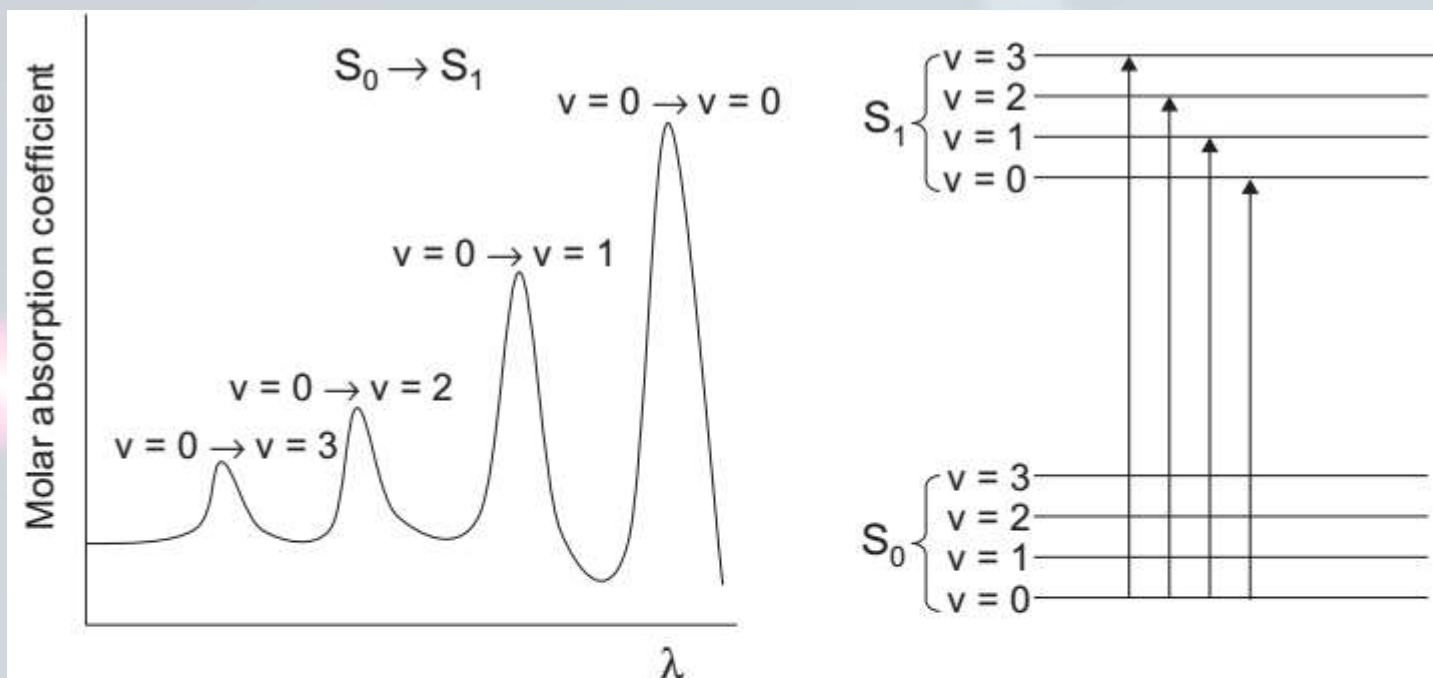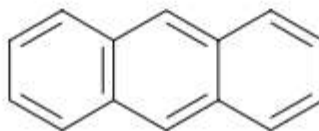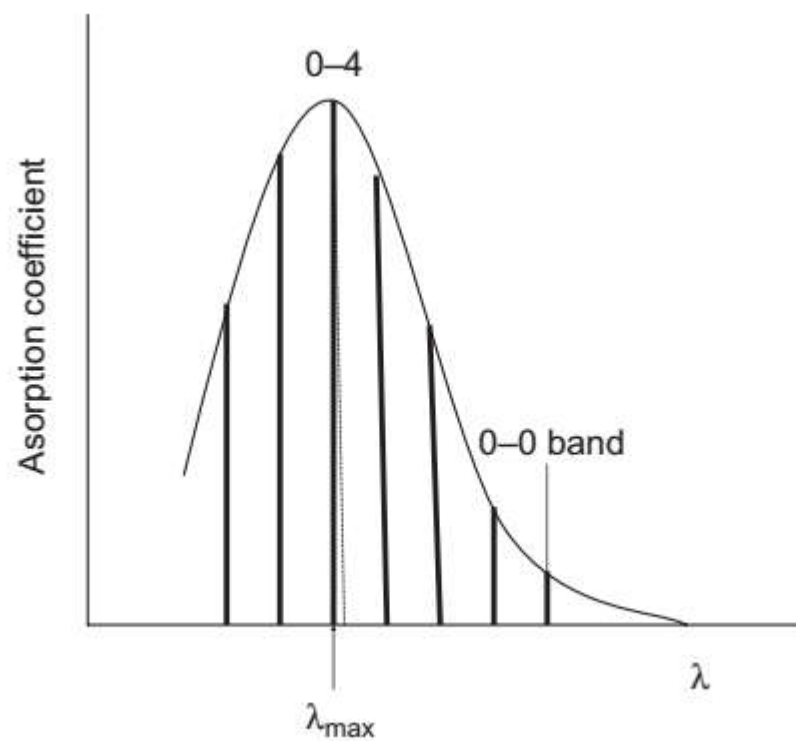# ABSORPTION OF LIGHT BY ORGANIC MOLECULES:

Absorption spectrum of a solution of anthracene in benzene, and the vibronic transitions responsible for the vibrational fine structure

The spectrum shows that many vibronic transitions are allowed, and that some are more probable than others; that is, the intensities of the different vibronic transitions vary. In the absorption spectrum of anthracene, the $v = 0 \rightarrow v = 0$ transition gives rise to the most intense absorption band because for this transition the overlap of the vibrational probability functions for $S_0(v = 0)$ and $S_1(v = 0)$ is greatest; that is, the Franck –Condon factor for this transition is greatest. The $v = 0 \rightarrow v = 0$ transition gives rise to the 0 –0 band.

Broad, featureless absorption spectrum of the solution of an organic compound

The absorption spectra of rigid hydrocarbons in nonpolar solvents may show vibrational fine structure, but absorption spectra of other organic molecules in solution tend to be broad, featureless bands with little or no vibrational structure (Figure). This is due to the very large number of vibrational levels in organic molecules and to blurring of any fine structure due to interaction between organic molecules and solvent molecules. The hypothetical spectrum shown in Figure shows the vibrational structure hidden by the enveloping absorption spectrum, and the peak of the absorption curve does not correspond to the 0–0 band because the most probable vibronic transition here is the $0 \rightarrow 4$ transition.

In principle, six types of electronic transition, designated σ → σ*, σ → π*, π → π*, π → σ*, n → σ* and n → π*. The σ → σ* transitions correspond to absorption in the inaccessible far-ultraviolet (**the shortest wavelengths of radiation in the ultraviolet spectrum and especially those between 100 and 300 nanometers**), and both σ → π* and π → σ* are obscured by the much stronger π → π* absorptions. Of the possible electronic transitions, the ones we shall be most concerned with in molecular organic photochemistry are the π → π* and n → π* transitions, which produce (π,π*) and (n,π*) electronically-excited states, respectively.

SOME SELECTION RULES:

Transitions between energy levels in organic molecules are subject to certain constraints, referred to as selection rules.

1. Spin selection rule: An electronic transition takes place with no change in the total electron spin – that is, $\Delta S = 0$ – hence singlet $\leftrightarrow$ triplet transitions are forbidden or very weakly allowed. For example, the $S_0 \rightarrow T_1$ transition in anthracene has a molar absorption coefficient, ε_{max}, some 108 times less than that corresponding to the $S_0 \rightarrow S_1$ transition.
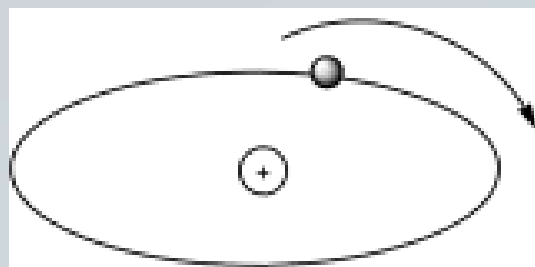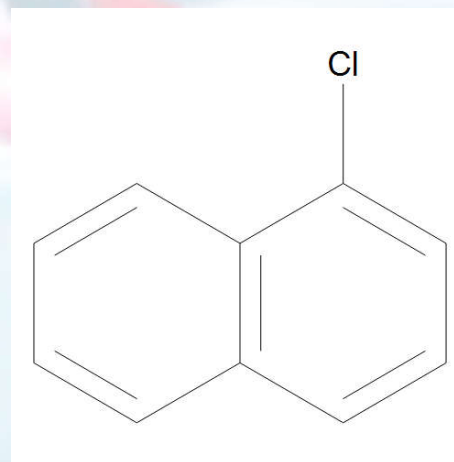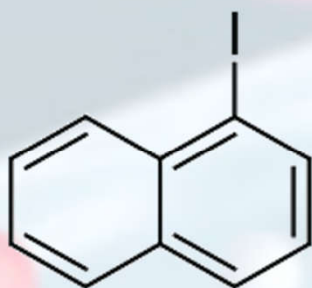
Orbital motion
of electron

Spin of electron

L

v

μ
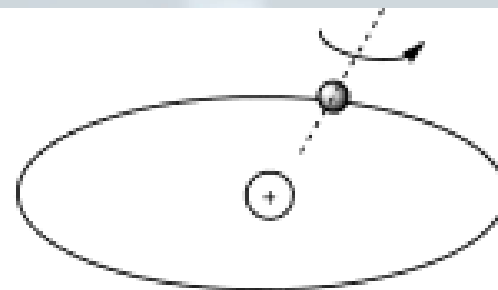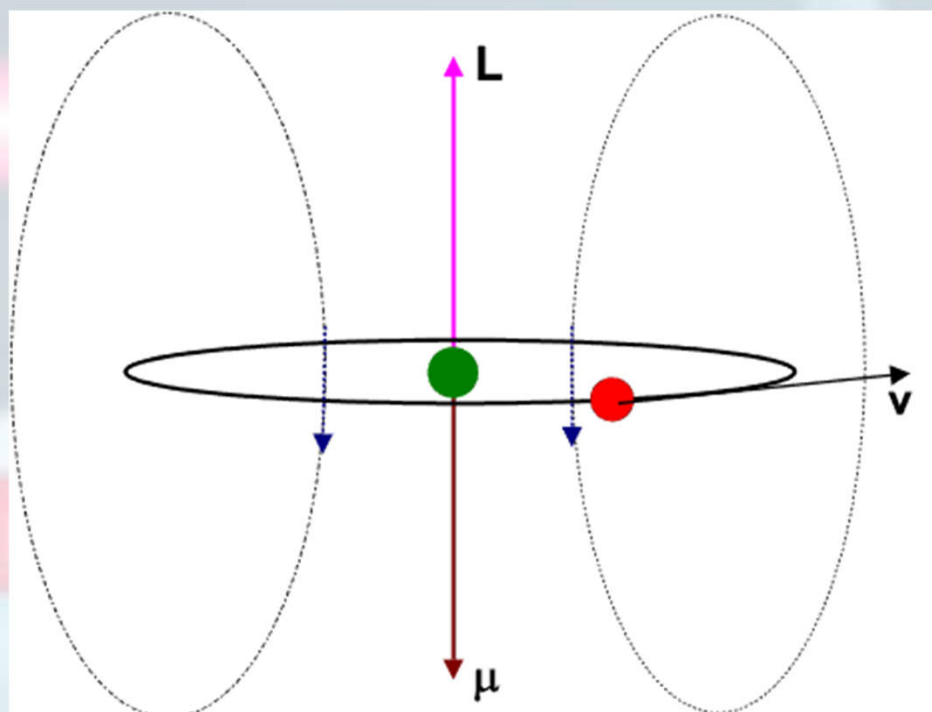
The heavy atom effect can show itself as the internal heavy atom effect, where incorporation of a heavy atom in a molecule will enhance $S_0 \rightarrow T_1$ absorption due to spin–orbit coupling. For example, 1-iodonaphthalene has a much stronger $S_0 \rightarrow T_1$ absorption than 1-chloronaphthalene.

The external heavy atom effect shows itself when a heavy atom is incorporated in a solvent molecule. For example, 1- chloronaphthalene has a much stronger $S_0 \rightarrow T_1$ absorption in iodoethane solution than in ethanol.
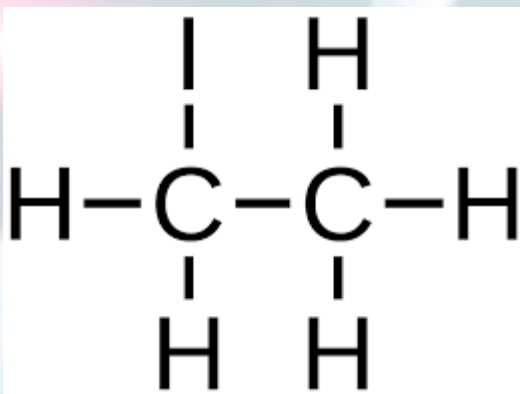
2. Orbital symmetry selection rule: According to the quantum theory, the intensity of absorption by molecules is explained by considering the wavefunctions of the initial and final states (ψ and ψ^*, respectively). An electronic transition will proceed most rapidly when ψ and ψ^* most closely resemble each other; that is, when the coupling between the initial and fi nal states is strongest.
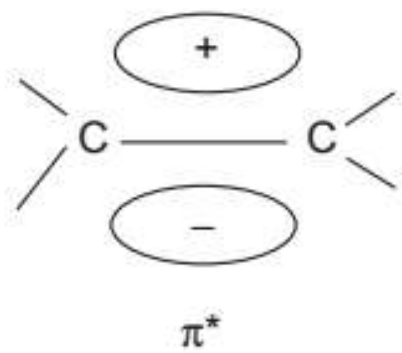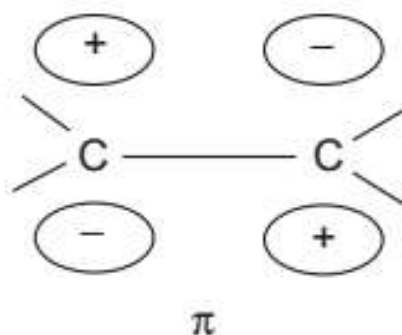
π and π* molecular orbitals associated with the >C=C< chromophore. Both the π- and π*-orbitals lie in the plane of the paper

Transitions involving a large change in the region of space the electron occupies are forbidden. The orbital overlap between the ground state and excited state should be as large as possible for an allowed transition. π- and π^* -orbitals occupy the same regions of space, so overlap between them is large. The orbital overlap between n- and π^* -orbitals is very much smaller, as these orbitals lie perpendicular to each other.
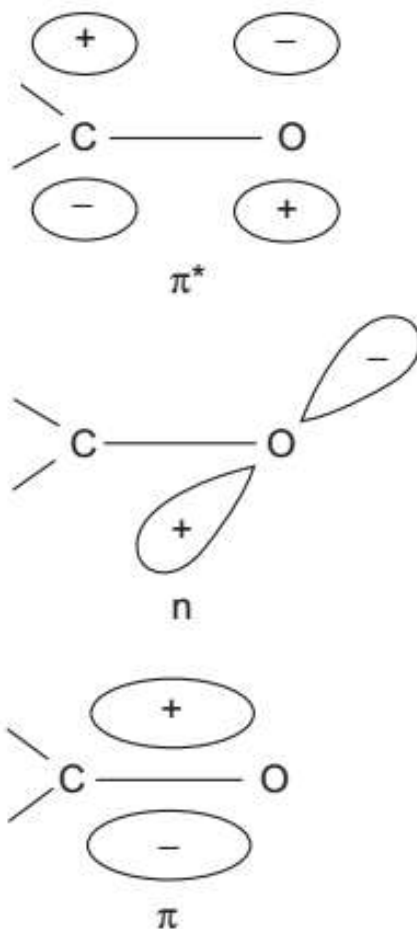
Molecular orbitals associated with the >C=O chromophore. The π- and π^*-orbitals lie in the plane of the paper but the n-orbitals are perpendicular to the plane of the paper
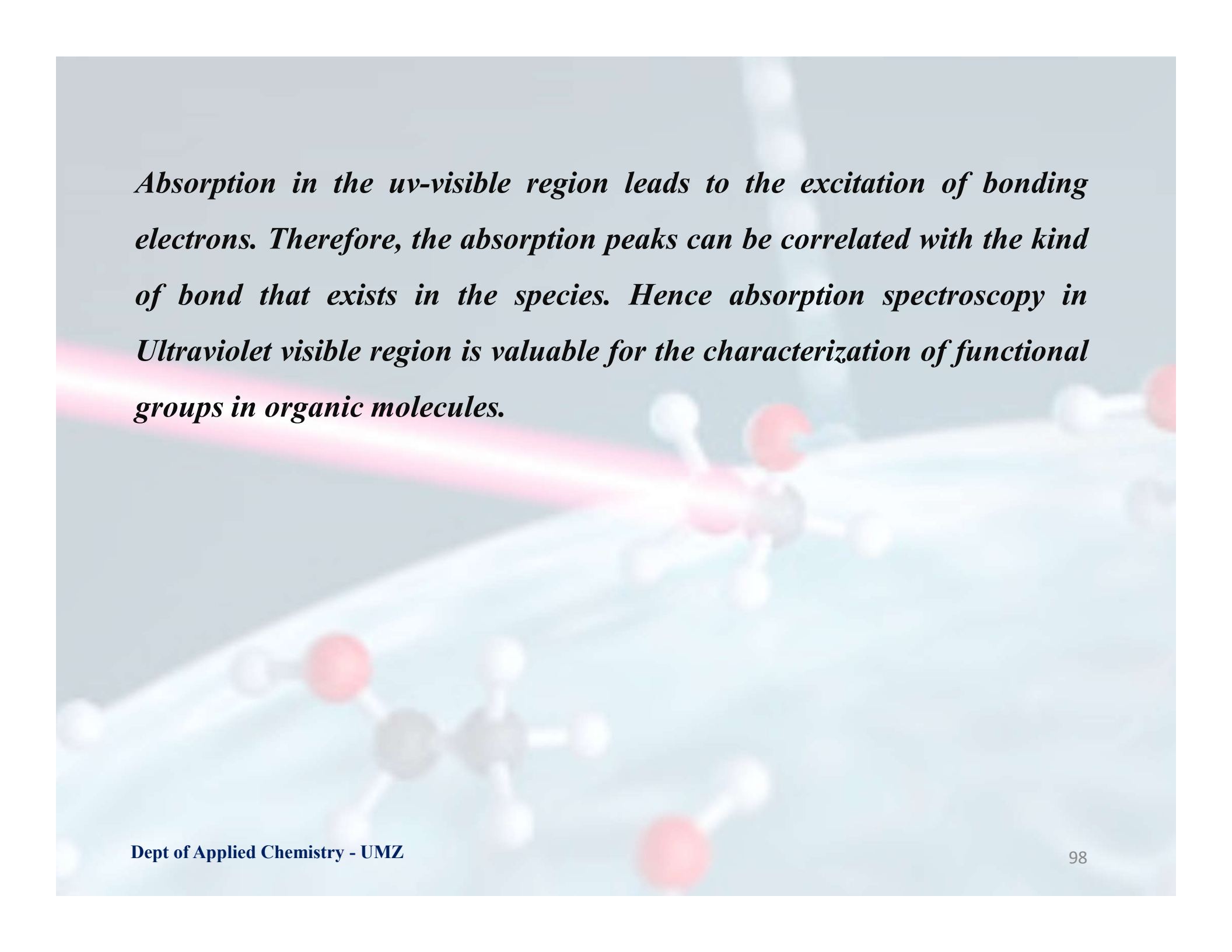
Types of excitations:
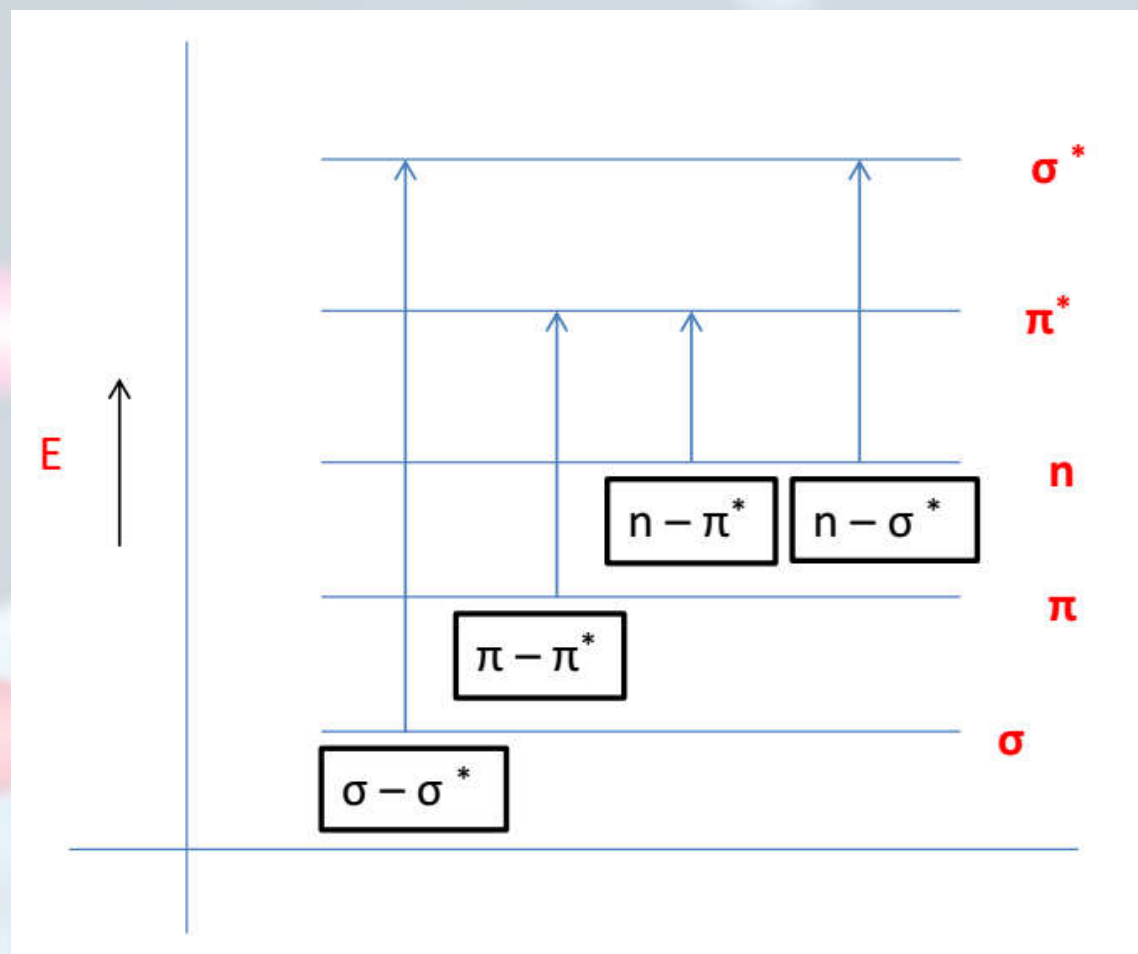
Absorption in the uv-visible region leads to the excitation of bonding electrons. Therefore, the absorption peaks can be correlated with the kind of bond that exists in the species. Hence absorption spectroscopy in Ultraviolet visible region is valuable for the characterization of functional groups in organic molecules.

Theory of Ultraviolet–Visible Absorption:

The UV-Visible spectroscopy principle is based on the absorption of ultraviolet light or visible light by chemical compounds. To occur a chemical reaction, the reacting molecules must be activated by acquiring activation energy.

In photochemical reactions, the activation energy is obtained by absorption of radiation or light energy. In order to study the mechanism of the photochemical reaction, we need to study the following types of electronic transition:

Sigma to sigma star transition (σ → σ∗)

n to sigma star transition (n → σ∗)

n to pi star transition (n → π∗)

**Pi to pi star transition (π → π∗)**

1. $\sigma - \sigma^{*}$ $\longrightarrow$ alkanes (no n or pi electrons)
2. $n - \sigma^{*}$ $\longrightarrow$ alcohols, amines , ethers etc
3. $\pi - \pi^{*}$ $\longrightarrow$ aldehydes, carboxylic esters, alkenes etc.
4. $n - \pi^{*}$ $\longrightarrow$ aldehydes, ketones,carboxylic esters(can undergo above three transitions also)

$$\sigma - \sigma^{*} > n - \sigma^{*} > \pi - \pi^{*} > n - \pi^{*}$$

$\longrightarrow$

Decreasing energy

✓ **However, the order may sometimes be altered in some solvents.**

✓ **More conjugation in a molecule, the more the absorption is displaced towards higher wavelengths.**

Interaction of two C=C units in a conjugated system
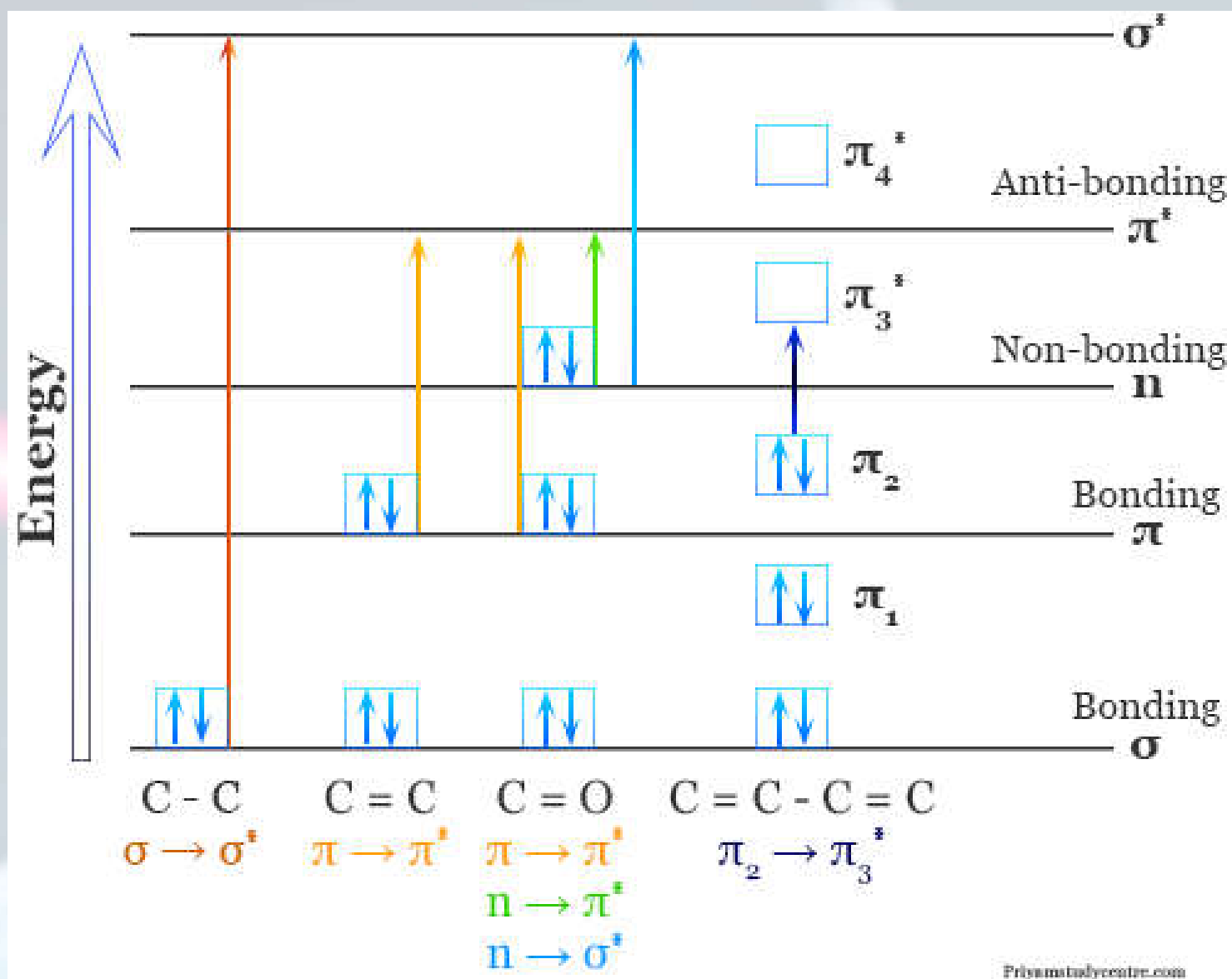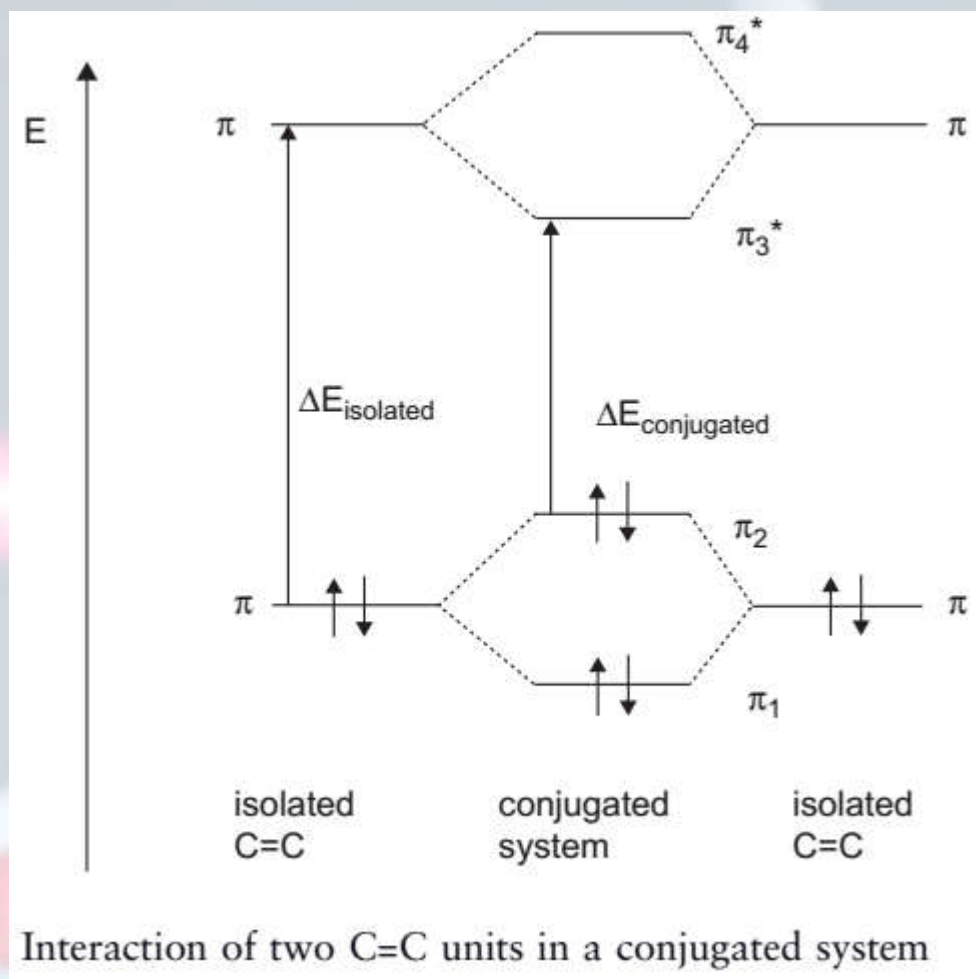
Lowest energy absorption bands of conjugated polyenes $H(CH=CH)_n H$

n	λ_{max}/nm
2	217
3	268
4	304
5	334
6	364
7	390
8	410

Absorption peaks (λ_{max}) and molar absorptivity (ϵ_{max}) and possible electronic transition of some common compounds are given below the table:

Compounds	λ_{max} (nm)	ϵ_{max} (L/cm/mol)	Electronic transition
Alkenes	177	1.3×10^4	$n \rightarrow \pi^*$
Alkyne	178 – 225	$10 \times 10^3 - 150$	$n \rightarrow \pi^*$
Carbonyl	186 – 280	$1.0 \times 10^3 - 16$	$n \rightarrow \pi^*$
Carboxyl	204	41	$n \rightarrow \pi^*$
Amide	214	60	$n \rightarrow \pi^*$
Azo	339	5	$n \rightarrow \pi^*$
Nitro	280	22	$n \rightarrow \pi^*$
Ketone	282	27	$n \rightarrow \pi^*$
Water	167	1.48×10^3	$n \rightarrow \sigma^*$
Methyl alcohol	184	15	$n \rightarrow \sigma^*$
Benzene	204	7.9×10^3	$n \rightarrow \sigma^*$

Absorptions due to $\pi \rightarrow \pi^*$ transitions	Absorptions due to $n \rightarrow \pi^*$ transitions
Occur at shorter wavelengths than do absorptions due to $n \rightarrow \pi^*$ transitions	Occur at longer wavelengths than do absorptions due to $\pi \rightarrow \pi^*$ transitions
Substitution moves the absorption to longer wavelength	Substitution moves the absorption to shorter wavelength
Relatively strong absorptions with ε_{max} values of ~10^3 to ~10^5 l mol^{-1}cm^{-1}	Relatively weak absorptions with ε_{max} values of ~1 to ~10^2 l mol^{-1}cm^{-1}
The absorption band occurs at longer wavelength in a polar solvent than in a nonpolar solvent (the absorption shows a **red shift** or **bathochromic shift**)	The absorption band occurs at shorter wavelength in a polar solvent than in a nonpolar solvent (the absorption shows a **blue shift** or **hypsochromic shift**)

It is possible for excited electrons in atoms and molecules to have some other kind of interaction which lowers their energy before they can make a downward transition. In that case they would emit a photon of lower energy and longer wavelength. This process is called fluorescence if it happens essentially instantaneously. It is also possible that material can hold onto the energy of excitation for a long time, gradually making downward transitions with emission. This delayed emission is called phosphorescence.
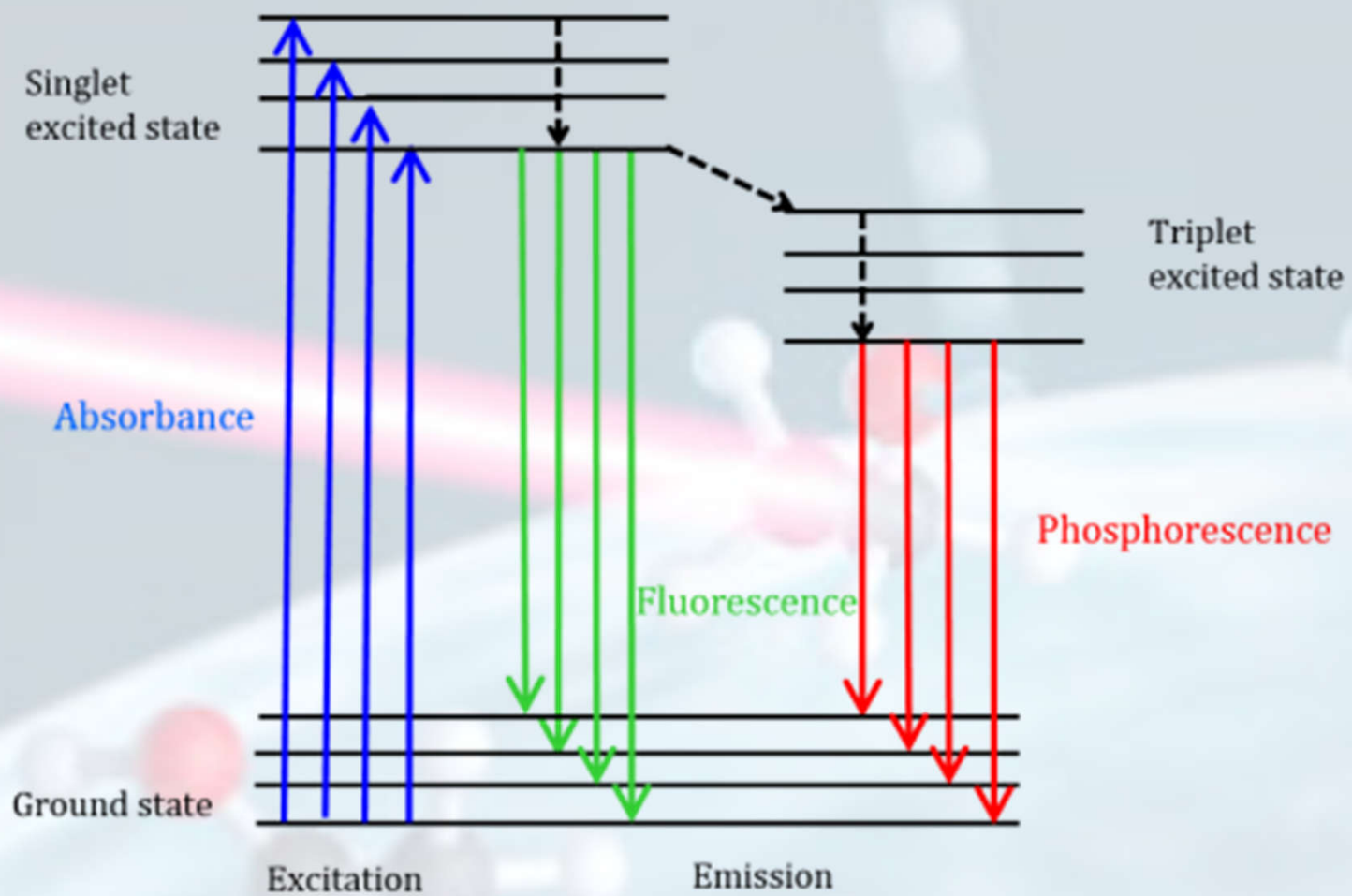
Fluorescence:

Fluorescence, a type of luminescence, occurs in gas, liquid or solid chemical systems. Fluorescence is brought about by absorption of photons in the singlet ground state promoted to a singlet excited state. The spin of the electron is still paired with the ground state electron, unlike phosphorescence.

Phosphorescence:

Phosphorescence is a type of photoluminescence related to fluorescence. When exposed to light of a shorter wavelength, a phosphorescent substance will glow, absorbing the light and reemitting it at a longer wavelength. Unlike fluorescence, a phosphorescent material does not immediately reemit the radiation it absorbs.

Jablonski Diagram:

The Jablonski diagram, typically used to illustrate fluorescence in molecular spectroscopy, demonstrates the excited states of a molecule along with the radiative and non-radiative transitions that can occur between them.

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a written representation that generally shows a portion of the possible consequences of applying photons from the visible spectrum of light to a particular molecule.
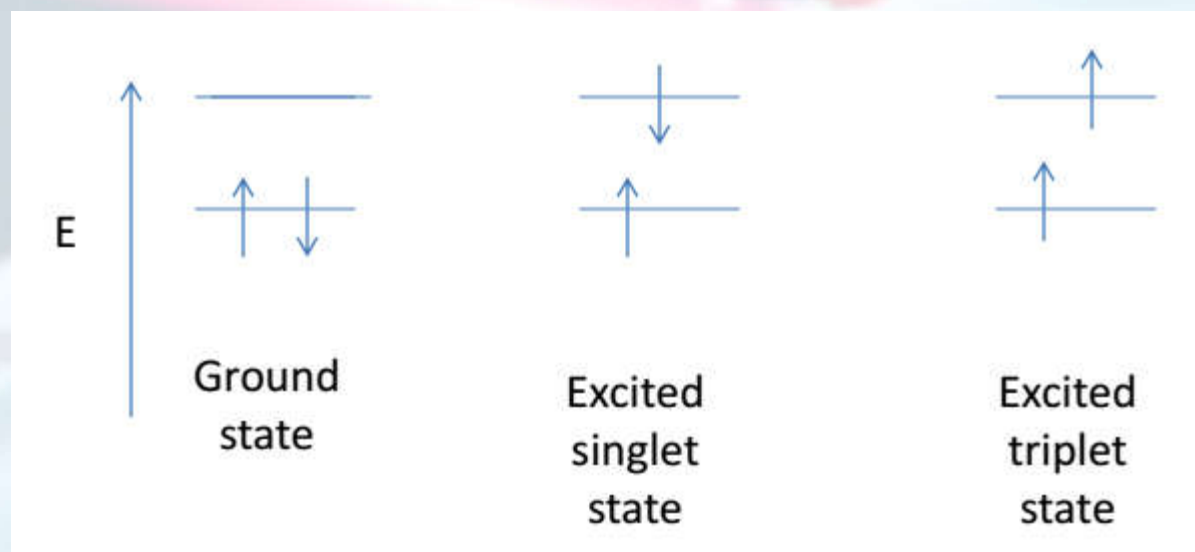
Jablonski Diagram
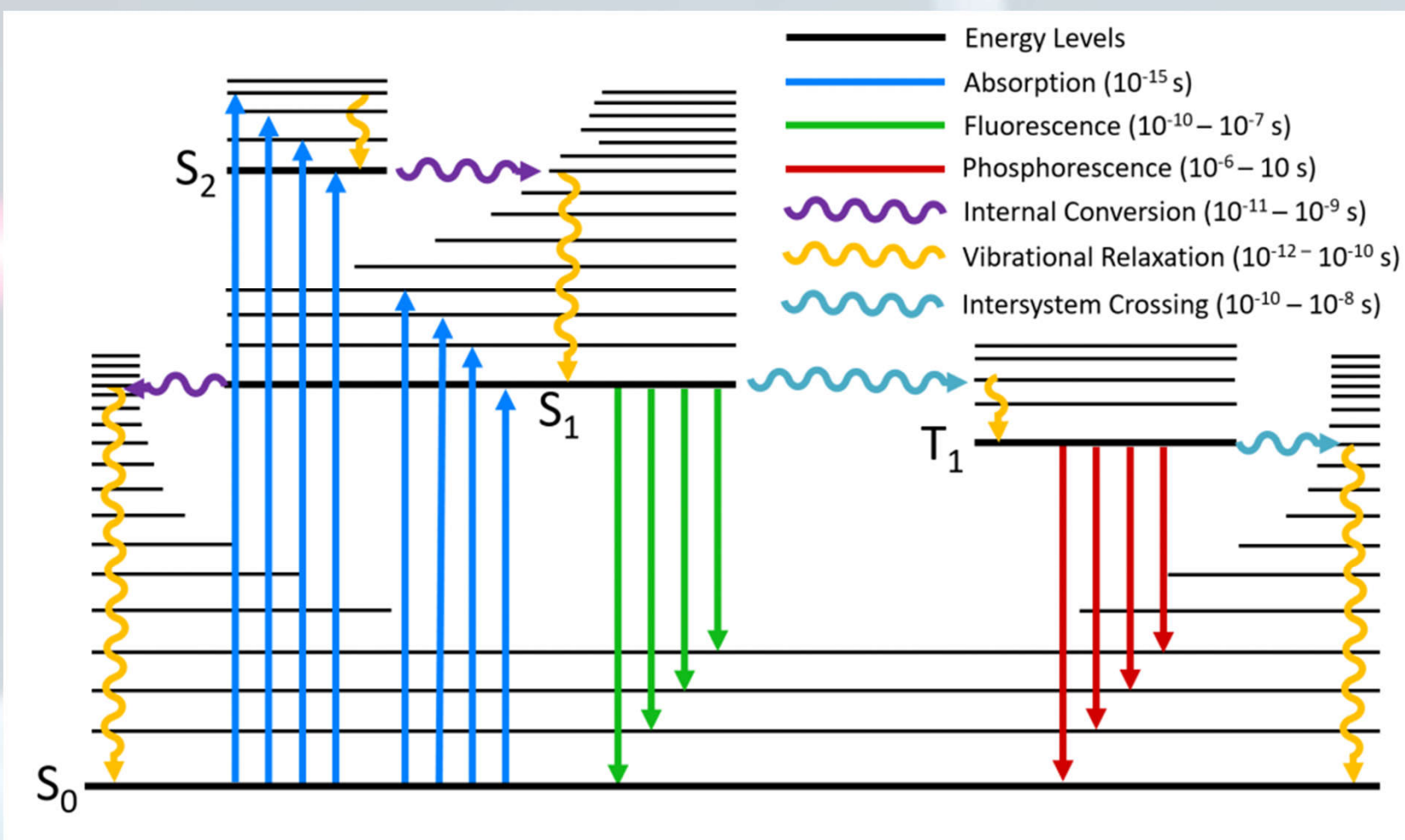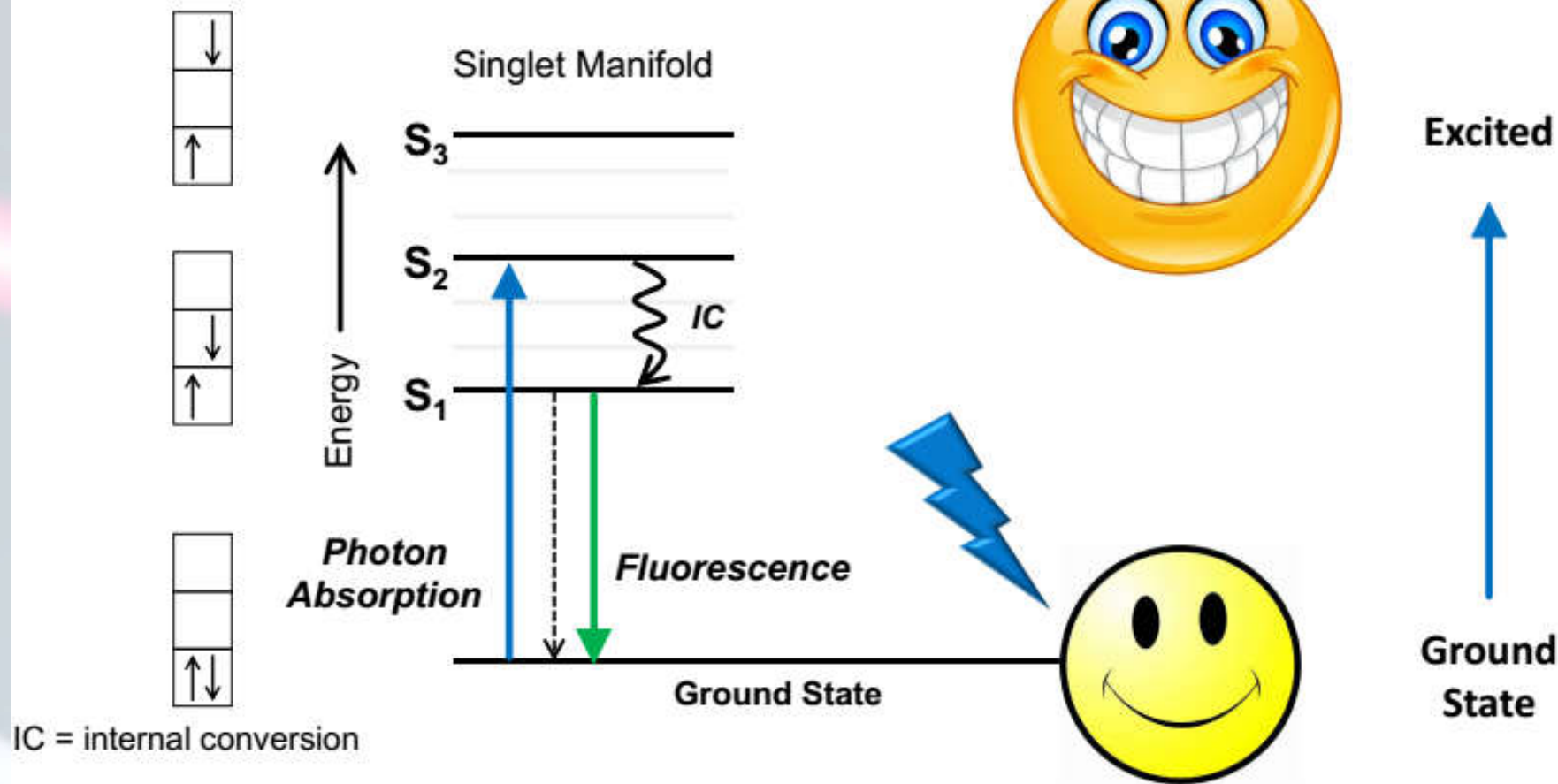
- Intersystem crossing (ISC): transition from S_1 in ground vibrational level to T_1 state

- IC = 10^{-14} - 10^{-10} s, ISC= 10^{-10} - 10^{-8} s

- Transitions

- Radiative transitions: excited molecules emit light and return to ground state.

- Non radiative transitions: some or all of the energy of the absorbed photon is ultimately converted to heat by collisions

- spin multiplicity of singlet state = 2S + 1 = 1

- spin multiplicity of triplet state = 2S + 1 = 3

in figure :

$h\nu_f$ = flourescence (10^{-9} - 10^{-6} s)
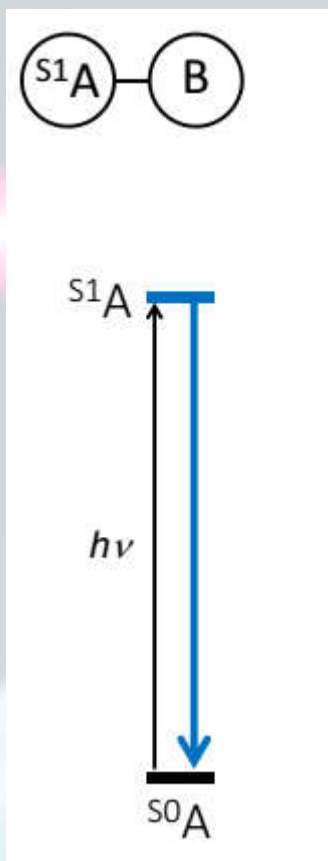
$h\nu_p$ = phosphorescence(10^{-3} - 10^3 s)

- Both singlet and triplet give different products.

Fluorescence Emission

BLUE Light
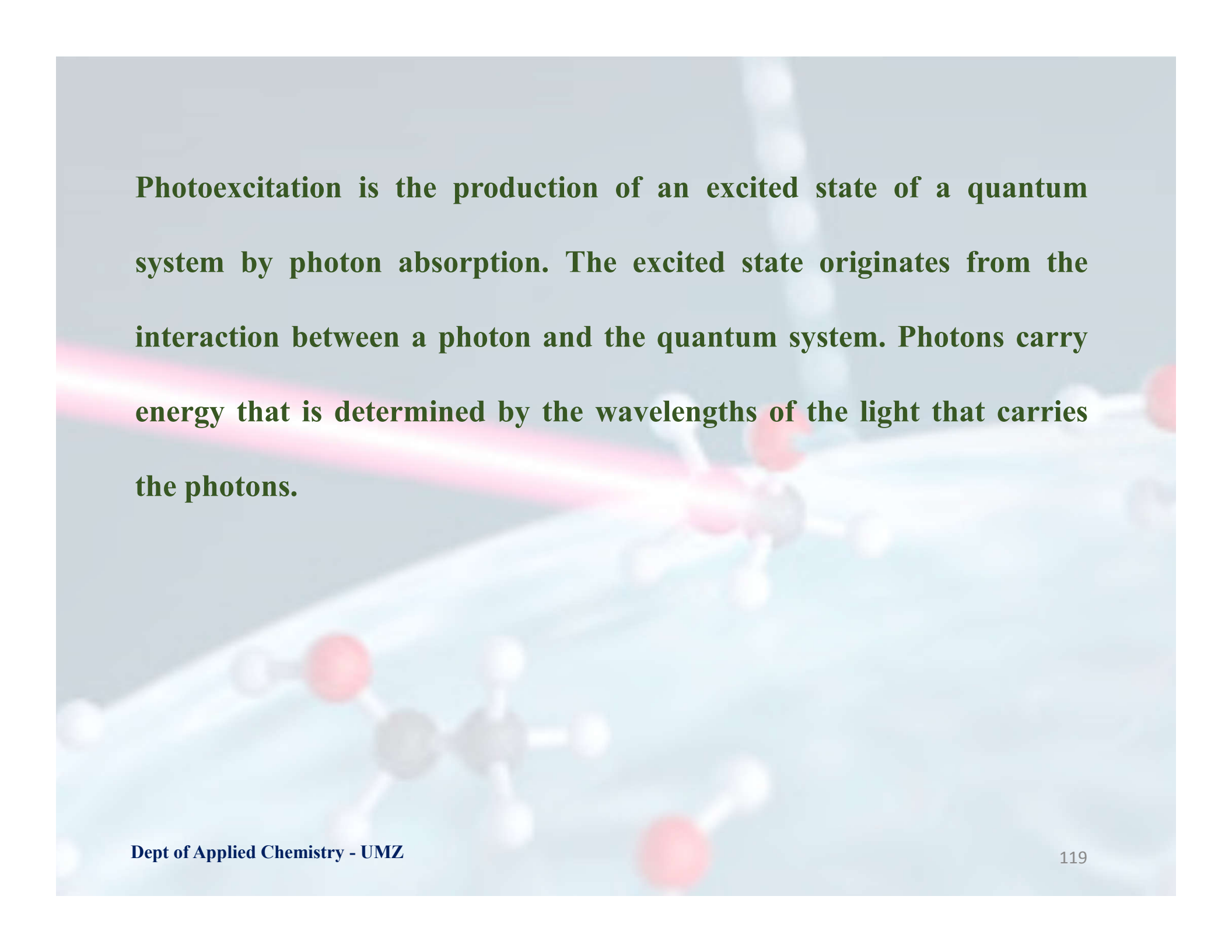
Photo-induced Electron Transfer (ET):

Photo-induced Electron Transfer (ET):

Photoinduced electron transfer (PET) is a term reserved to describe the transfer of an electron between photoexcited and ground-state molecules. The energetics and dynamics of PET are shown to depend on the structure of the reactants, the distance separating the reactants, the nature and polarity of the medium, and Coulombic effects.

Photoexcitation is the production of an excited state of a quantum system by photon absorption. The excited state originates from the interaction between a photon and the quantum system. Photons carry energy that is determined by the wavelengths of the light that carries the photons.

RP=radical pair
or
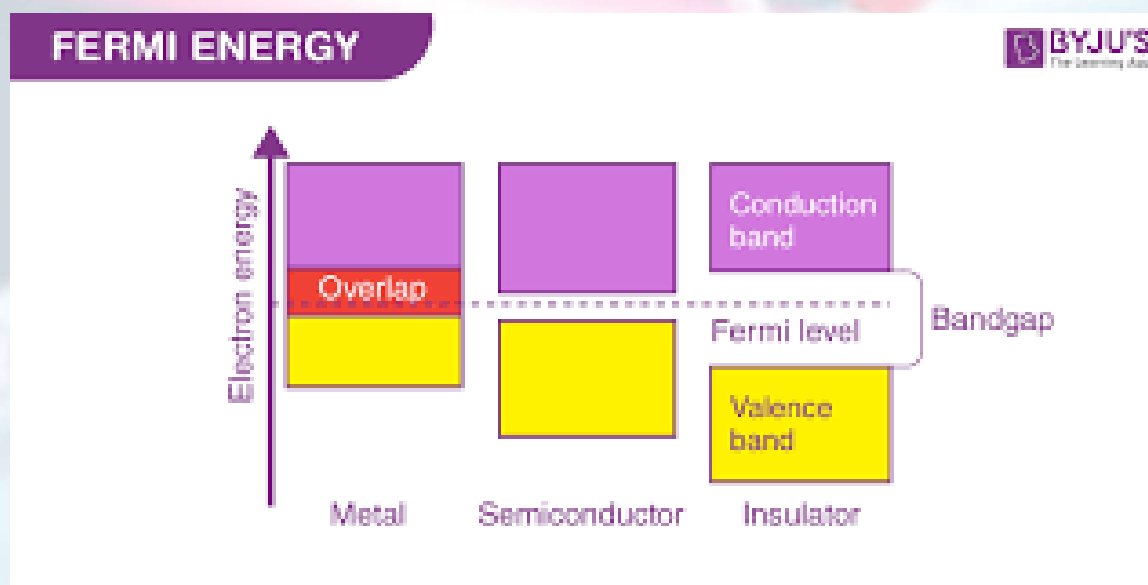CS = charge-separated state
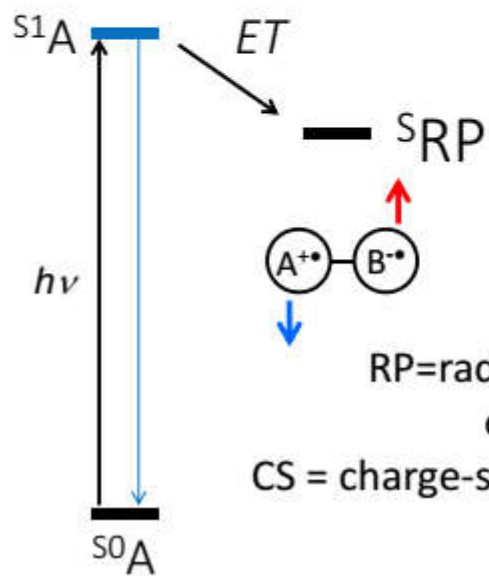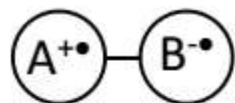
Rudolph A. Marcus
1992 Nobel Prize

What is the charge separation process?

Charge separation is defined by the process of exciting an electron. Electrons are excited from lower energy level to higher energy level. After separation, electrons leave the atom and make the atom positively charged. So charged particles are created by Charge separation.
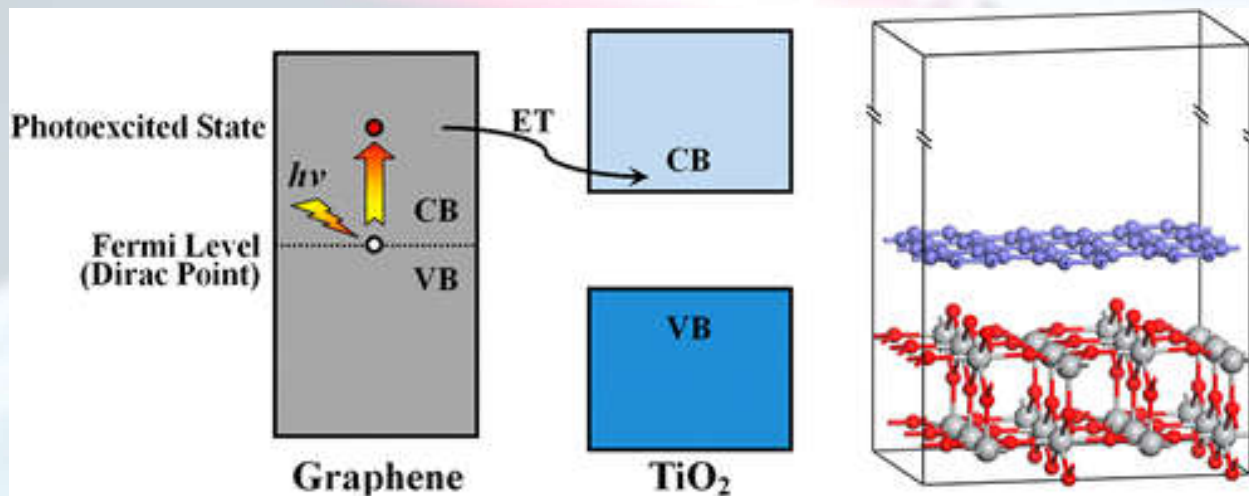
What is meant by Fermi level?

The highest energy level that an electron can occupy at the absolute zero temperature is known as the Fermi Level. The Fermi level lies between the valence band and conduction band because at absolute zero temperature, the electrons are all in the lowest energy state.
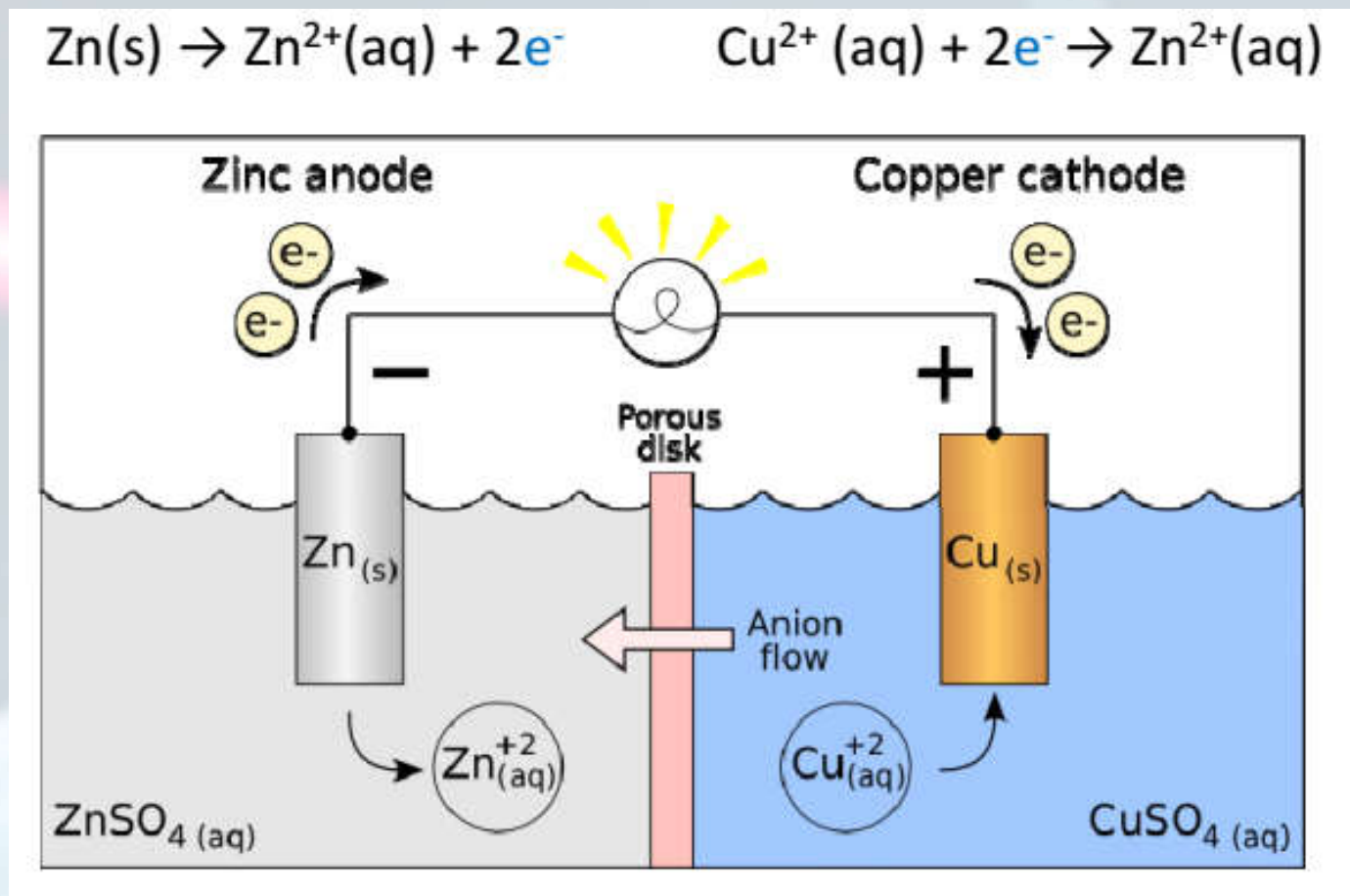

FERMI ENERGY

BYJU'S

Electron energy

Overlap

Conduction band

Fermi level

Bandgap

Valence band

Metal   Semiconductor   Insulator

Photo-induced Electron Transfer (ET): Orbital View
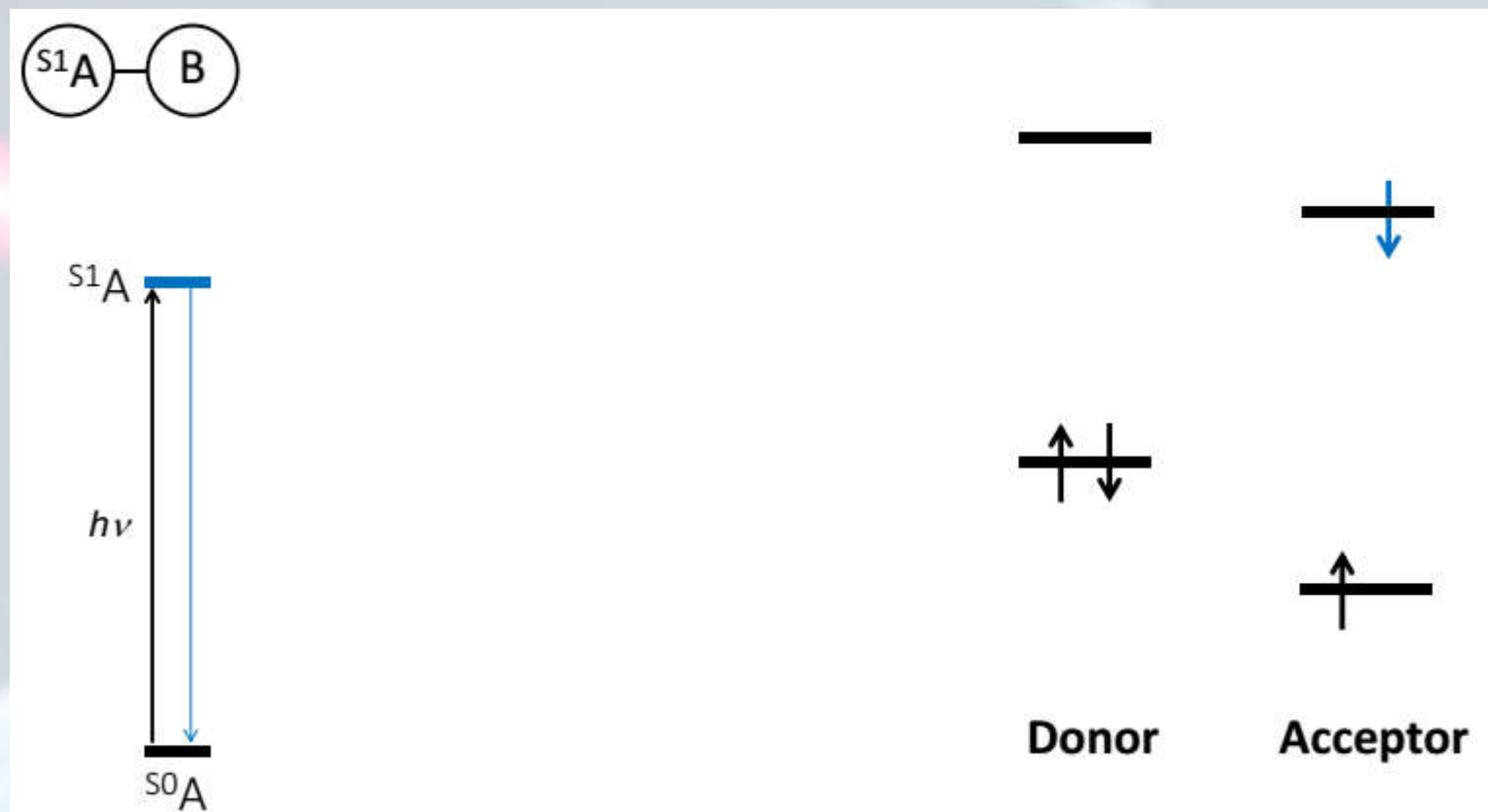
Electron Transfer is one of the Most Fundamental Chemical Reactions.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$ $$Cu^{2+}(aq) + 2e^- \rightarrow Zn^{2+}(aq)$$

Zinc anode

Copper cathode

e-

e-

−

+

e-

e-

Porous disk

$Zn_{(s)}$

$Cu_{(s)}$

Anion flow

$Zn^{+2}_{(aq)}$

$Cu^{+2}_{(aq)}$

$ZnSO_4 \text{ }_{(aq)}$

$CuSO_4 \text{ }_{(aq)}$

What is Galvanic Cell?

What is Galvanic Cell? An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell. Galvanic cell Voltaic cell is an electrochemical cell that makes use of chemical reactions to generate electrical energy.

The anode may be called the electron donor and the cathode the electron acceptor. In a Galvanic cell, the anode is negative and the cathode positive.

Photo-induced ET at the Heart of Sciences & Applications:
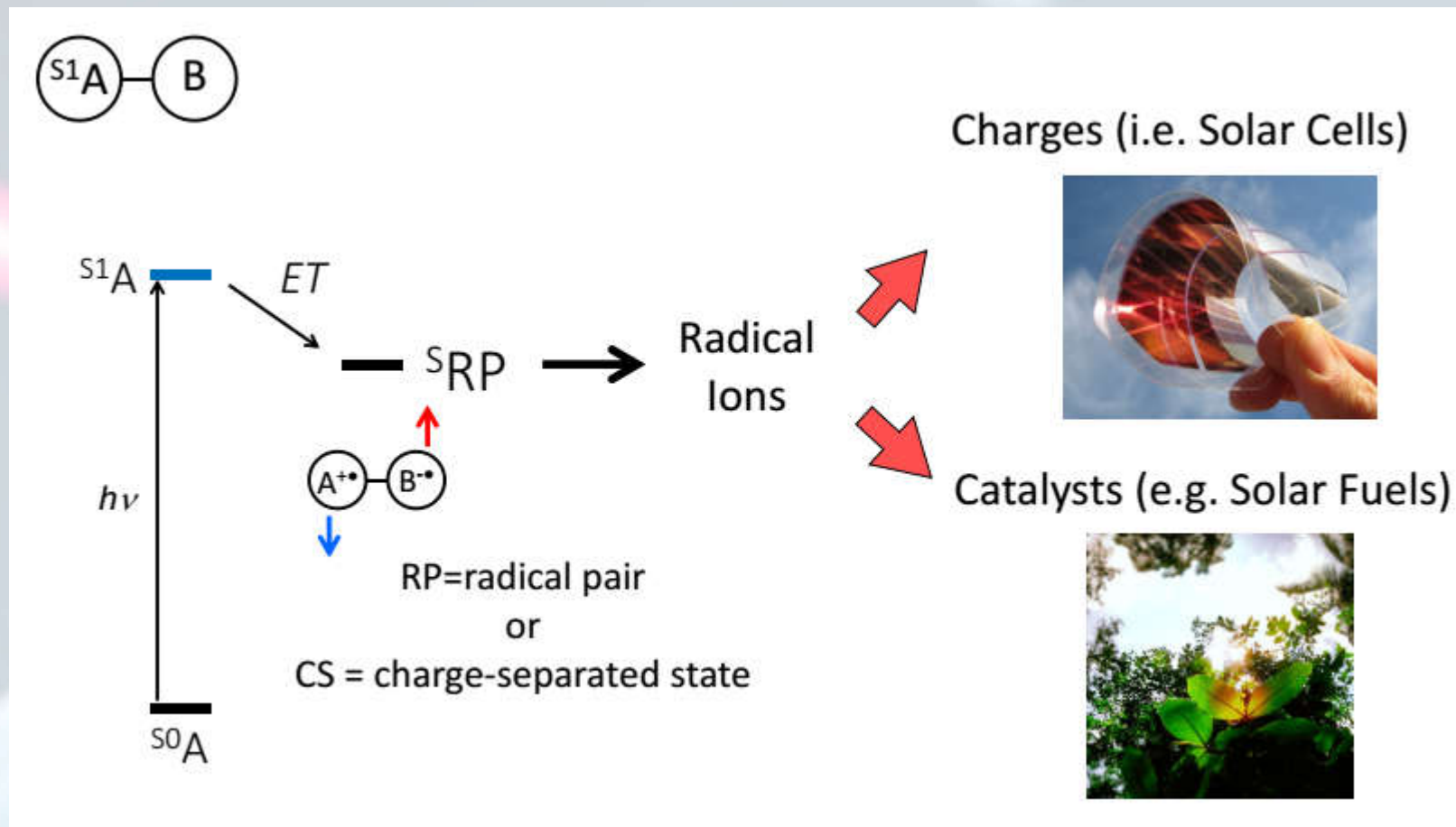
Solar Cells: Charge Separation and Transport are Critical Steps:


Non-polar Environment
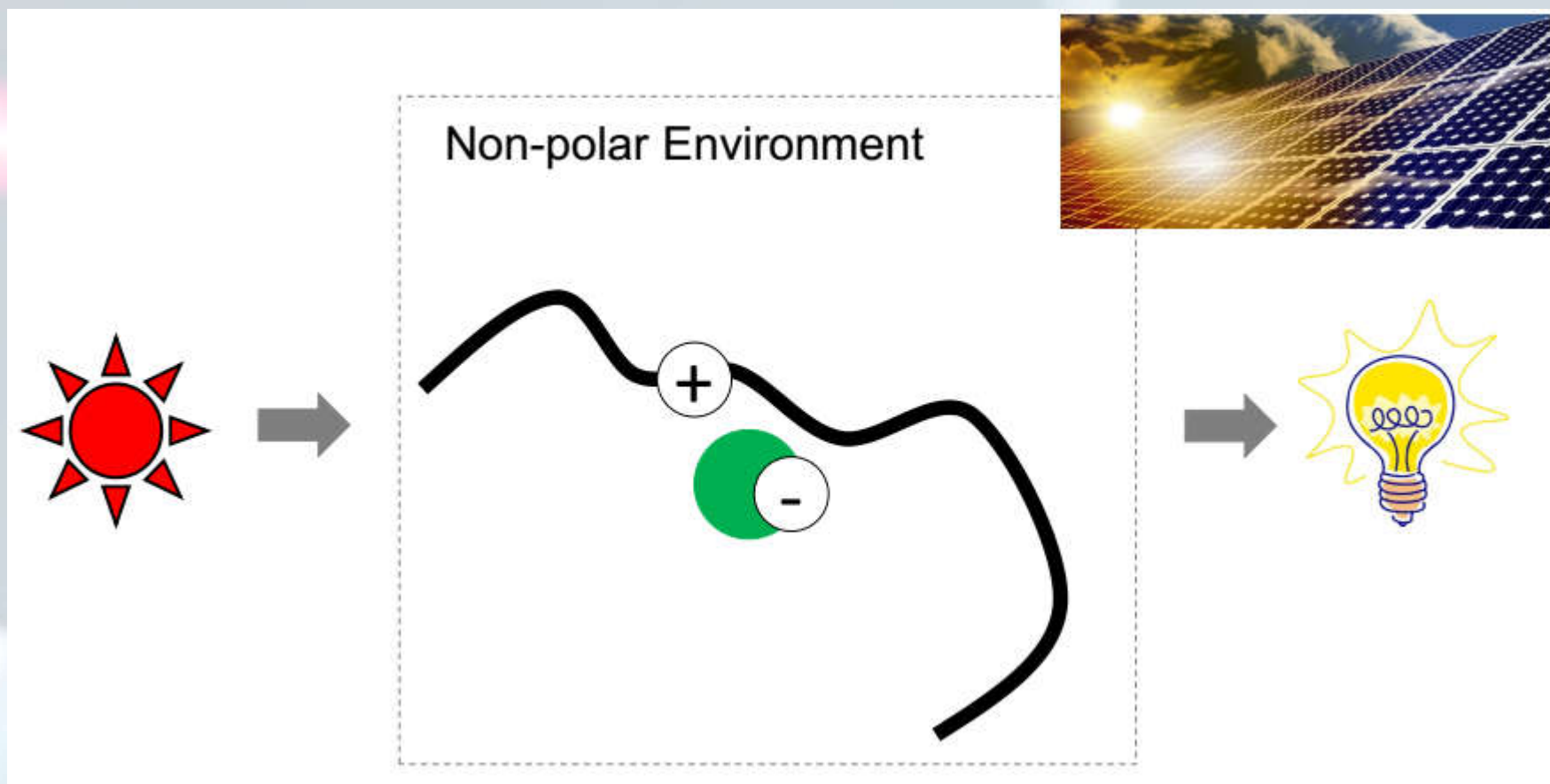
How a Solar Cell Works?

A solar cell is made of two types of semiconductors, called p-type and n-type silicon. The p-type silicon is produced by adding atoms—such as boron or gallium—that have one less electron in their outer energy level than does silicon. Because boron has one less electron than is required to form the bonds with the surrounding silicon atoms, an electron vacancy or "hole" is created.

The n-type silicon is made by including atoms that have one more electron in their outer level than does silicon, such as phosphorus. Phosphorus has five electrons in its outer energy level, not four. It bonds with its silicon neighbor atoms, but one electron is not involved in bonding. Instead, it is free to move inside the silicon structure.
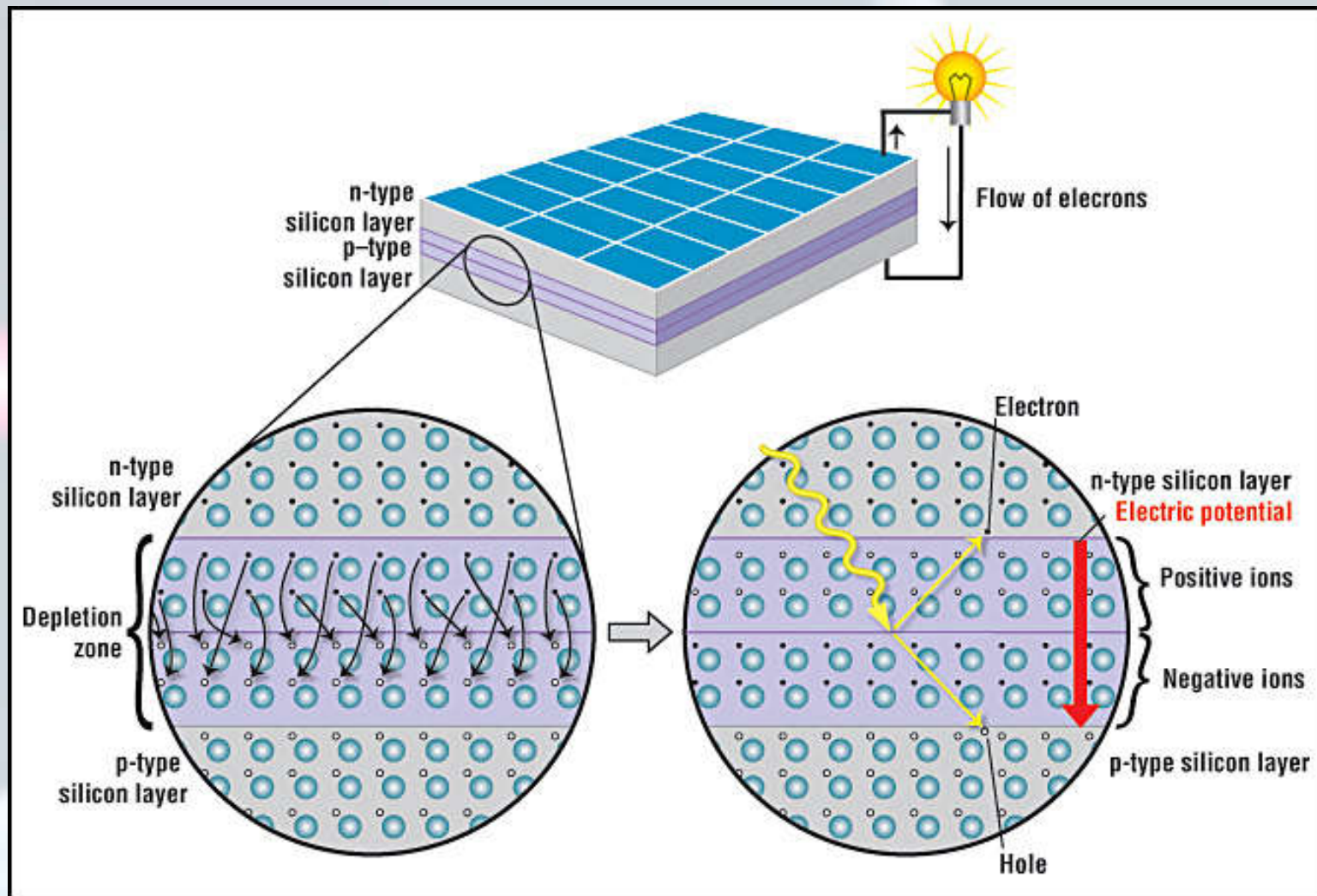
A solar cell consists of a layer of p-type silicon placed next to a layer of n-type silicon. In the n-type layer, there is an excess of electrons, and in the p-type layer, there is an excess of positively charged holes (which are vacancies due to the lack of valence electrons). Near the junction of the two layers, the electrons on one side of the junction (n-type layer) move into the holes on the other side of the junction (p-type layer). This creates an area around the junction, called the depletion zone, in which the electrons fill the holes.

When all the holes are filled with electrons in the depletion zone, the p-type side of the depletion zone (where holes were initially present) now contains negatively charged ions, and the n-type side of the depletion zone (where electrons were present) now contains positively charged ions. The presence of these oppositely charged ions creates an internal electric field that prevents electrons in the n-type layer to fill holes in the p-type layer.

When sunlight strikes a solar cell, electrons in the silicon are ejected, which results in the formation of "holes"—the vacancies left behind by the escaping electrons. If this happens in the electric field, the field will move electrons to the n-type layer and holes to the p-type layer. If you connect the n-type and p-type layers with a metallic wire, the electrons will travel from the n-type layer to the p-type layer by crossing the depletion zone and then go through the external wire back of the n-type layer, creating a flow of electricity.
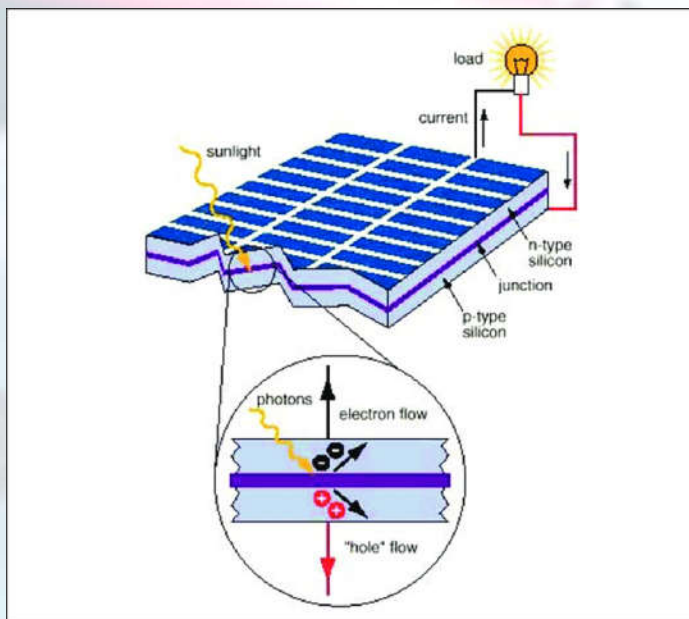
Light Absorption: How Do We See Colors?
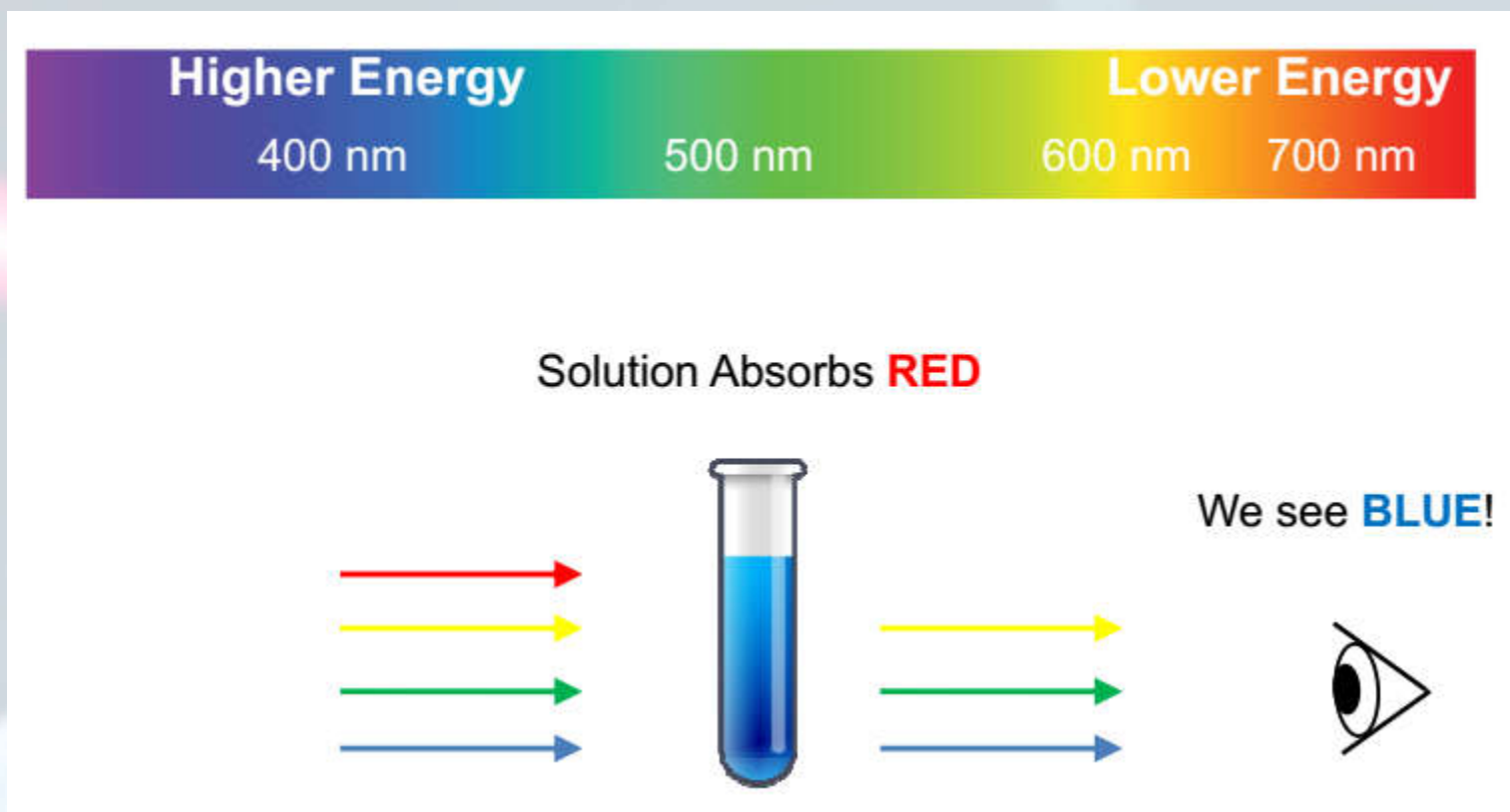
Molecules that Absorb Different Wavelength have Different Colors.