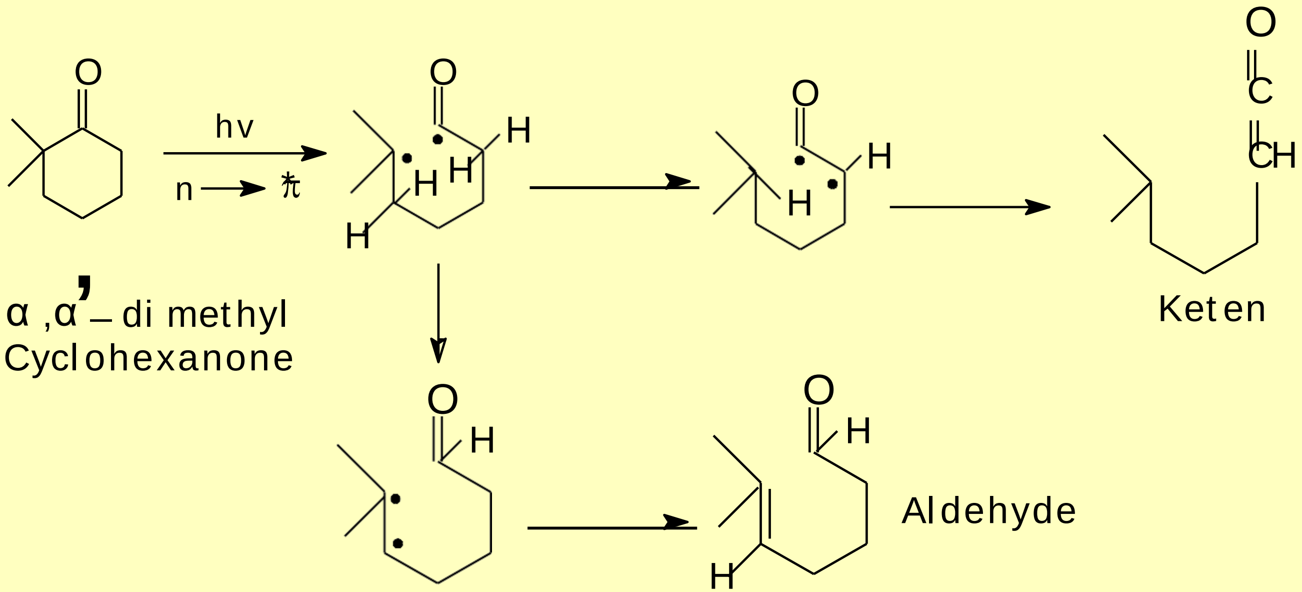
cyclic ketones may give rise to an unsaturated aldehyde by hydrogen transfer to the carbonyl group.



α ,α' – di methyl Cyclohexanone

Keten

Aldehyde

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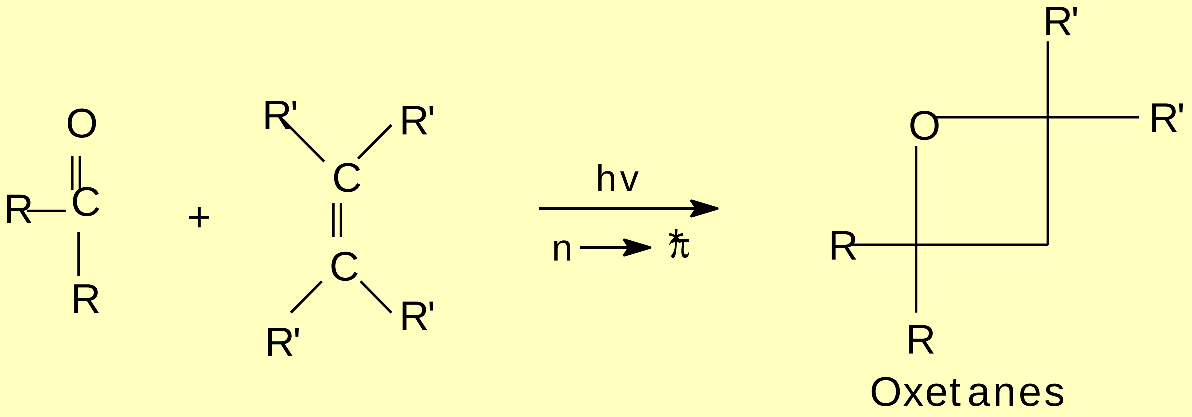
Paterno-Buchi Reaction

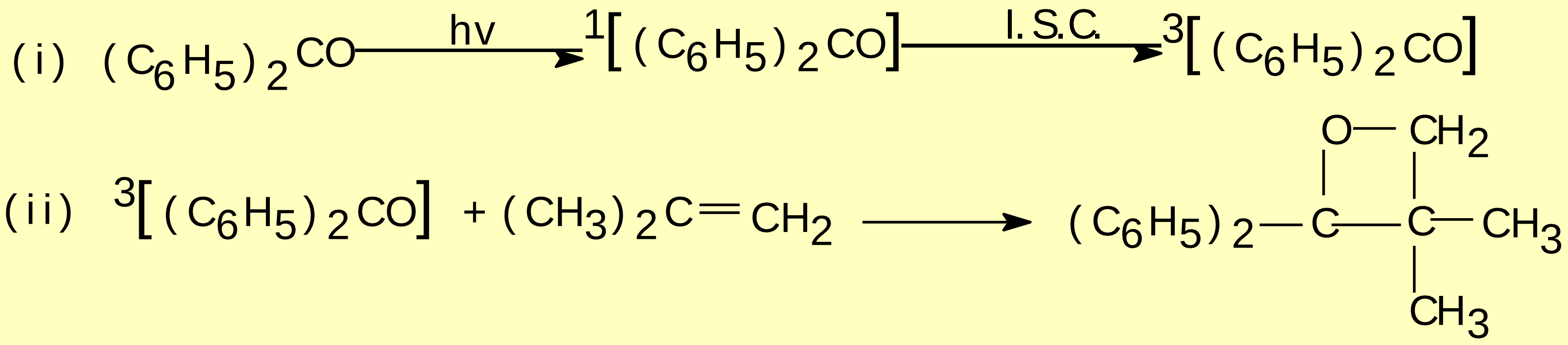
Photocycloaddition of carbonyl compounds with olefins upon irradiation yields oxetanes, is known as paterno-buchi reaction.



Photocycloaddition is performed by irradiation with the light of wave length absorbed only by the carbonyl group, it involves the triplet excited state of the carbonyl comp rather than that of olefin.

Mechanism of pateron-buchi reaction

Unsymmetrical Olefins:

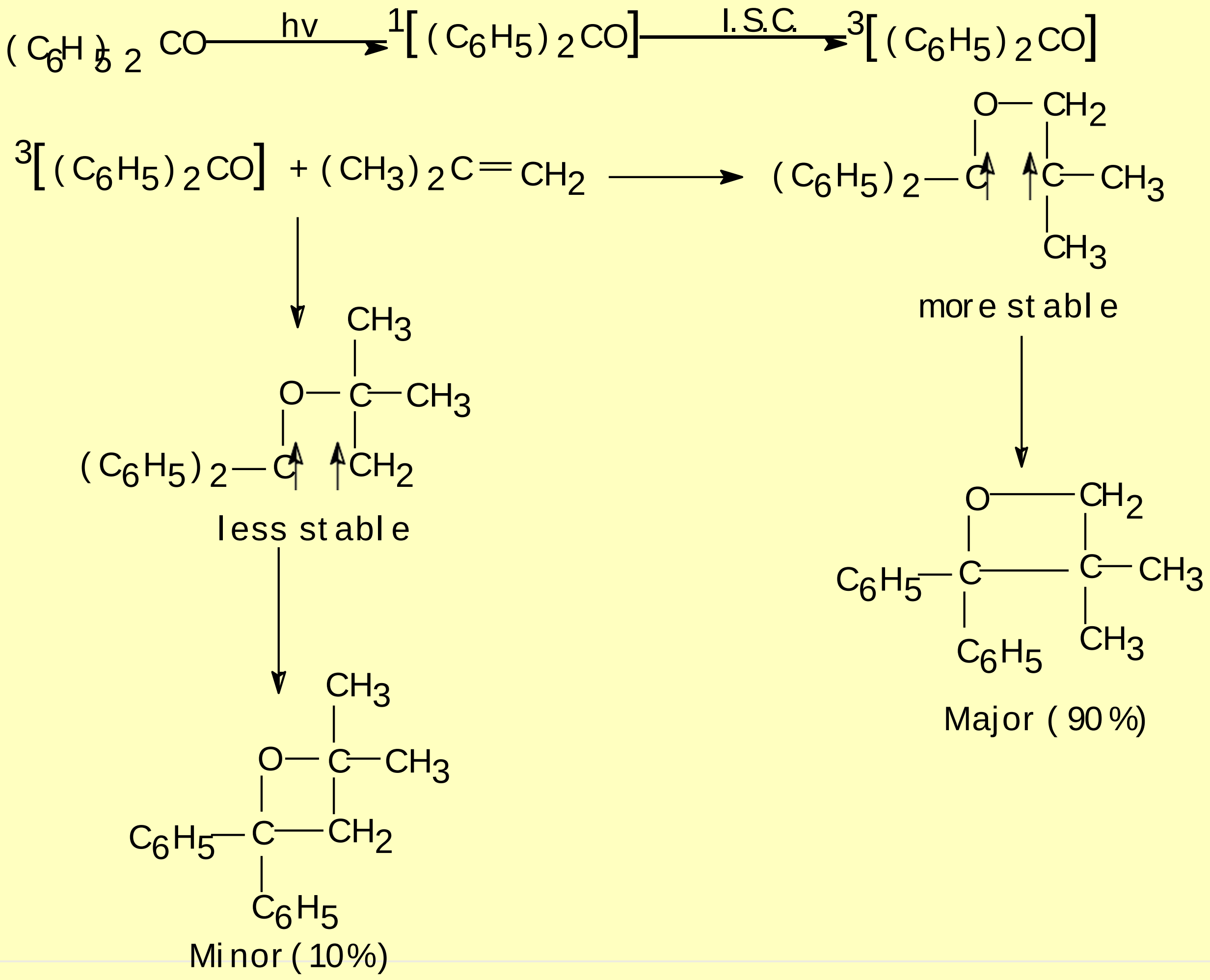


$$(i)\quad (C_6H_5)_2CO \xrightarrow{hv} {}^{1}[(C_6H_5)_2CO] \xrightarrow{I.S.C.} {}^{3}[(C_6H_5)_2CO]$$

$$(ii)\quad {}^{3}[(C_6H_5)_2CO] + (CH_3)_2C{=}CH_2 \longrightarrow \begin{array}{lcccl} & O & - & CH_2 & \\ & | & & | & \\ (C_6H_5)_2- & C & - & C & -CH_3 \\ & & & | & \\ & & & CH_3 & \end{array}$$

Since the olefin is unsymmetrical, two products will be obtained. The product in which the most stable biradical intermediate forms, will be the major and other will be minor.

Mechanism of pateron-buchi reaction



$$(C_6H_5)_2CO \xrightarrow{h\nu} {}^1[(C_6H_5)_2CO] \xrightarrow{I.S.C.} {}^3[(C_6H_5)_2CO]$$

$$^3[(C_6H_5)_2CO] + (CH_3)_2C{=}CH_2 \longrightarrow$$

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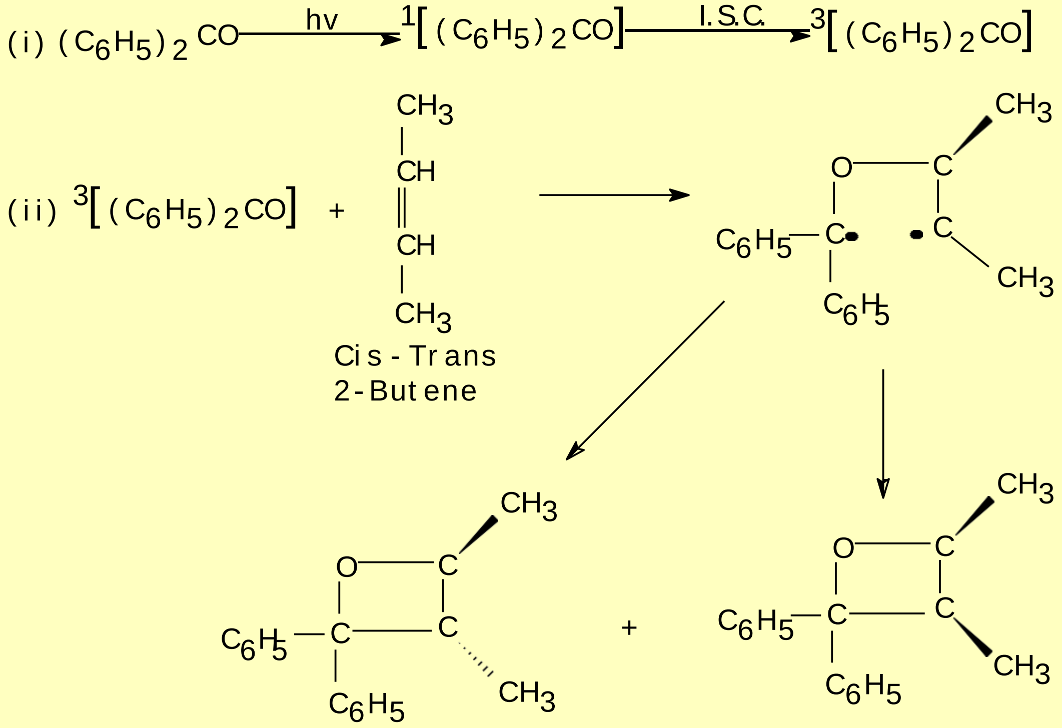
(ii) Symmetrical Olefins:

Irradiation of benzophenone with either cis or trans-2-butene yields the same mixture of both isomeric oxetanes.

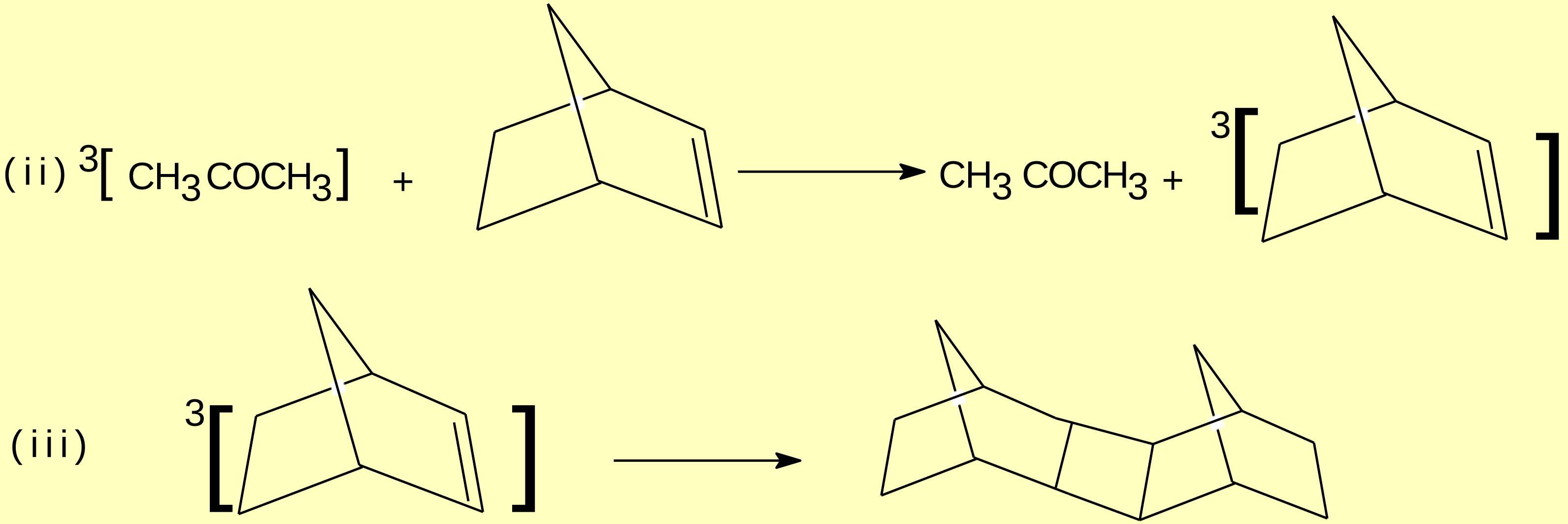


$$(i)\ (C_6H_5)_2CO \xrightarrow{hv} {}^1[(C_6H_5)_2CO] \xrightarrow{I.S.C.} {}^3[(C_6H_5)_2CO]$$

Limitation of paterno-buchi reaction

Paterno-buchi reaction fails when the triplet excitation energy of ketone exceeds that of olefins. Under such condition oxetane formation does not take place but energy transfer take place from triplet excitation state of ketone (T_1) to the olefins (S_0). There by olefin is excited to triplet state and is dimerize. e.g. Irradiation of acetone with Norborene, yields dimmers of norbornene rather than Oxetanes.

$$(i)\ CH_3COCH_3 \xrightarrow{h\nu} {}^1[CH_3COCH_3] \xrightarrow{I.S.C.} {}^3[CH_3COCH_3]$$



Dimer of Norborene

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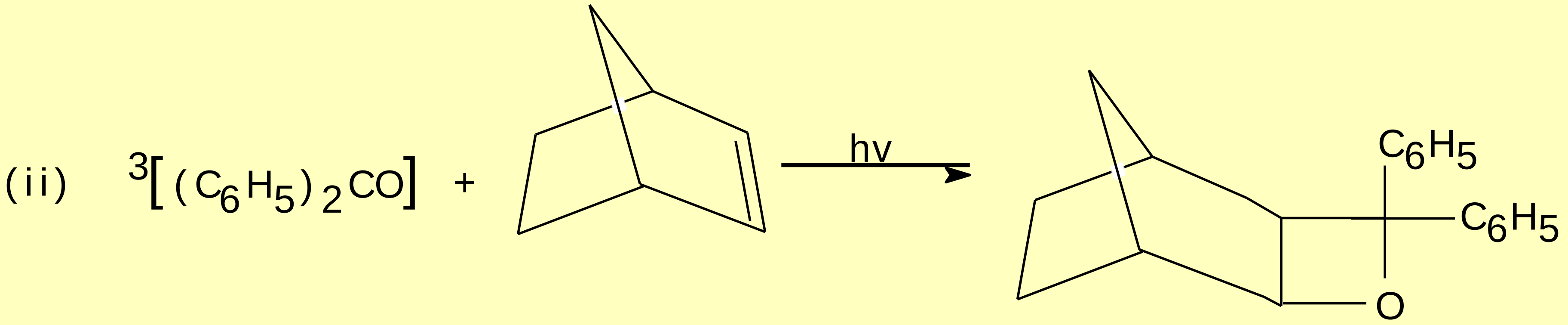
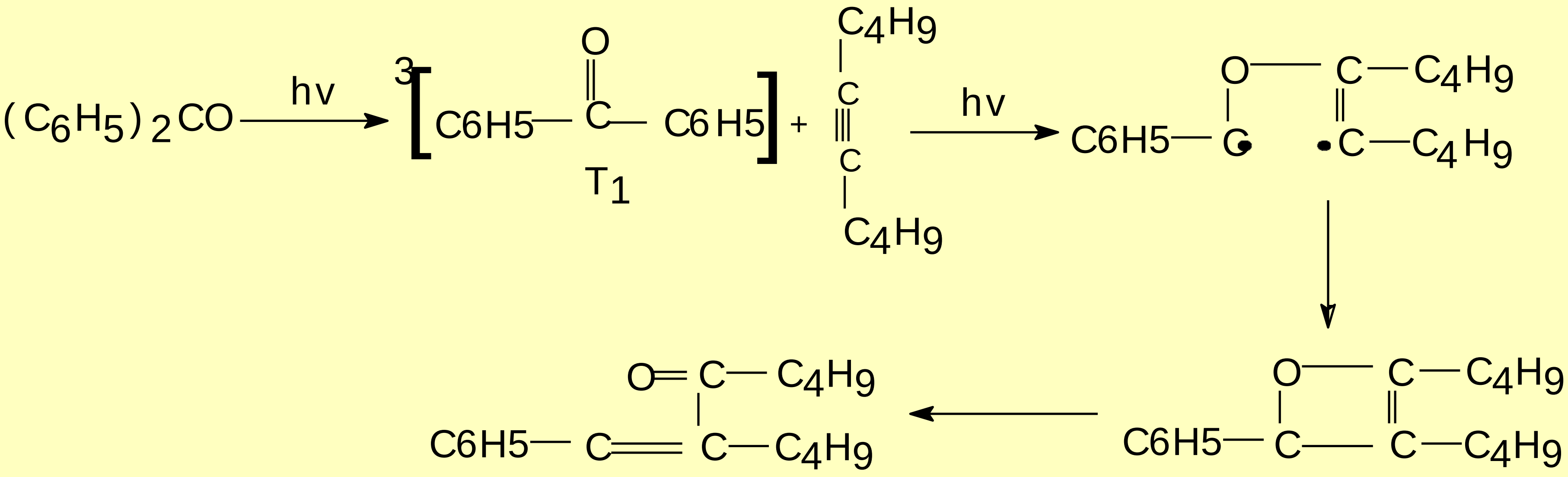
When a ketone (Benzophenone) having less triplet energy is used will leads to paterno – buchi reaction to form Oxctanes of a nonrborene.

(i) $(C_6H_5)_2CO \xrightarrow{h\nu} {}^1[(C_6H_5)_2CO] \xrightarrow{I.S.C.} {}^3[(C_6H_5)_2CO]$



Paterno – buchi reaction also fails to occur with conjugated dienes.



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Photochemistry of α, β – unsaturated ketone:

α, β – unsaturated ketone displays two absorption maxima at 220 nm (π - π*) and at 310 nm(n - π*) and irradiation may induce either of these transition. The excited state in such ketone has more π -π* transition than n - π* triplet even though there may be an initial n - π* excitation.

Two important reactions initiated by π - π* states of the α, β – unsaturated ketone

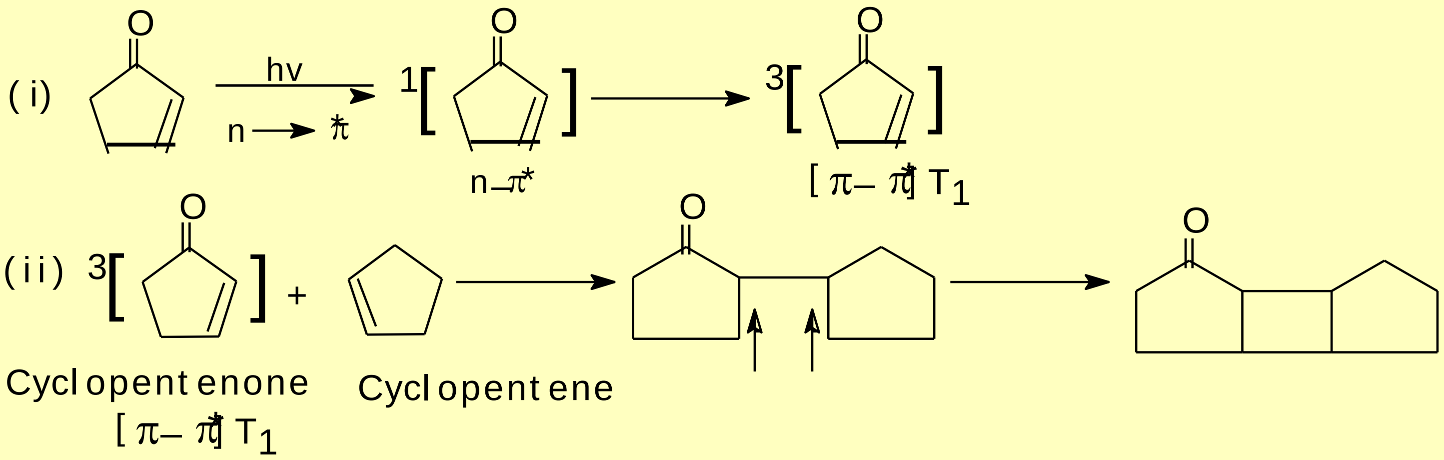
(i) Olefin addition across the double bond. and

(ii) photocyclodimerization.

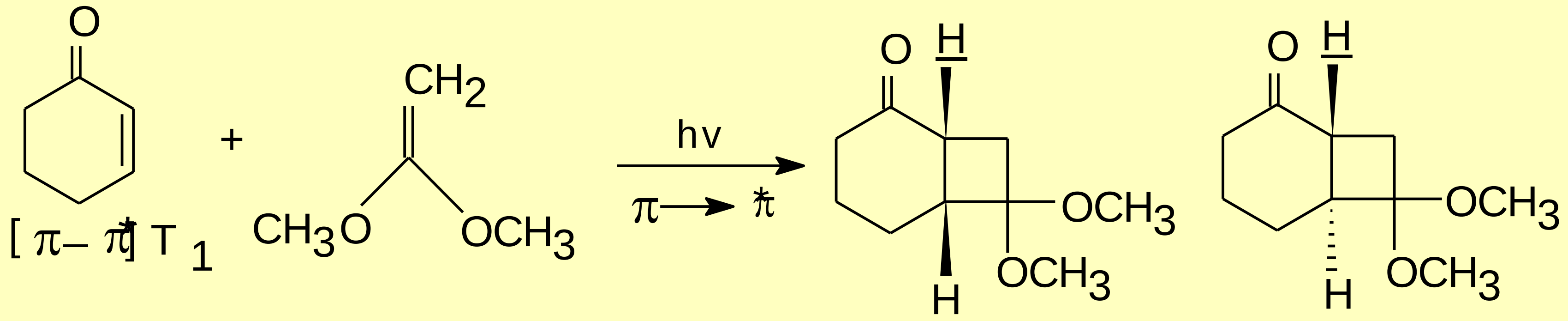
(i) Olefin addition:

Photocycloaddition reaction involves, initial formation of a carbon – carbon bond between the α–carbon of α, β–unsaturated ketone and the olefin, followed by cyclization.

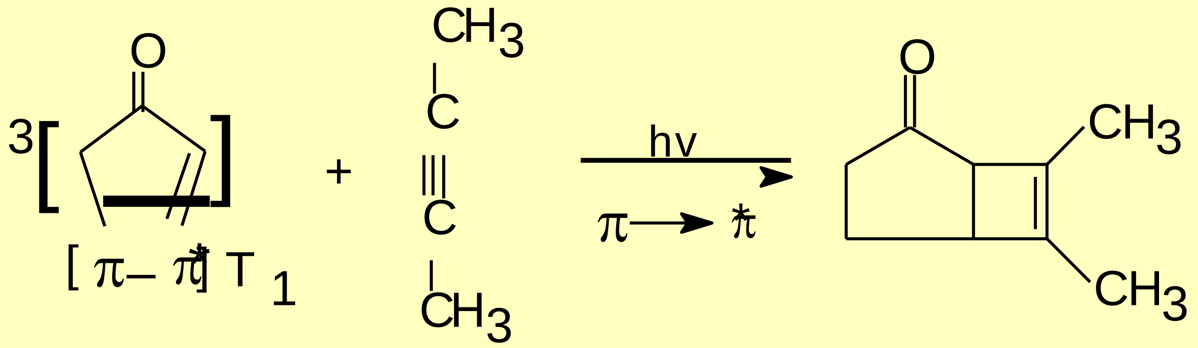
Cyclopentenone + Cyclopentene



Cyclohexenenone + 1,4,-dimethoxyethylene



Cyclopentenone + Acetylene



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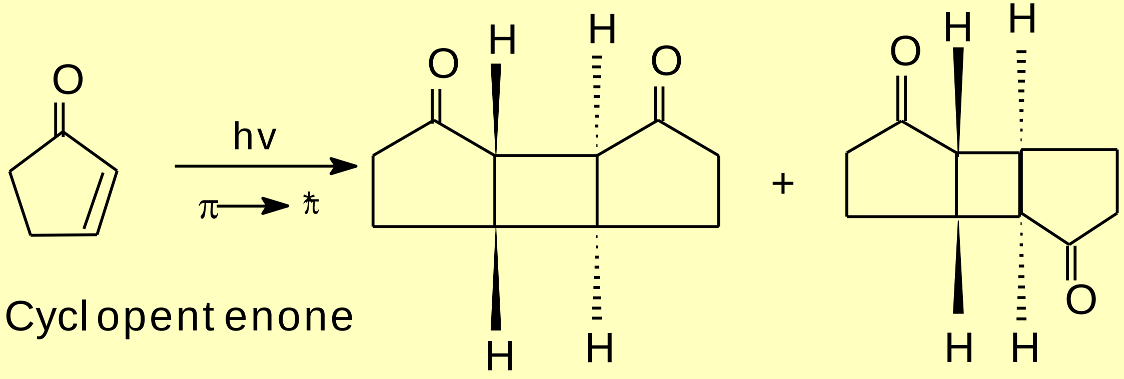
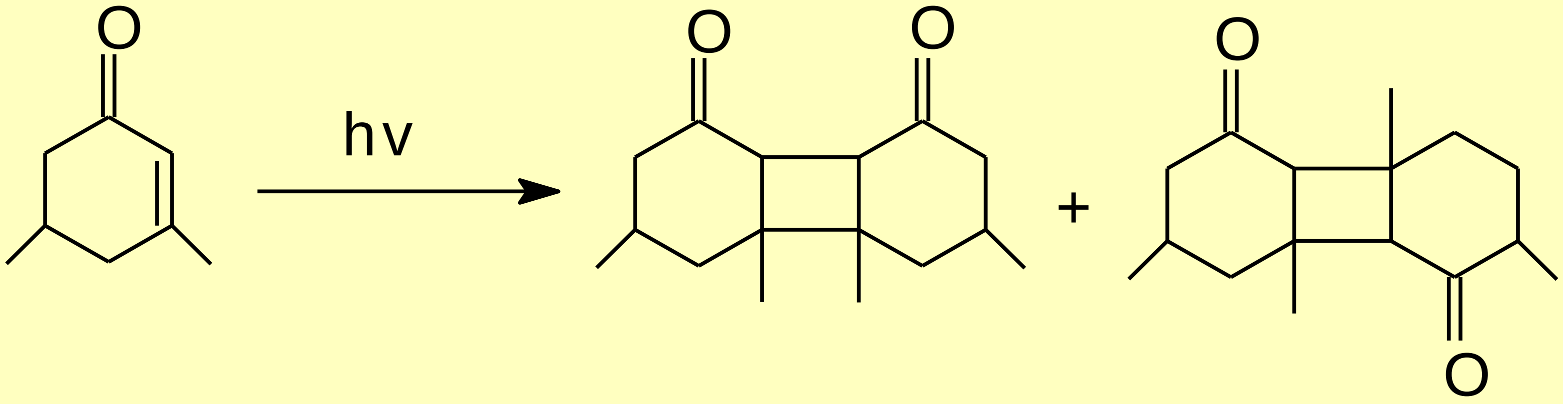
(ii) Photodimerization:

The photodimerization of α, β – unsaturated ketones occurs readily in cyclic systems. Irradiation of cyclopentenone yields head to head to and head to tail dimmers in almost equal amount. However, head to head dimmers are preferred in polar solvent, while head to tail dimmers are favoured in non – polar media.



The dimerization of cyclohexenene derivative occurs in a similar manners.



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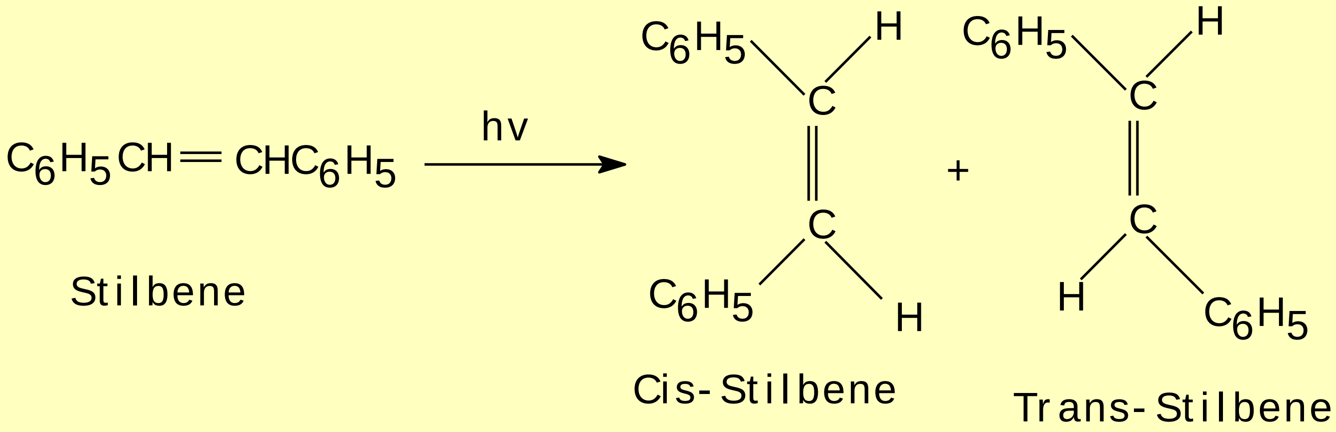
Photochemistry of olefins:

The photochemistry of olefin involves only two types of electronic excitations i.e. $\sigma-\pi^*$ and $\pi-\pi^*$. Promotion of an electron from $\sigma-\pi^*$ requires more energy (available from the light of wavelength longer then 150 nm) and hence difficult to achieve under usual experimental conditions. The $\pi-\pi^*$ excitation is experimentally accessible as it requires the absorption of light of about 180 – 210 nm for non - conjugated olefins and of about 220 nm or more for the conjugated olefins. Because of this reason most of the photochemical studied involve only $\pi-\pi^*$ excitation.

Photoisomerization of cis and trans Stilbene.

Direct irradiation of solution of either cis – or trans – stlbene yields a mixture consisting of 60% cis – stilbene and 40% trans- stilbene.



Electronic excitation of cis - trans alkenes leads to two distinct states; the trans excitation (E_T=48) state being of lower energy then the cis excited state. (E_T=57 kcal/mole). As a result the trans alkene is more heavily populated either by direct or through sensitization than cis isomer these excited state may either intermediated from trans to cis isomer through a rotational process or return to the respective electronic state. Thus initial absorption of light by either of there isomer is rapidly followed by intersystem crossing to the respective triplet states. Photoisomerization then occurs via a common triplet intermediate.

$$\begin{tikzcd}
\text{Cis-Stilbene} \arrow[r, "h\nu"] & {}^{1}[\text{Cis-Stilbene}] \arrow[r] & {}^{3}[\text{Cis-Stilbene}] \arrow[d, shift left] \\
\text{Trans-Stilbene} \arrow[r, "h\nu"] & {}^{1}[\text{Trans-Stilbene}] \arrow[r] & {}^{3}[\text{Trans-Stilbene}] \arrow[u, shift left]
\end{tikzcd}$$

$$C_6H_5CH\overset{\text{—}}{\text{---}}CHC_6H_5 \longrightarrow \underset{(60\%)}{\text{Cis-Stilbene}} + \underset{(40\%)}{\text{Trans-Stilbene}}$$

The intermediates either interconverts to the triplet of the other or goes to a common triplet intermediate called the phantom triplet or photostalionary state. Which leads finally to the cis isomer.

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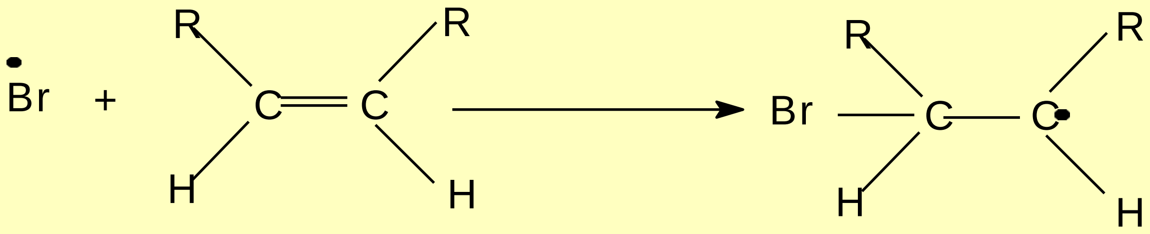
Photochemical cis – trans isomerization in presence of halogens.

In presence of halogens photochemical cis-trans isomerization takes place as shown below:

Upon photochemical irradiation halogen radical produced.

$$Br_2 \xrightarrow{h\nu} \dot{Br} + \dot{Br}$$

Halogen radical is than add to the olefin yielding an alkyl radica



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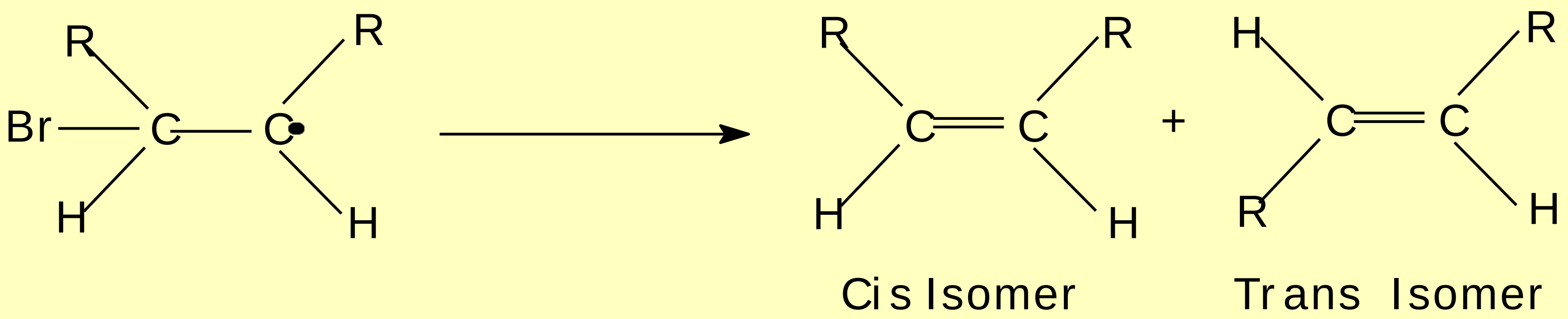
Elimination of halogen atom from alkyl halide radical yields a constant ratio of cis- and trans- isomers.



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Cyclic olefins may undergo addition reactions, instead of dimerization upon irradiation in methanol. The reaction of 4-isopropyl-1-methyl cyclohexene with methanol is sensitized by xylene as shown below.

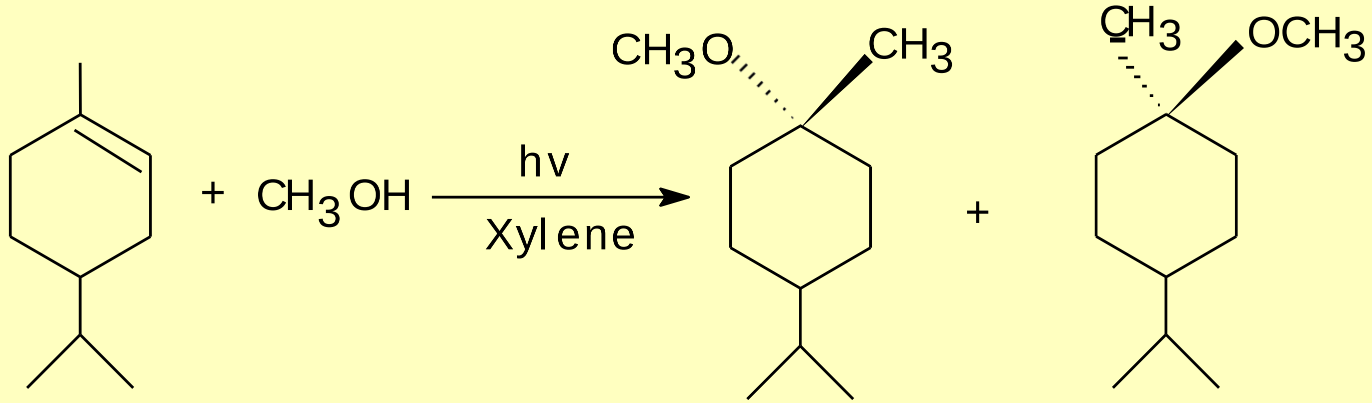
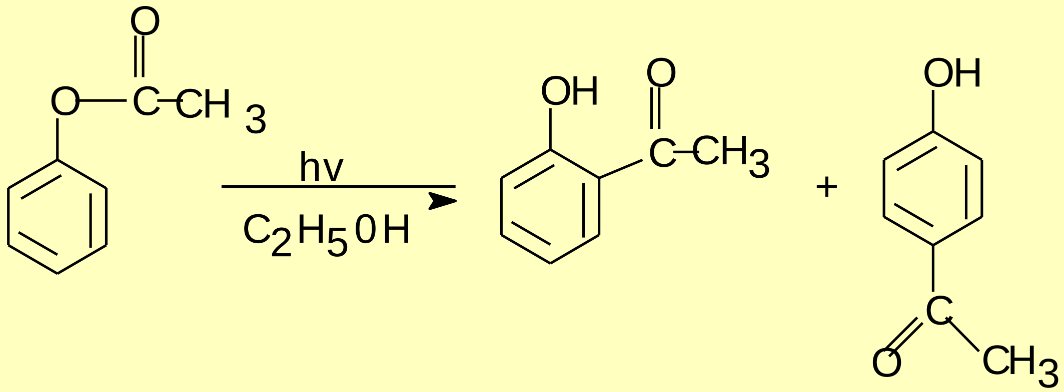
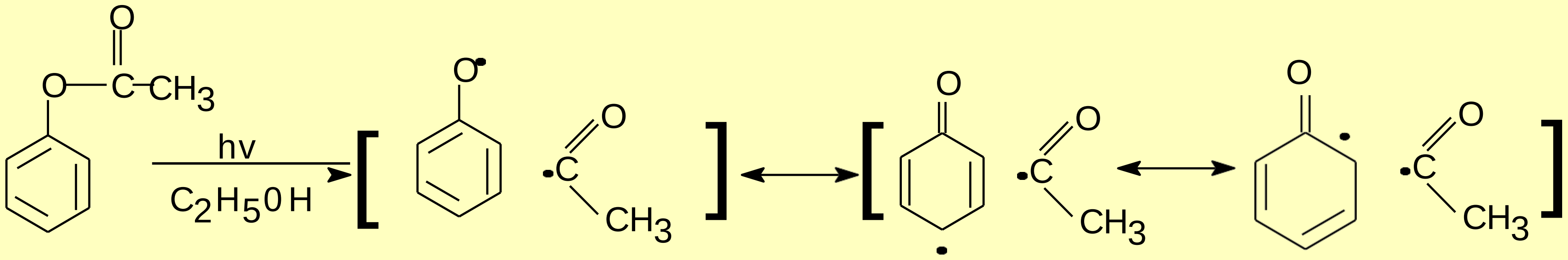


Photo-Fries rearrangement

This rearrangement involves the conversion of a phenolic ester (phenyl acetate) to a hydroxy ketone in presence of light.

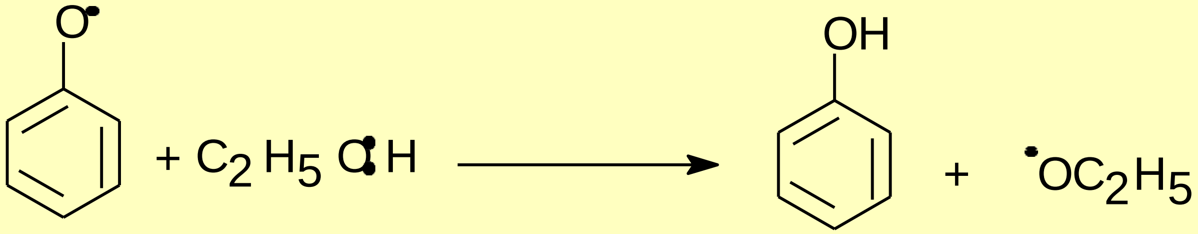


Mechanism of this reaction involves a homolytic cleavage of the acyl – oxygen bond and formation of a radical pair intermediate, which is held together in a solvent cage.



The coupling of radical pair then yields the stable products. During photo-fries rearrangement a small amount of phenol is also formed.

This might be due to the abstraction of hydrogen atom from the solvent by the phenoxy radical.



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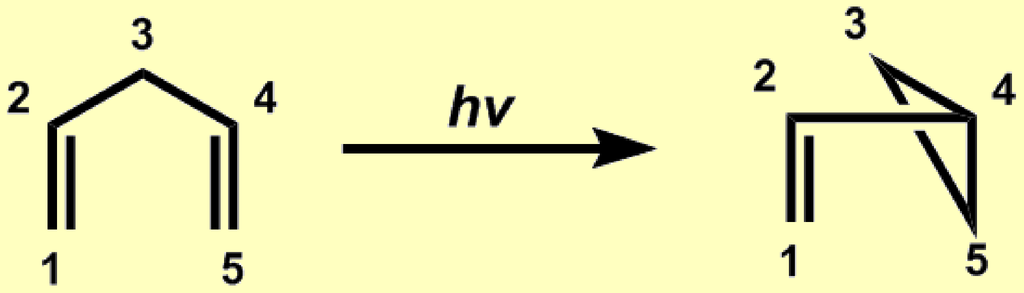
Di-π methane rearrangement

The **di-pi-methane rearrangement** is a photochemical reaction of a molecular entity that contains two π-systems separated by a saturated carbon atom (a 1,4-diene or an allyl-substituted aromatic ring), to form an ene- (or aryl-) substituted cyclopropane.

The rearrangement reaction formally amounts to a 1,2 shift of one ene group (in the diene) or the aryl group (in the allyl-aromatic analog) and bond *formation* between the lateral carbons of the non-migrating moiety.



It is called as **Zimmermann rearrangement**

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Reference Books:

- Fundamentals of photo chemistry, K.K. Rothagi-Mukheriji, Wiley-Eastern.
- Essentials of Molecular Photochemistry, a Gilbert and J. Baggott, Blackwell Scientific Publication.
- Molecular Photochemistry, N. J. Turro, W.A. Benjamin.
- Introductory Photochemistry, A. Cox and t. Camp, McGraw Hill.