PHOTOCHEMISTRY

The study of photochemistry embraces all of the phenomena associated with the absorption & emission of radiation by chemical system.
It includes phenomena that are mainly spectroscopic, such as fluorescence & phosphorescence, luminescent chemical reaction such as flames & the gleam of the firefly & photostimulated reaction such as photography, photo synthesis, photolytic reaction of various kinds.

Photochemistry deals with the study of chemical reactions which are caused by the absorption of light radiations (photons). The energy carried by this radiation (UV & visible) is sufficient to cause electronic excitation in molecules & making it reactive resulting in chemical reactions.
Only the absorbed radiation can cause a chemical change. The light radiations of the visible & UV regions lying between 200 & 800 nm wavelengths bring about such reaction.
The related photons should be of sufficient energy (given by $h\nu$) to raise the atom or the molecules from the ground electronic state to an excited electronic state which essentially involves the promotion of electron from bonding to anti-bonding molecular orbital.
In the excited state, the atom or the molecule is more likely to undergo a chemical reaction than the ground state.

Laws of Photochemistry:

1.) Grotthus - Draper law

(Principle of photochemical activation)

Only that light which is absorbed by a system can bring about a photochemical change.
However, it is not necessary that the light which is absorbed must bring about a photochemical change. The absorption of light may result in a number of other phenomena.

2.) Stark - Einstein law of Photochemical Equivalence

(Principle of Quantum Activation)

Given by Stark in 1908 & Einstein in 1912, independently.

1 molecule is activated by the absorption of 1 quantum of radiation in the primary (or first) step of a photochemical reaction.

However, it does not imply that 1 molecule must react for each photon absorbed.

E = Energy of absorbed per mole of the reacting substance $= N_A h\nu$

Energy absorbed per molecule $= h\nu$ (1 quantum)

1 Einstein

ν = frequency of the radiation absorbed.

$h\nu$ = corresponding quantum of energy absorbed per molecule.

Light absorbed may be used to excite molecule.

It may:

(1.) Cause only a decrease in the intensity of the incident radiation (Beer-lambert's law).

(2.) be re-emitted almost instantaneously in 1 or more steps.

Two types of reactions:

Thermal Reaction (or Dark Reaction)	Photochemical Reaction
- Activation energy results from random collisions.	- Ea (Activation Energy) is acquired by the absorption of photons of light with a particular amount of energy. (Monochromatic light of particular wavelength)
- Reaction rate is independent of intensity of light	- Rate of reaction depends on intensity of light
- The energy needed is in range of 10^{4} to 10^{5} cal mol^{-1}	- Energy needed varies from 23 to 230 kcal mol^{-1} (200-800 nm)
- Thermal excitation increases in a random manner. Translational, rotational & vibrational energy of all the molecules resulting in the excitation of all the molecules to almost the same extent.	- Only a single selected species (atom or molecules) can be promoted to an excited state, independent of the other species present in the reaction system.
- Not specific, spontaneous	- very specific, non-spontaneous
- Effected by Temperature	- Temperature has no effect

Applications of Photochemistry:

- Importance of photochemistry in research.
- Synthesis of complex molecules such as proteins & nucleic acids through photochemical reaction between simple gaseous molecules such as CO_2, NH_3 & CH_4.
- Formation of Vitamin D, O_3 from O_2 in the Earth's stratosphere, smog, skin cancer.
- Photobiology

It deals with photochemistry of biological reactions & has helped in partially understanding the mechanism of photosynthesis & other complex biological phenomena.

- Organic compounds such as vitamin D, cubane (antiviral agents), caprolactam (a monomer of nylon) & several insecticides & cleaning solvents have also been synthesized photochemically.
- Photochromic materials.
They have peculiar property of changing color when exposed to radiations of suitable wavelength.
spiropyrans - used in photochromic sunglasses.
They are used in production of information storage & self developing, self erasing films in digital computers.
- To understand phenomena of fluorescence & phosphorescence. They have useful applications in the development of X-ray & TV screens, fluorescent tubelights, optical brighteners in white dress materials, luminescent dials for watches, microanalytical reagents for tracing the course of rivers through caves.
- Development of laser techniques. ~~They have~~

~~application of~~
- Photochemistry in medicine
Photodynamic therapy (PDT): Laser radiation (usually delivered to diseased tissue through a fibre optic cable) is absorbed by a drug which in its first excited triplet state, photosensitizes the formation of an excited singlet state of oxygen. The singlet oxygen molecules are very reactive & destroy cellular components & cell membranes are the primary cellular targets.

Resulting photochemical cycle leads to the shrinkage (& sometimes the total destruction) of the diseased tissue.

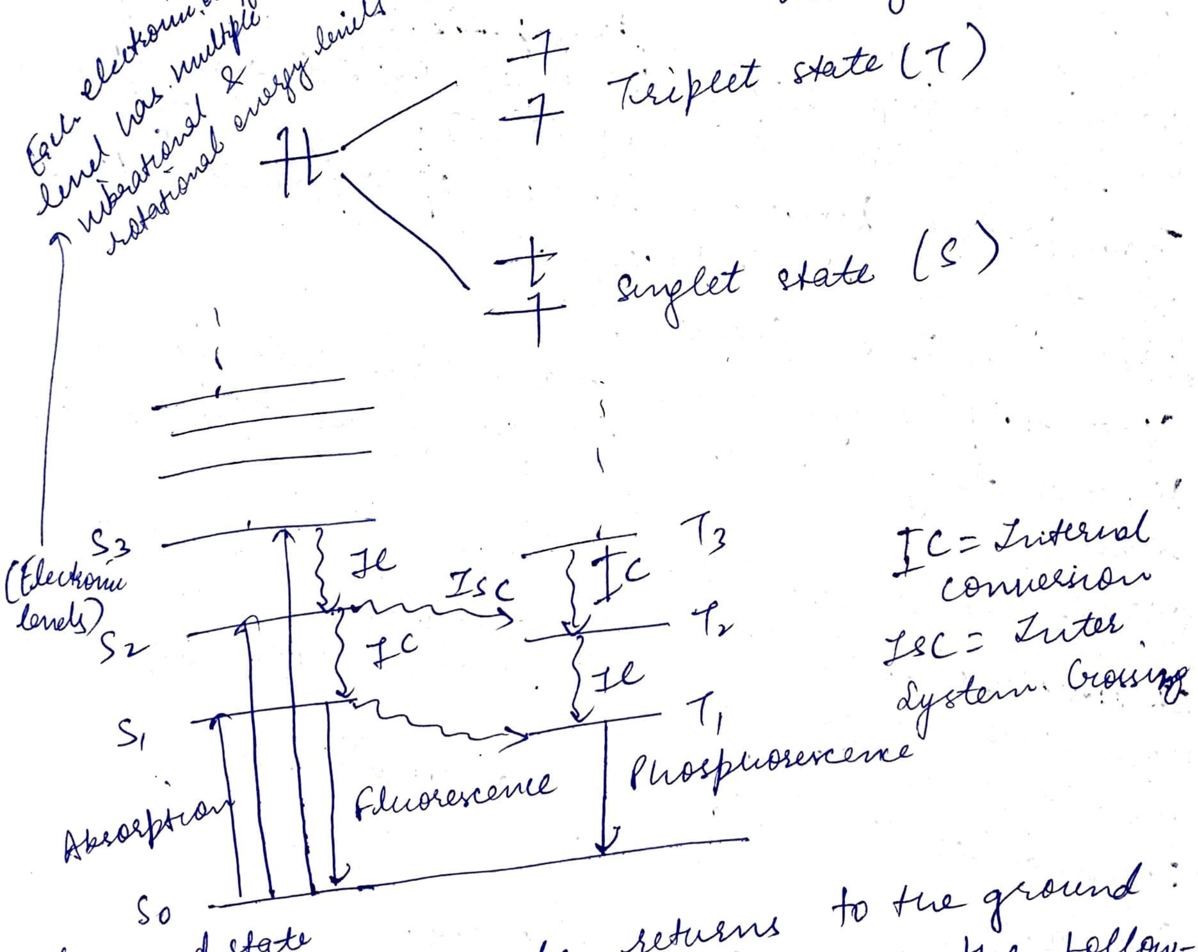
- Solar energy (using photovoltaic cells) is another application.

JABLONSKI DIAGRAM (It is an Energy diagram arranged with energy on a vertical axis)

$A_0 + h\nu \longrightarrow A^*$

Ground state

Excited state (can be in triplet or singlet state)



The activated molecule returns to the ground state by dissipating its energy through the following types of processes: