PHOTOCHEMISTRY-RADIATIVE AND NON-RADIATIVE DECAY

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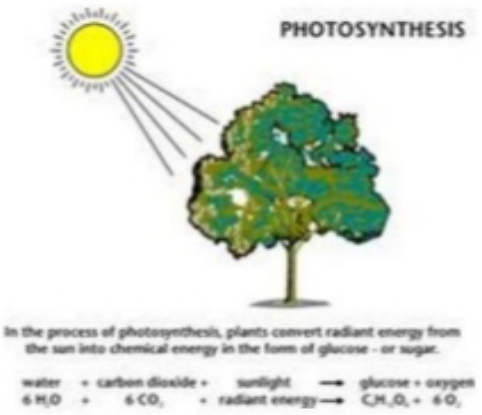
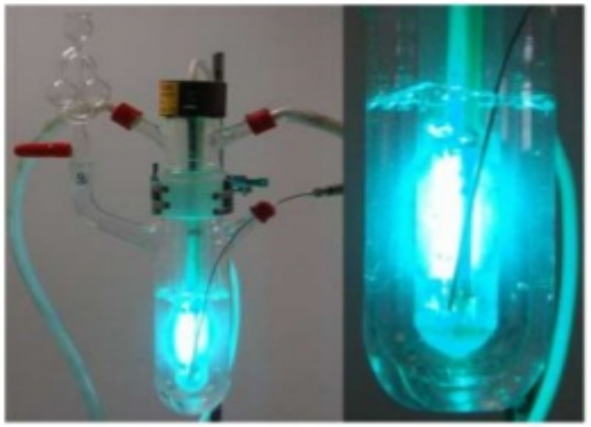
Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction .

EXAMPLES OF PHOTOCHEMICAL REACTIONS

Photosynthesis



Photochemistry



Primary Processes

- One molecule is excited into an electronically excited state by absorption of a photon, it can undergo a number of different primary processes.
- **Photochemical** processes are those in which the excited species dissociates, isomerizes, rearranges, or react with another molecule.
- **Photophysical** processes include radiative transitions in which the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions in which some or all of the energy of the absorbed photon is ultimately converted to heat.

Laws Governing Absorption Of Light

- **Lambert's Law:** This law states that decrease in the intensity of monochromatic light with the thickness of the absorbing medium is proportional to the intensity of incident light.

  $-dI/dx \propto I$

or $-dI/dx = KI$, which on integration changes to

$$I = I_0 e^{-Kx}$$

Where I_0 = intensity of incident light.

I = intensity of transmitted light.

K = absorption co efficient.

- **Beer's Law :** It states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration 'c' of the solution.

  Mathematically, $-dI/dx \ \alpha \ Ic$

  or $-dI/dx = \epsilon Ic$,which on integration changes to $I=I_0 e^{-\epsilon cx}$

Where, ϵ = molar absorption coefficient or molar extinction coefficient.

Laws governing Photochemistry

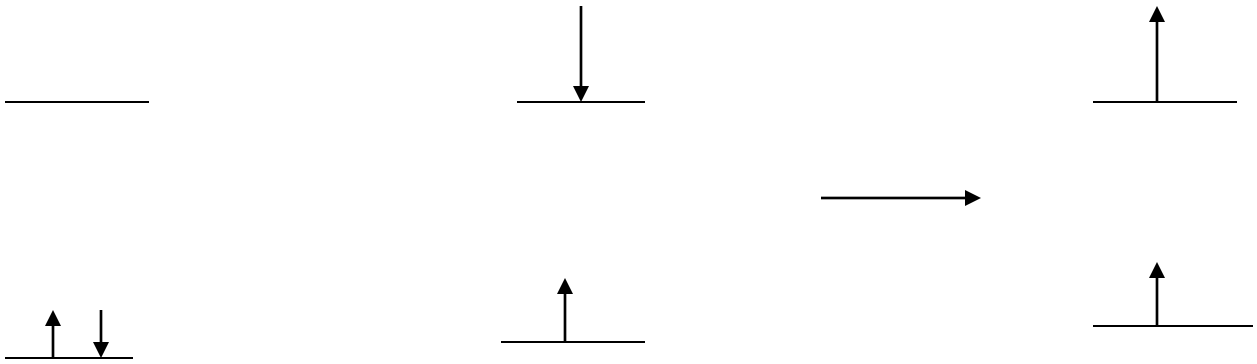
- **Grotthus-Draper Law:**

  Only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule.

- **Stark-Einstein's Law (Second Law of Photochemistry):**

  It states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. The energy absorbed by one mole of the reacting molecules is given by E=Nhv. This energy is called one einstein.

Fluorescence and phosphorescence in terms of excitation of electrons:



Singlet ground state So

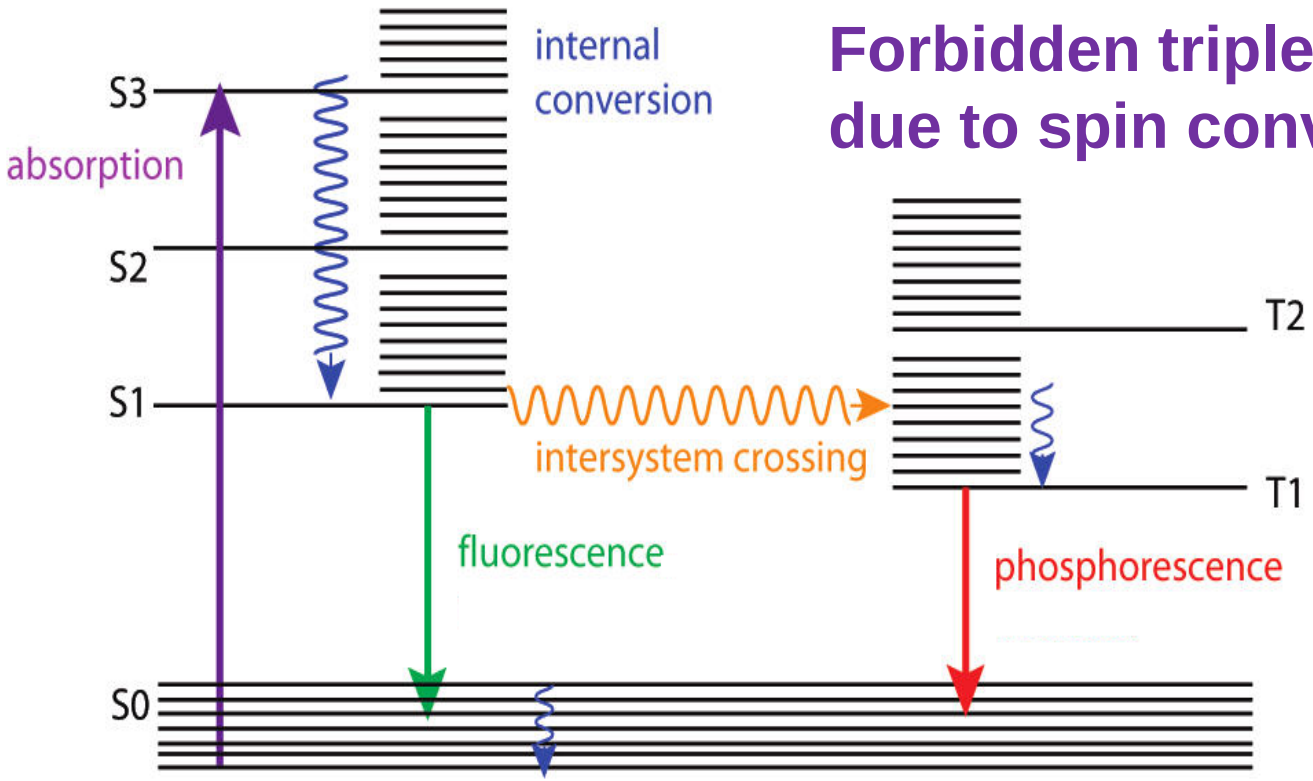
Singlet excited state S_1 (pair of electorns with Opposite spins but each in different orbital)

Triplet excited state T_1 (pair of electrons with parallel spins in different Orbitals)

The exicted species can return to the ground state by losing all of its excess energy by any one of the paths shown in Jablonski diagram.

Jablonski Diagram

Allowed singlet states



Forbidden triplet states due to spin conversion

Ground state

Explanation of Jablonski Diagram

non-radiative process

Path I: The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative.

Internal Crossing(IC): The first step is the transition from higher excited singlet states to the lowest excited singlet state S_1.This is called internal conversion (IC).

It is a **non-radiative** process and occurs in less than 10^{-11} second .Now from S_1 the molecule return to ground state by any of the following paths.

- **Path II:**
- **Intersystem crossing (ISC):** Some energy may be lost in Tranfer from S_1 to T_1 in the form of heat.

It is called intersystem crossing (ISC). This path is **non-radiative.**

Radiative process

Path III:

- **Fluorescence:** Molecule releases energy in the form of light or uv radiation.This is called **Fluorescence. Its Radiative Process**

Path IV:

- **Phosphorescence:**
- After ISC, the molecule may lose energy in the form of light in going from the excited triplet state to the ground state.This is called phosphorescence. **Its Radiative Process**

Fluorescence: Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence .

e.g Organic dyes such as eosin,fluorescein etc.

vapour of sodium,mercury,iodine etc.

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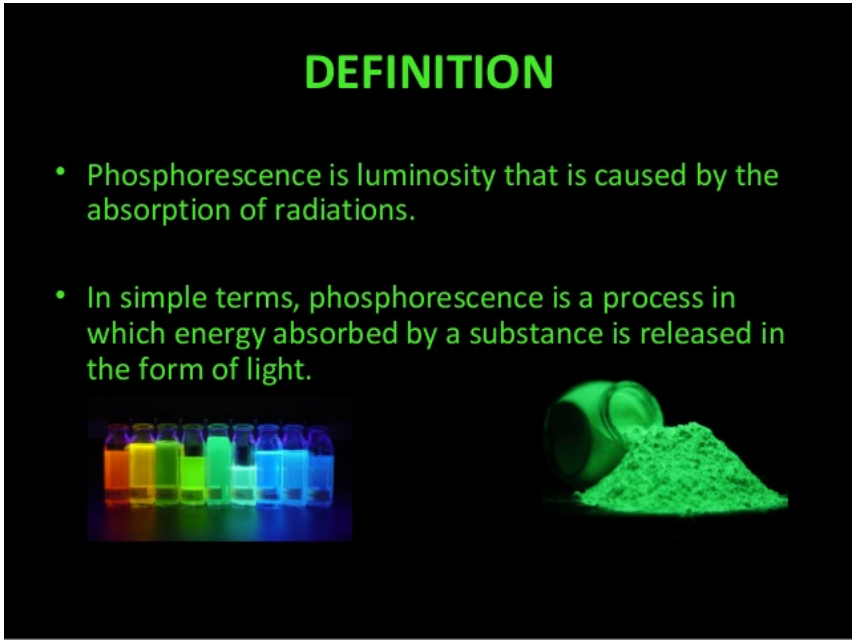
Phosphorescence: There are certain substances which continue to glow for some time even after the external light is cut off. Thus, phosphorescence is a slow fluorescence



Photosensitisation

Photosensitized reactions:

- An electronically excited molecule can transfer its energy to a second species which then undergoes a photochemical process even though it was not itself directly excited.
- Mercury acting as a photosensitizer:

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

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

- Chlorophyll acting as a photosensitizer

$$CO_2 + H_2O + h\nu \xrightarrow{\text{chlorophyll}} 1/6(C_6H_{12}O_6) + O_2$$

THANK YOU