

## Uni-t-I: Light and Matter Engineering

### Syllabus

**Electro-magnetic spectrum-Applications in Engineering, Interaction of EM radiation with matter, work function of matter, Electrons in matter. Bonding theories: MOT, Band structure of matters HOMO-LUMO. Photochemical and thermal reactions: Laws of photochemistry, quantum yield, high and low quantum yield reactions. Jablonski diagram – photo physical and photochemical processes, photo-sensitization, photo- polymerization and commercial application of photochemistry.**

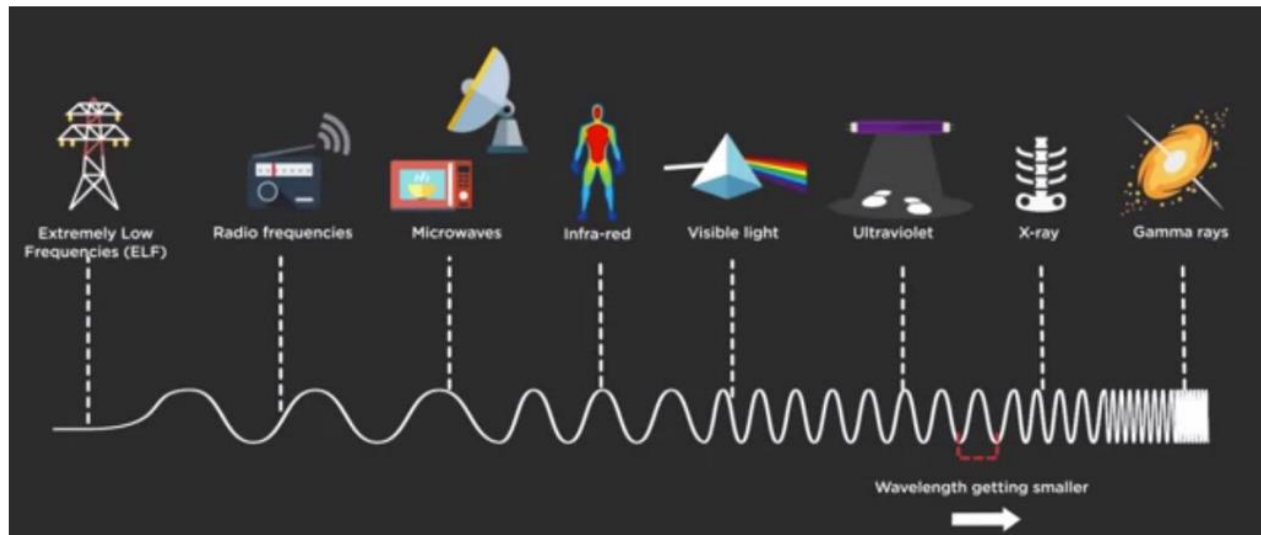
### 1. Electromagnetic Spectrum

Radiation that has both electric and magnetic fields and travels in waves. It comes from natural and man-made sources. Electromagnetic radiation can vary in strength from low energy to high energy.

EM Spectrum includes radio waves, microwaves, infrared light, visible light, ultraviolet light, x-rays, and gamma rays. Also called EMR.

As the wavelengths grows smaller in size, their frequency increases, along with their energy.

Such radiation travels through space at the speed of light. That is about  $3 \times 10^8$  m/s.



### EMR Spectrum:

Short Wave					Long Wave		
Cosmic rays	Gamma rays	X - rays	UV rays	Visible rays	IR rays	Micro waves	Radio waves
	Less than $10^{-12}$ m	$6 \times 10^{-12}$ m to $5 \times 10^{-12}$ m	0.2 to 0.4 micron	0.4 to 0.76 micron	0.76 to 3000 micron	1mm to 30 cm	0.1 cm to 100 km

1Picometer =  $10^{-12}$  m, 1 nanometer =  $10^{-9}$  m,  
1 micron (micrometer) =  $10^{-6}$  m, 1millimeter= $10^{-3}$ m

## **Applications**

### **Microwaves:**

It is used in Satellite signals. (Frequency of microwaves pass easily through atmosphere and clouds)

Cooking - Microwaves are absorbed by water molecules. These water molecules become heated and heat food. It is also used in extending TV signals to larger distances.

Dangers: microwaves are absorbed by living tissue Internal heating will damage or kill cells.

### **Infrared Radiation (remote controls, toasters):**

Any object that radiates heat radiates Infrared Radiation

It is used for night vision and security cameras as Infrared Radiation is visible in daytime or night-time.

It is also used in remote controls

### **Ultraviolet:**

Over-exposure to UVA and B damages surface cells and eyes and can cause cancer.

UVC is germicidal, destroying bacteria, and viruses in the air, in water and on surfaces.

### **X-rays:**

X-rays detect bone breaks.

### **Gamma Rays:**

Gamma Rays cause and treat cancers.

In high doses, gamma can kill normal cells.

## **2. Electro-magnetic spectrum-Applications in Engineering**

- Imaging with electromagnetic waves
- Sensing with electromagnetic waves
- Electromagnetic applications in biomedicine
- Electromagnetic applications in nanotechnology
- Electromagnetic measurements
- Electromagnetic modeling of devices and circuits
- Inverse scattering and inverse electromagnetic problems
- Electromagnetic radiators and antennas
- Wireless power transfer based on electromagnetic waves
- Radio-frequency identification (RFID)

### 3. Interaction of EM radiation with matter

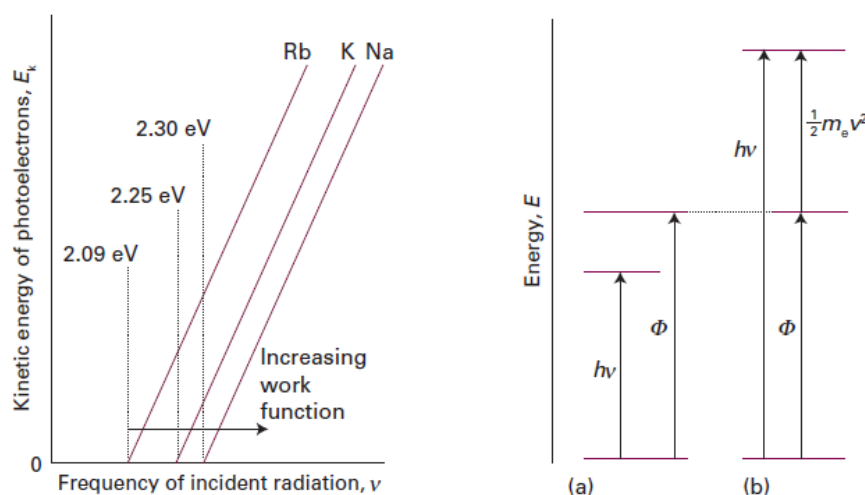
EM radiation interacts with matter that has a similar size to its own wavelength. But, depending on the wavelength, they interact with matter in different ways. For wavelengths larger than new UVC, the processes of interaction are; transmission, reflection, scattering, and absorption.

Wavelengths from UVC on-wards are so small that they can directly interact with matter at the atomic level. They can pass through the space of an atom and they can ionize atoms. Ionization happens when electromagnetic radiation knocks off an electron from an atom. By doing so, they have direct and indirect effects.

Various materials are transparent at various wavelengths. For example, lead glass is transparent to visible light but not X-rays, whereas several thicknesses of black paper sheets are transparent to X-rays, but not visible light. No known material is perfectly transparent.

### 4. Work function of matter – Light – matter interaction

The light radiation incident on the matter the electron emission occurs when the threshold frequency of energy is supplied (Photoelectric effect). This depends on the work function of matter. The wave like EMR radiation also behave as particle in nature (Wave-particle duality of light).



- The emission of electrons from the matter depends of the energy or frequency of the incident radiation.
- When the threshold frequency of light is applied the electron emission occur even at low intensity.

### 5. Molecular orbital (MO) theory

We will understand how the molecular orbitals are formed from the interaction of atomic orbitals.

We will see how the electrons occupy these molecular orbitals.

Molecular orbitals are formed from the combinations of atomic orbitals.

Since orbitals are wavefunctions, they can combine either constructively to form bonding molecular orbitals or destructively to form antibonding molecular orbitals.

Why do we need Molecular Orbital theory? Valence bond theory generally fails to explain the bonding in simple molecules.

With the help of molecular orbital one can understand the electronic transitions in molecules.

if we consider two hydrogen atoms to form hydrogen molecule, we expect that the wavefunctions of two hydrogen atoms  $\phi(a)$  and  $\phi(b)$  will interact constructively or destructively.

If they interact constructively then the molecular wavefunction.

In MO theory, valence electrons are delocalized over the entire molecule, not confined to individual atoms or bonds.

Molecular orbitals (wavefunctions) arise from adding together (superimposing) atomic orbitals or wavefunctions.

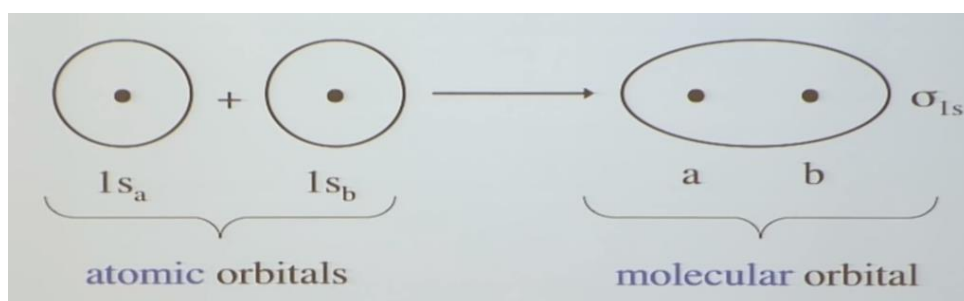
A linear combination of atomic orbitals (LCAO) creates molecular orbitals (bonding and antibonding orbitals).

N molecular orbitals can be constructed by N atomic orbitals.

### Molecular orbital theory

- A. Homonuclear diatomic molecules with MOs originating from s orbitals
- B. Homonuclear diatomic molecules with s and p orbitals
- C. Heteronuclear diatomic molecules

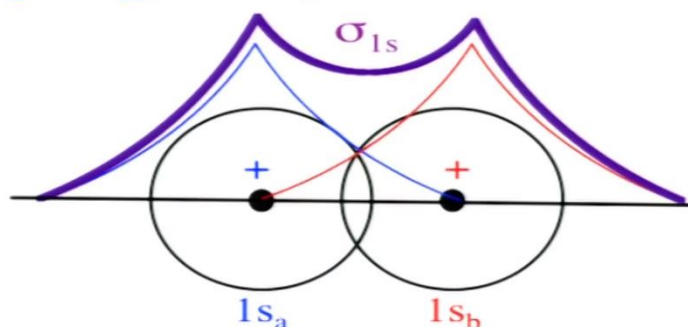
**Bonding orbitals arise from a linear combination of atomic orbitals (LCAO) (constructive interference)**



$\sigma$ : Cylindrically symmetric about the bond axis. No nodal plane along bond axis.

$1s_a + 1s_b = \sigma_{1s}$  (bonding molecular orbital (MO)).

**$1s_a + 1s_b = \sigma_{1s}$  (bonding MO) and a wavefunction**



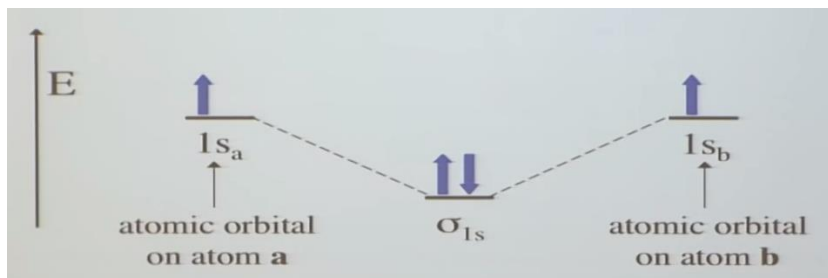
When waves interfere constructively, amplitude increases where they overlap

**Increased** amplitude in the internuclear region translates to an **enhanced** probability density ( $\Psi^2$ ) between the nuclei.

An electron on a bonding MO will be attracted to BOTH nuclei, and will be **lower in energy** compared to an atomic orbital for single nuclei.

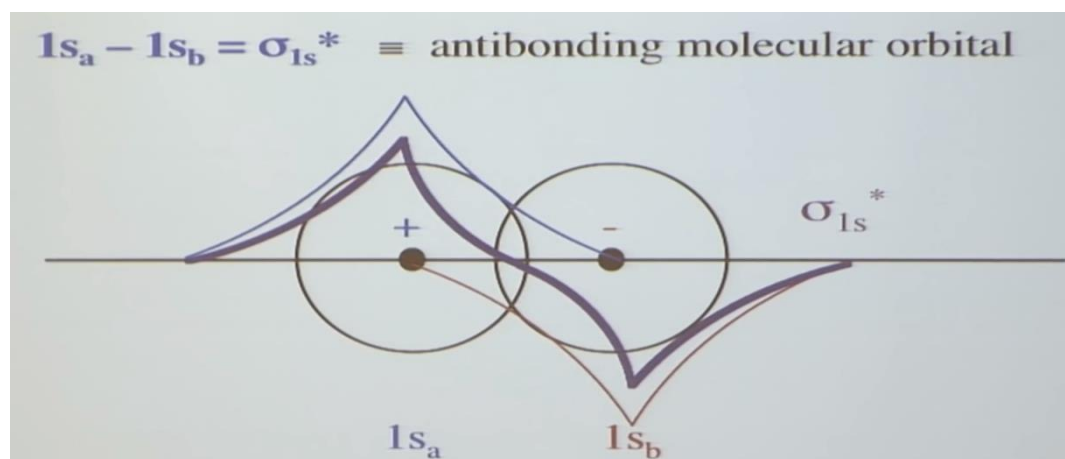
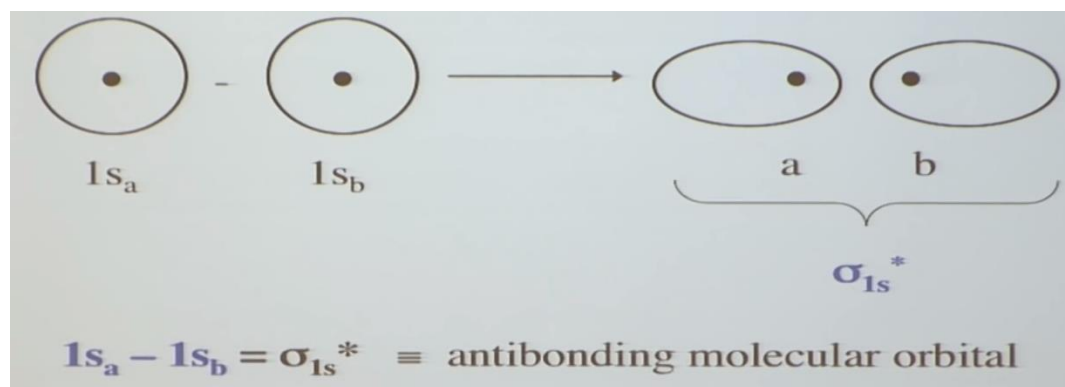
### Energy of interaction

The energy of a **bonding orbital** is **decreased** compared to the atomic orbitals

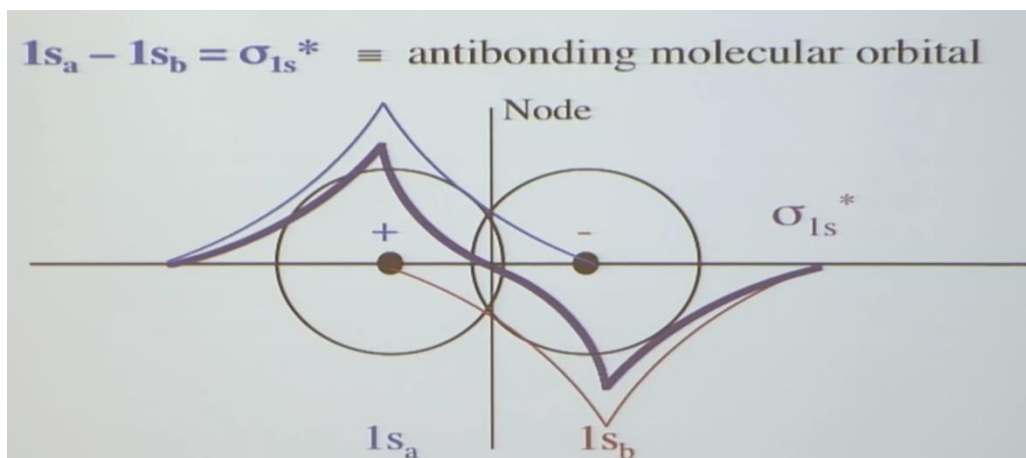


For H<sub>2</sub>, when its two electrons both occupy the bonding orbital, the molecule is **more** stable.

**Antibonding** orbitals arise from linear combination of atomic orbitals (LCAO) (destructive interference).



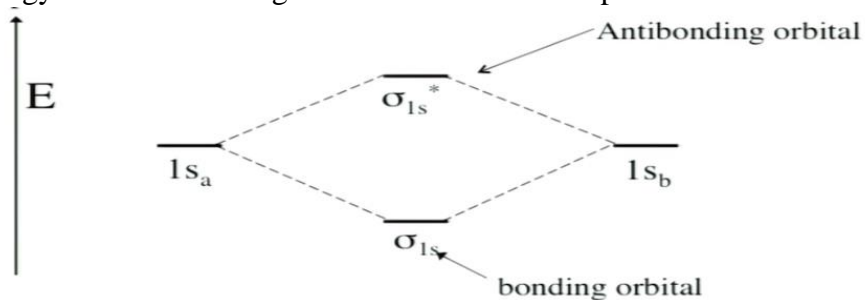
When wavefunctions interfere **destructively**, the amplitude **decreases** where they overlap.



When wavefunctions interfere destructively, the amplitude decreases where they overlap.

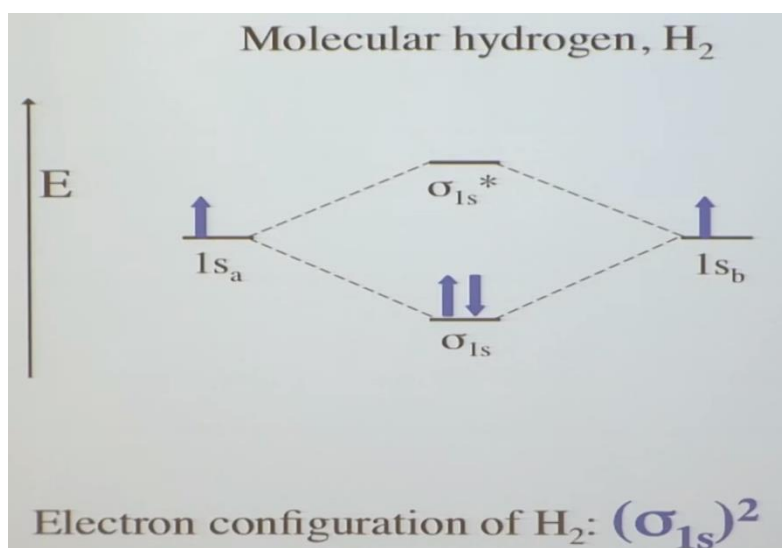
Decreased amplitude translates to a diminished probability density ( $\Psi^2$ ) between the nuclei and a node between the two nuclei.

The energy of an antibonding orbital is increased compared to the atomic orbitals.

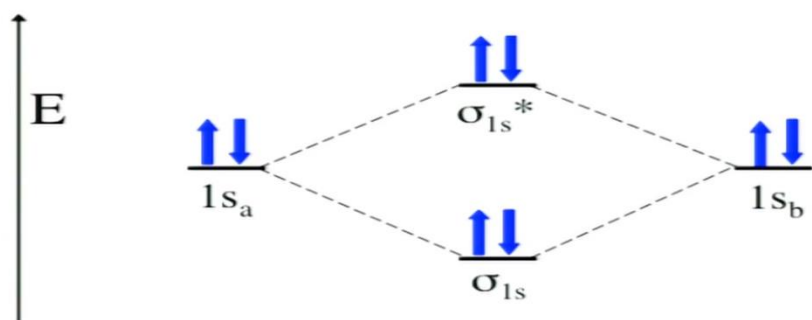


The antibonding orbital is raised in  $E$  by the amount as the bonding orbital is lowered.

Two atomic orbitals generate two MO (one is bonding (lower  $E$ ) and one is antibonding (higher  $E$ )).



## MO diagram of He<sub>2</sub>



Electron configuration of He<sub>2</sub>:  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$

**No net gain or loss** in energy for He<sub>2</sub> compared to 2 He

MO theory predicts that He<sub>2</sub> does not exist

BOND ORDER =  $\frac{1}{2} (\text{\# of bonding electrons} - \text{\# of antibonding electrons})$

He<sub>2</sub> bond order =  $\frac{1}{2} (2 - 2) = 0$ , no bond

H<sub>2</sub> bond order =  $\frac{1}{2} (2 - 0) = 1$ , single bond

Reality: He<sub>2</sub> does not exist

He-He

Weakest chemical bond known. Discovered in 1993.

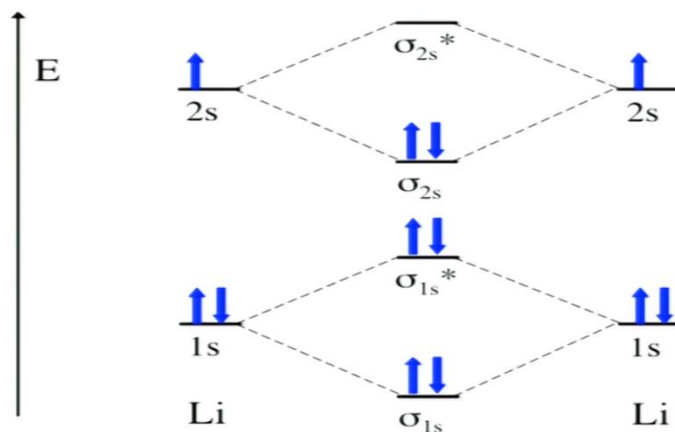
$\Delta E_d = 0.01$  kJ/mol for He<sub>2</sub>

$\Delta E_d = 432$  kJ/mol for H<sub>2</sub>

Li<sub>2</sub>

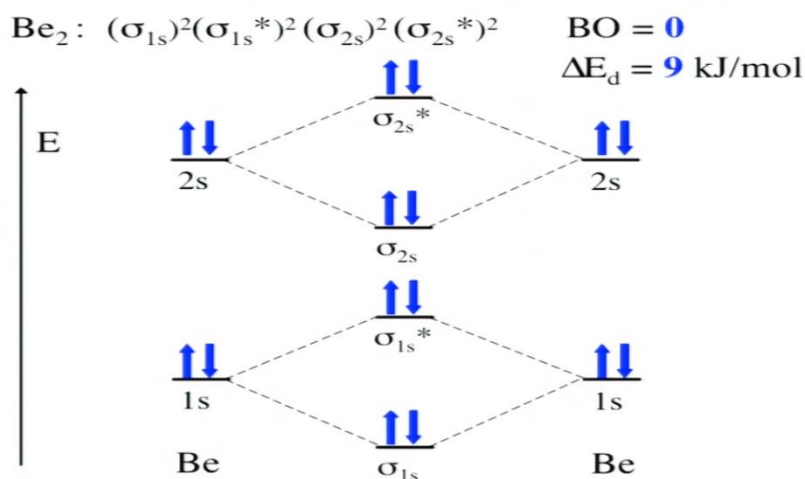
Electron configuration:

$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2$

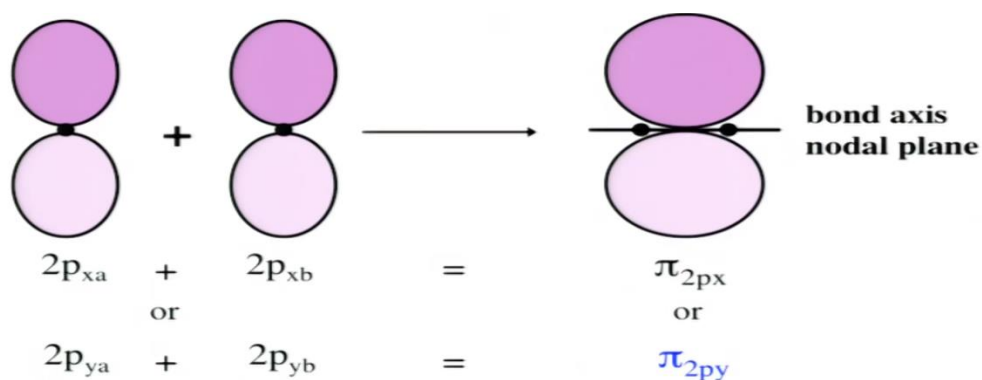


BO =  $\frac{1}{2} (4 - 2) = 1$

$\Delta E_d = 105$  kJ/mol

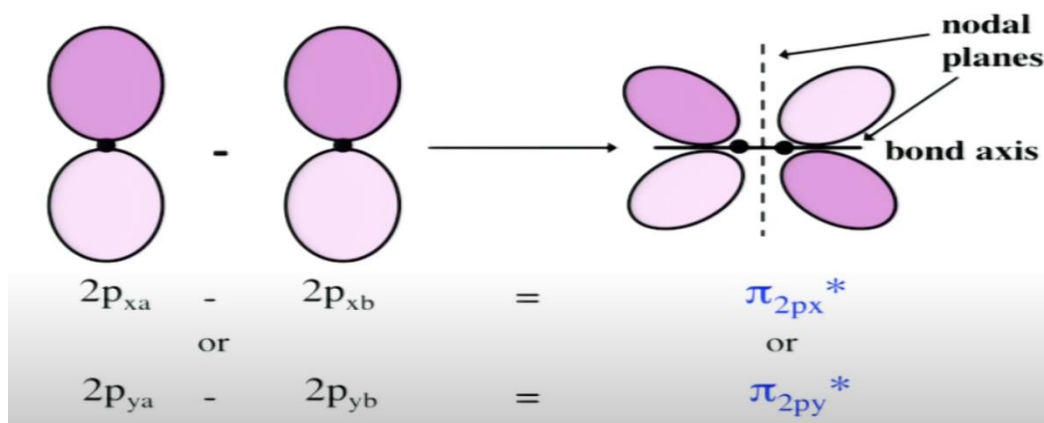


**Bonding orbitals** formed by LCAO of  $2p_x$  and  $2p_y$  via **constructive** interference



$\pi$ -orbital: Molecular orbital with a nodal plane through the **bond** axis.

**Antibonding orbitals** formed by LCAO of  $2p_x$  and  $2p_y$  via **destructive** interference

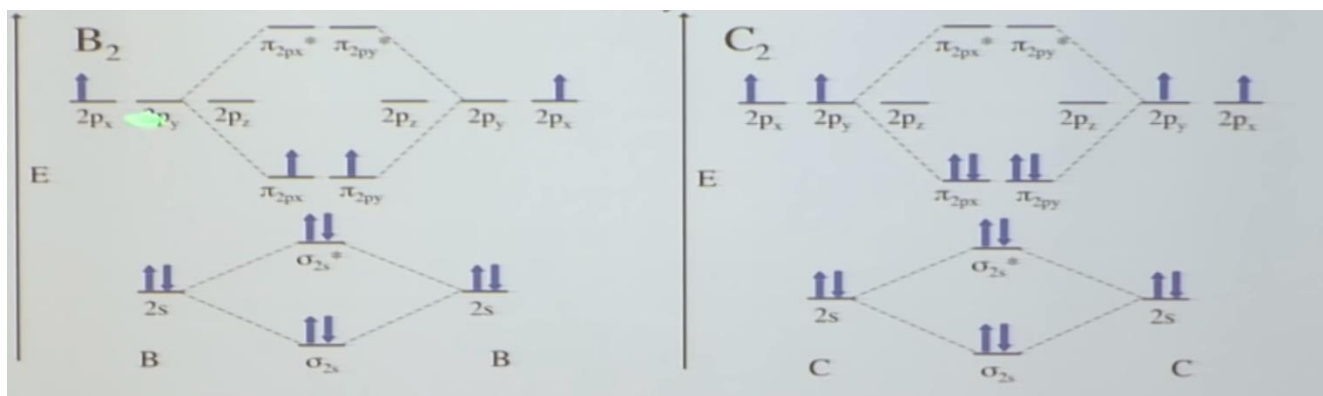


$\pi^*$ -orbitals: MO with two nodal planes.

Please note that the following MO diagrams for  $\text{B}_2$  and  $\text{C}_2$  are rated I for incomplete since they do not include the  $2p_z$  molecular orbitals!

Just considering  $2s$  and  $2p_x$  and  $2p_y$  for the moment, let's sum it up



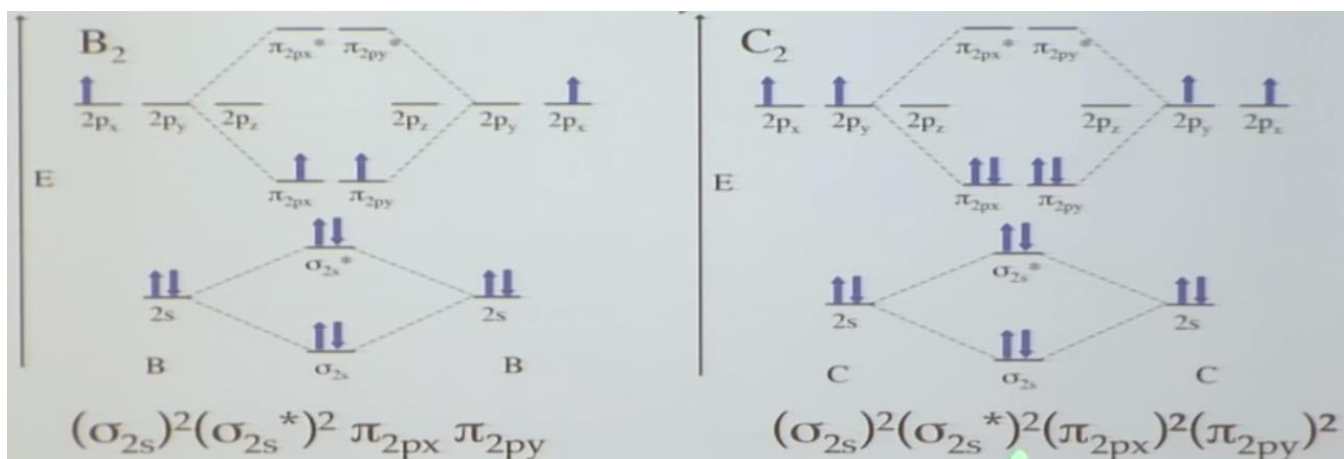


Two 2s atomic orbitals generate two σ<sub>2s</sub> molecular orbitals (one lower in energy (σ<sub>2s</sub>) and one higher (σ<sub>2s</sub><sup>\*</sup>))

Two 2p<sub>x</sub> atomic orbitals generate two π<sub>2px</sub> molecular orbitals (one lower in energy (π<sub>2px</sub>) and one higher (π<sub>2px</sub><sup>\*</sup>))

Two 2p<sub>y</sub> atomic orbitals generate two π<sub>2py</sub> molecular orbitals (one lower in energy (π<sub>2py</sub>) and one higher (π<sub>2py</sub><sup>\*</sup>))

**Just considering 2s and 2p<sub>x</sub> and 2p<sub>y</sub> for the moment, let's sum it up**



4 electrons in lower E (bonding MO)

2 electrons in lower E (antibonding MO)

**B.O.** = ½ (4-2) = 1

Which is more stable? has a higher dissociation energy?

ΔE<sub>d</sub> = 289 kJ/mol

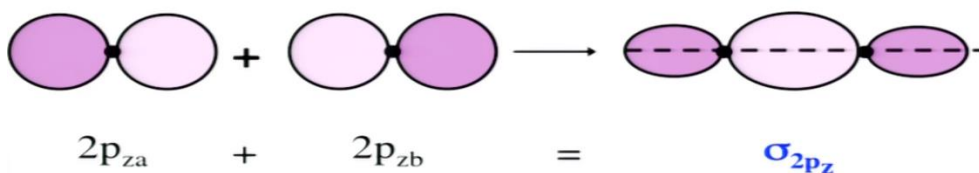
6 electrons in lower E (bonding MO)

2 electrons in lower E (antibonding MO)

**B.O.** = ½ (6-2) = 2

ΔE<sub>d</sub> = 599 kJ/mol

**Bonding orbitals**  
formed by LCAO of 2p<sub>z</sub>



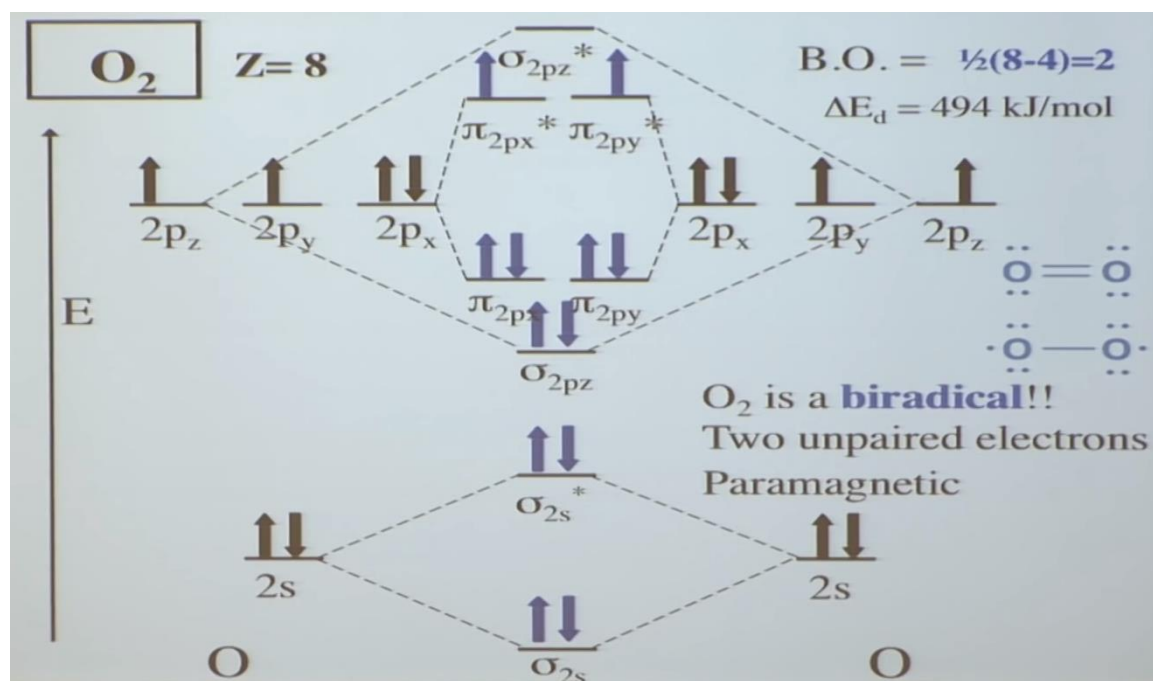
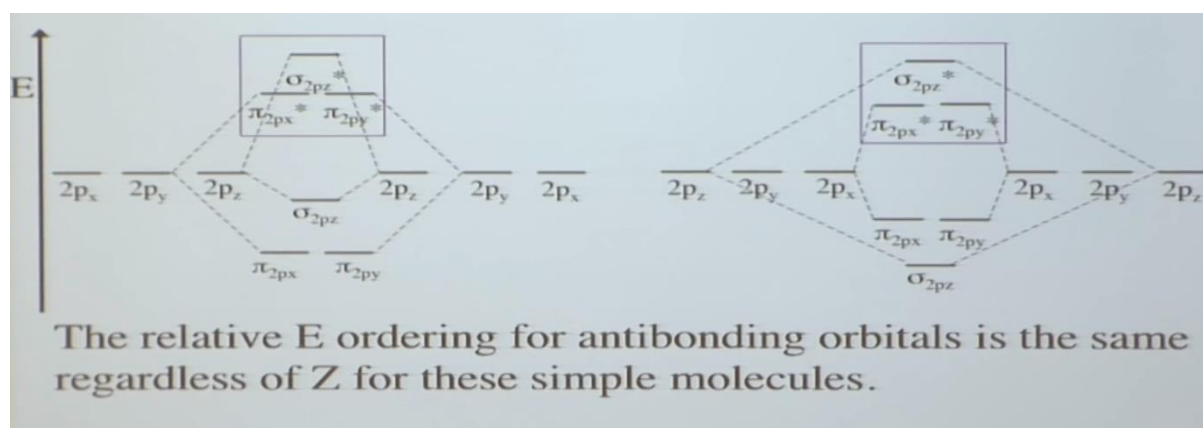
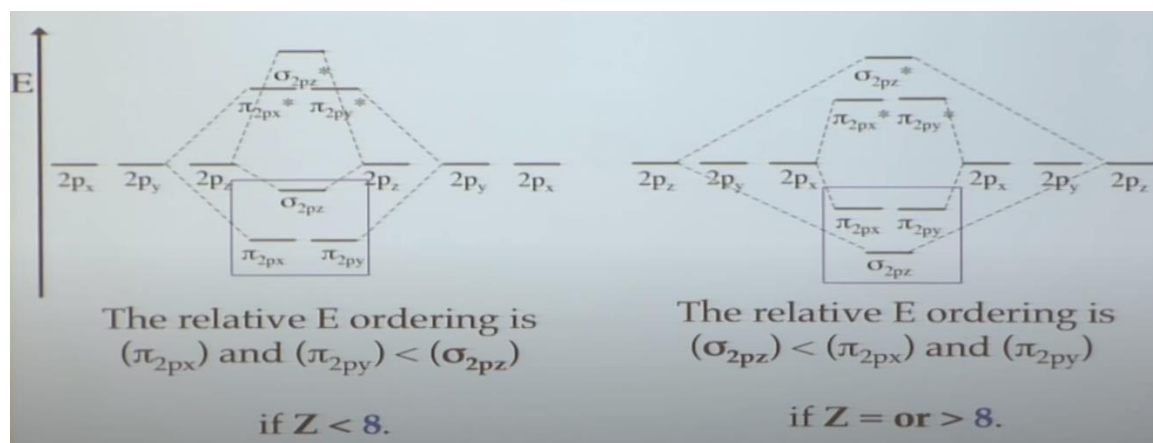
$\sigma$ : cylindrically symmetric with no nodal plane along the bond axis

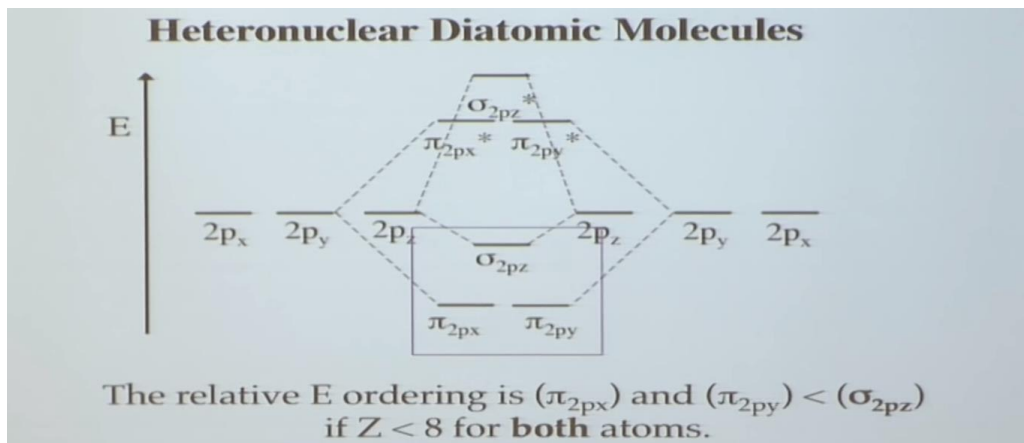
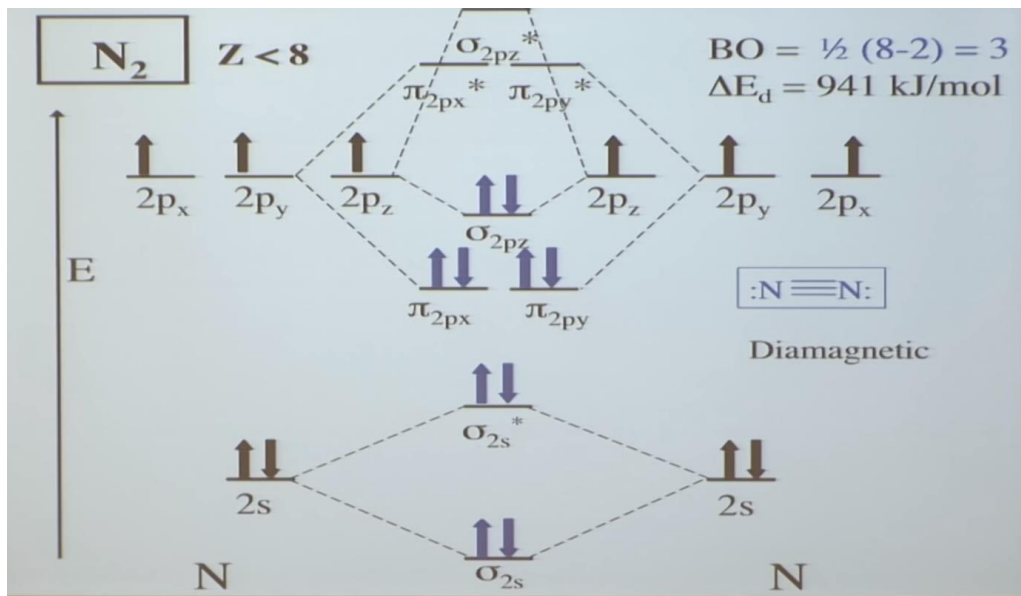
**Nodes** pass through nuclei, but no nodes along the bond axis.

**Constructive** interference-**increased** amplitude between nuclei-**increased** probability density between nuclei-**lower** energy MO.

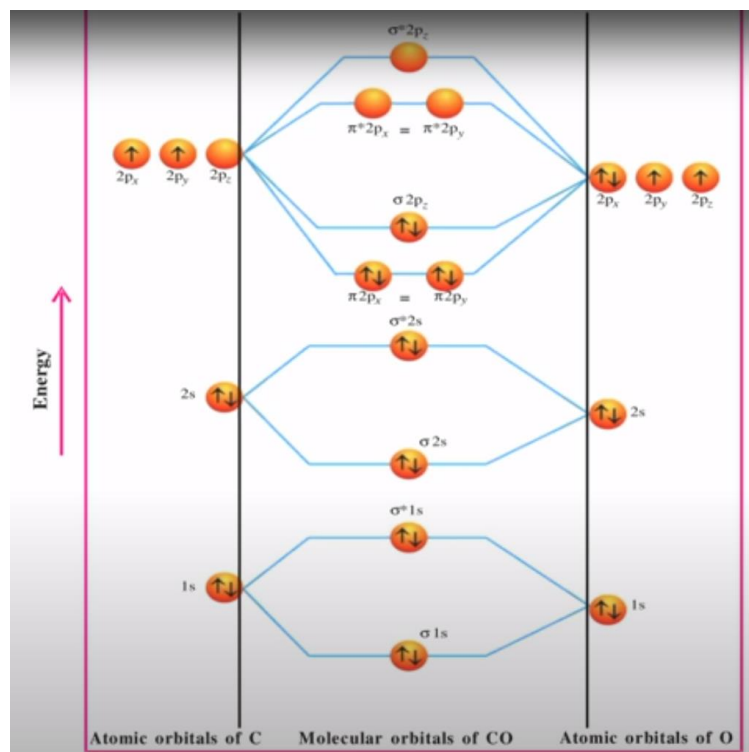
The relative energies of the  $\sigma_{2pz}$  orbital compared  $\pi_{2px}$  or  $\pi_{2py}$  depend on Z value of the atoms.

The relative energies of the  $\sigma_{2pz}$  orbital compared to the  $\pi_{2px}$  or  $\pi_{2py}$  orbitals depend on the Z value of the atoms.

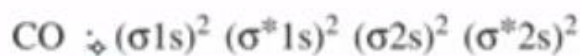




Let us take another example of CO and NO as shown in below figure.



The arrangement of fourteen electrons present in carbon monoxide molecule, can be written in molecular orbitals as follows :



$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

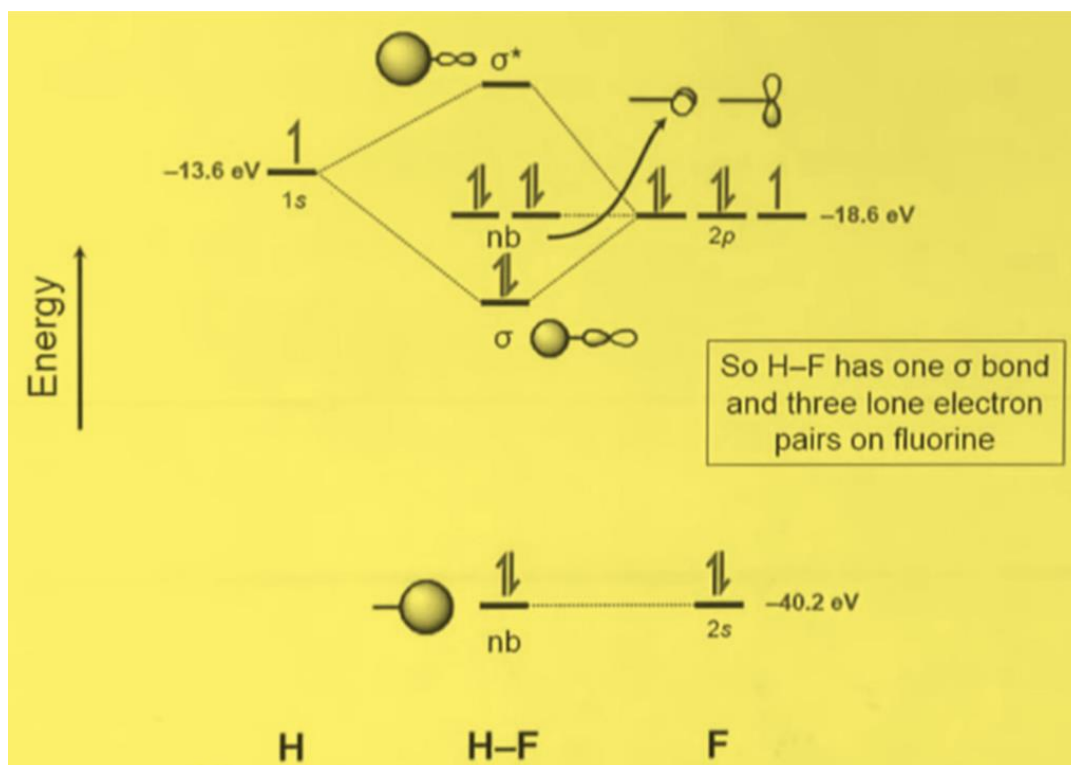
$$= \frac{1}{2} [10 - 4]$$

$$= 3$$

Hence,  $\text{C} \equiv \text{O}$  will be in CO.

### Molecular Orbital Diagram for HF

The AO energies suggest that the 1s orbital of hydrogen interacts mostly with 2p orbital of fluorine. The F 2s is nonbonding.



$$\text{Bond order} = \frac{1}{2} (2-0)$$

$$= 1$$

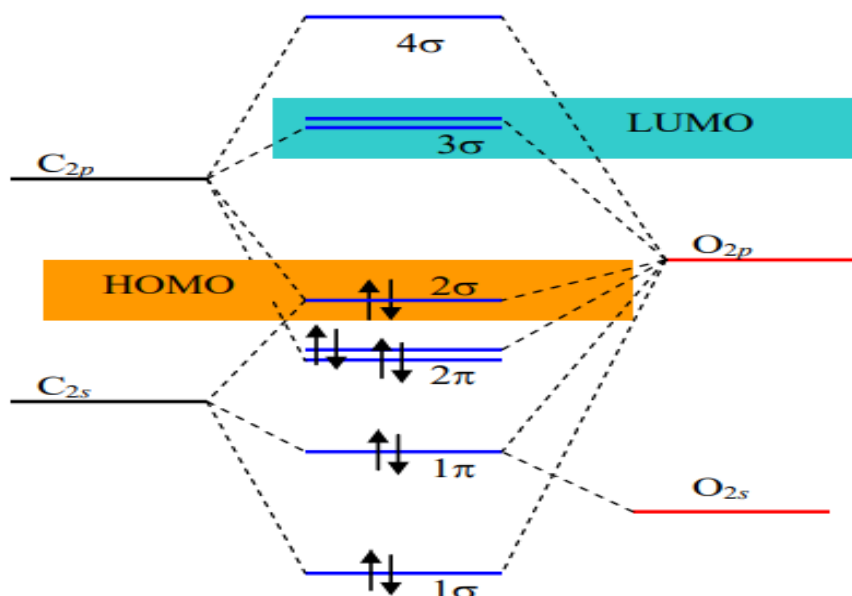
Magnetic property= diamagnetic property

## 6. Band structure of matters HOMO-LUMO

Generally, to simplify the things, interactions of the orbitals contains valence electrons are considered to form the molecular orbitals.

The molecular orbital  $2\sigma$  is the highest filled orbital and is HOMO.

The molecular orbital  $3\sigma$  is the lowest unfilled orbital and is LUMO.



As MO for larger molecules tend to be more complicated (the electrons are spread out all over the big molecule). At this point we generally no longer focus on a comparison between the MOs and the AOs but instead just take the MOs as a set of orbitals for the whole molecule. There are many such orbitals (an infinite number), but we will always focus simply on the electrons that are most important for the chemistry. These are: the highest occupied molecule orbital or HOMO and the lowest unoccupied molecular orbital or LUMO. The HOMO is the highest energy MO that has any electrons in it. The LUMO is the next highest energy orbital (it will be empty). The LUMO is the lowest energy place to put or excite an electron.

The energy difference between the HOMO and LUMO or HOMO-LUMO gap is generally the lowest energy electronic excitation that is possible in a molecule. The energy of the HOMO-LUMO gap can tell us about what wavelengths the compound can absorb. Or alternatively, measuring the wavelengths a compound absorbs in the lab can be used as a measure of the HOMO-LUMO gap.

. The band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors.

It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current.

It is closely related to the HOMO/LUMO gap in chemistry. If the valence band is completely full and the conduction band is completely empty, then electrons cannot move in the solid; however, if some electrons transfer from the valence to the conduction band, then current *can* flow.

Therefore, the band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps or none, because the valence and conduction bands overlap.

The energy gap between the highest occupied and lowest unoccupied electronic levels is a critical parameter determining the electronic, optical, redox, and transport (electrical) properties of a material.

However, the energy gap comes in many flavors, such as the band gap, HOMO–LUMO gap, fundamental gap, optical gap, or transport gap, with each of these terms carrying a specific meaning.

## **7.Photochemical and Thermal reactions**

Photochemistry is the study on photochemical reactions between light and molecules. Photochemical reactions require that a photon is absorbed to begin the reactions. The excited state can undergo a variety of transition states, which can be divided into photochemical and photophysical processes.

Photochemical reactions can occur in natural processes and applications such as:

- Photosynthesis: plants use solar energy to convert carbon dioxide and water into glucose and oxygen.
- Sunburn
- Formation of ozone from oxygen in atmosphere
- Bioluminescence: *e.g.* In fireflies, an enzyme in the abdomen catalyzes a reaction that produced light.
- Photography
- Phototropism (orientation of plants towards the direction of sunlight)
- Treatment of jaundice of newborn babies
- Biosynthesis of vitamin D
- Photochromism (sunglasses)
- Polymerizations started by photo initiators, which decompose upon absorbing light to produce the free radicals for radical polymerization.
- Photodegradation of many substances, *e.g.* polyvinyl chloride and Fp. Medicine bottles are often made with darkened glass to prevent the drugs from photodegradation.



- Photoresist technology, used in the production of microelectronic components.
- Photochemical production of artemisinin, anti-malaria drug.
- Photochemistry for biomedical applications has attracted much attention in the last few decades including oncology, molecular biology, chemotherapy, and surgery.

### Photochemical versus Thermal reactions

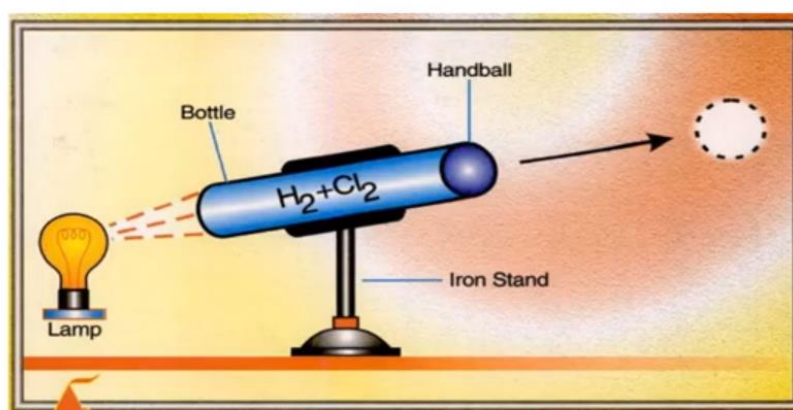
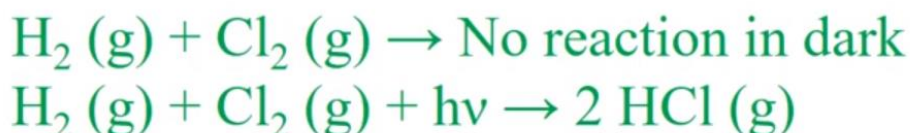
All chemical reactions need energy to occur. The reacting species need to acquire sufficient energy to get converted into the product

Two types

1. **Thermal reactions:** energy provided as heat
2. **Photochemical reactions:** energy provided as light or radiation

The photochemical reactions differ from thermal reactions. The activation of a photoreaction is provided by the absorption of light. In contrast, activation of a thermal reaction is based on heat. The electronic distribution and nuclear configuration of photo-activated molecules are different from those of thermally activated molecules.

A reaction which takes place by absorption of the visible and ultraviolet radiations is called a **photochemical reaction**



**The 'HCl-cannon' experiment**

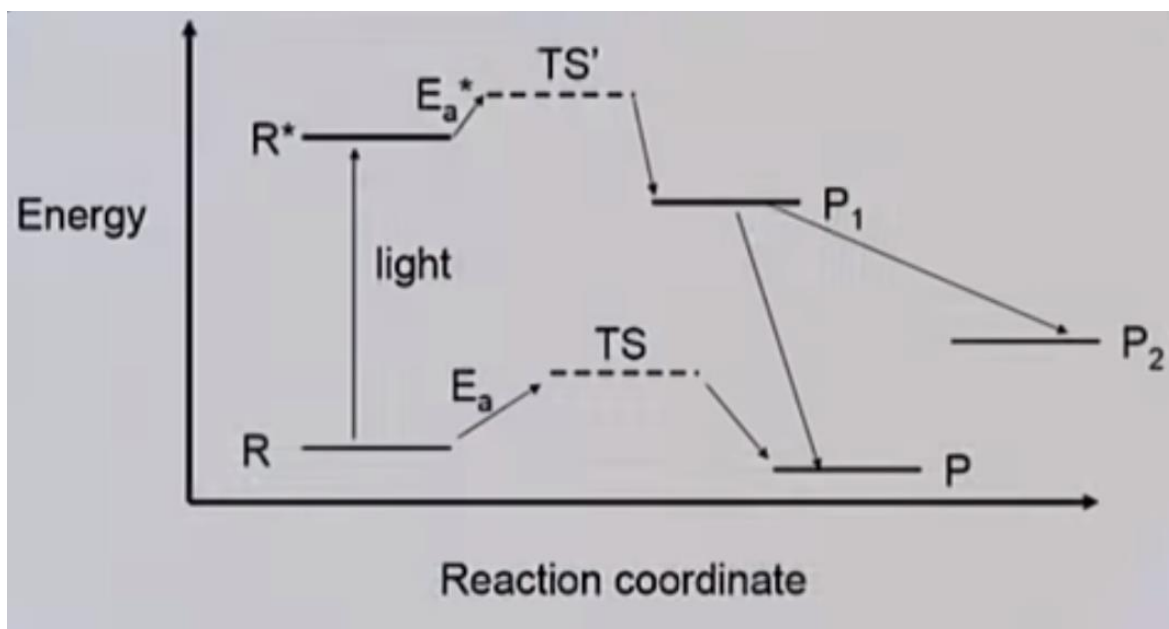
The reaction which are caused by heat and in absence of light are called **thermal or dark reaction**.

## Difference between Photochemical and Thermochemical reactions

	Photochemical reactions	Thermochemical reactions
1	These reactions involve absorption of light reactions.	These reactions involve of absorption or evolution of heat.
2	The presence of light is primary requirement of these reactions.	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.	Temperature has a significant effect on the rate of a thermochemical reactions.
4	Photo-activation with radiation of sufficiently large energy (200-800 nm) leads to electronic excitation followed by a reaction.	<p>Thermal activation leads to increase in the number of collisions between molecules of reactants or reactants and walls of container.</p> <p>The thermal energy gets distributed mainly amongst different translational, rotational, and vibrational excitations; very small fraction leads to electronic excitations followed by a reaction.</p>
5.	<p>In case of photo-excitation even the reaction accompanied by increase in free energy (non-spontaneous) may also occur.</p> <p>i.e <math>\Delta G</math> for photochemical spontaneous reaction +ve.</p>	<p>The thermal reactions are accompanied by decrease in free energy; i.e., these are spontaneous.</p> <p>i.e. <math>\Delta G</math> for thermochemical reaction reaction is always -ve.</p>
6.	Photochemical activation is highly selective.	Thermochemical activation is not selective in nature.
7.	$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow[\text{Chlorophyll}]{\text{Light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$	Formation of $\text{CO}_2$ , $\text{NH}_3$ , thermal decomposition reaction etc.



8	<p>In case of photochemical reactions, the rate of reaction is independent of temperature but depends on the intensity of radiation.</p> <p>The photo-excitation may cause reactions to occur at sufficient speed even at room temperature, whereas to do the same thermally, we need to raise temperature significantly.</p>	<p>The rate of thermal reactions depends on temperature.</p>
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## **7.Laws of photochemistry**

There are the two basic laws of photochemistry. The first law of photochemistry is the Grotthuss–Draper law. In 1817, the German physicist Theodor von Grotthuss first proposed a new phenomenon that a compound must absorb light for a photochemical reaction to take place. The American chemist John William Draper also noted that the rate of the reaction was proportional to intensity of absorbed light in 1841. The second law is the Stark–Einstein law. The German physicists of Johannes Stark and Albert Einstein independently formulated the law. They noted that each compound during the reaction absorbs only a single quantum or photon of light.

Two laws

1. Grotthus-Dropper law
2. Stark-Einstein's law

### **Grotthus-Draper law**

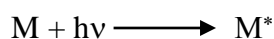
- Stated by Grotthus in 1817 and Drapper in 1843.
- Only those radiation that are absorbed by the reacting system can be effective in producing chemical change.
- The light that gets reflected or transmitted does not produce any chemical change.
- This is a simple concept, but it is the basis for performing photochemical and photobiological experiments correctly.
- If light of a particular wavelength is not absorbed by a system, no photochemistry will occur, and no photobiological effects will be observed, no matter how long one irradiates with that wavelength of light.

### **Stark-Einstein's law**

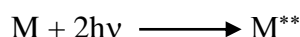
Proposed by Stark and Einstein from 1908 to 1912; also called law of photochemical equivalence.

#### **Statement**

Each atom or molecule absorb a single quantum of light (photon) in the process of getting excited



However, exception have been observed (intense lasers)



- The law concerns the primary step of activation of the molecule .
- The activated molecule may undergo a chain mechanism whereby a large number of molecules may undergo reaction.
- Alternatively, the activated molecule may deactivate without any reaction.
- Law of equivalence doesnot mean that one molecule would react per photon absorbed.

### **8.Absorption of Radiation**

The wavelength of the absorbed radiation determined by the Bohr's frequency rule

$$\nu = \frac{E_2 - E_1}{h}$$

Where,  $E_2$  and  $E_1$  are the energies of the final and the intial states respectively

The energy absorbed,  $I_a$  is generally expressed in terms of 'Einstein'.

It corresponds to amount of energy of one mole of photons of a given frequency absorbed by the system  
Given as:

$$\begin{aligned}
 1E &= N_A h\nu = (N_A h c) / \lambda \\
 &= (6.022 \times 10^{23} \text{ mol}^{-1} \times 6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}) / \lambda \times 10^{-9} \text{ m} \\
 &= (119666 / \lambda) \text{ J mol}^{-1} \quad \text{where } \lambda \text{ is expressed in nm.}
 \end{aligned}$$

### Einstein equivalents of photons of different wavelengths

$\lambda$ (nm)	einstein (kJ mol <sup>-1</sup> )
200	598.3
250	478.6
300	398.9
400	299.2
500	239.3
600	199.5
700	170.9

➤ Higher the wavelength, lower the energy

When a monochromatic light of intensity  $I_0$  is incident on a transparent medium, a part of light is absorbed by the media ( $I_a$ ), a part of light is reflected ( $I_r$ ) and the remaining part of light is transmitted ( $I_t$ ) i.e.,

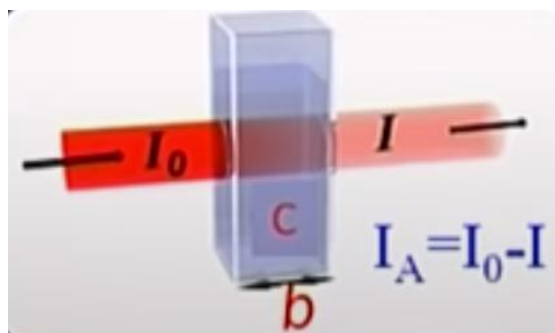
$$I_0 = I_a + I_r + I_t$$

For a glass-air interface,  $I_r$  is negligible

$$I_0 = I_a + I_t$$

Colorimetry is based upon Beer-Lambert Law.

When a monochromatic radiation of intensity  $I_0$  is made to fall on a sample taken in suitable container, a part of the radiation is absorbed, and a part is transmitted (ignoring reflection).



$I_0$  and  $I$  are related by Lambert-Beer's Law

### **Bouguer's law or Lambert's law**

Related the light absorption and the thickness of the absorbing medium;

### **Beer's law**

Related the light absorption and concentration of the absorbing sample.

The two laws are combined together to give Beer-Lambert's law.

### **Bouguer's law or Lambert's law**

Lambert's law: The intensity of transmitted light decreases exponentially as the thickness of the absorbing medium increase arithmetically.

### **Mathematically**

$$\log_{10} \frac{I_o}{I} = \frac{k''}{2.303} c$$

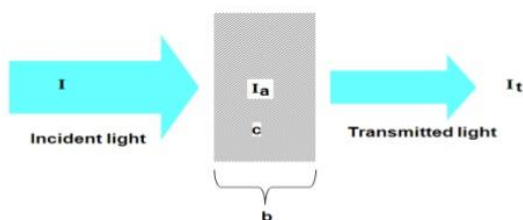
$I_o$  and  $I$  represent the intensities of the incident light and transmitted light after passing through a solution of concentration 'c' taken in a sample cuvette of unit thickness.

### **Beer-Lambert Law**

The intensity of transmitted beam of a monochromatic light decreases exponentially as the concentration and thickness of the absorbing medium increase arithmetically.

OR

It states that the absorbance of a monochromatic light is directly proportional to the path length,  $t$  and concentration,  $c$  of the light absorbing analyte.



Where

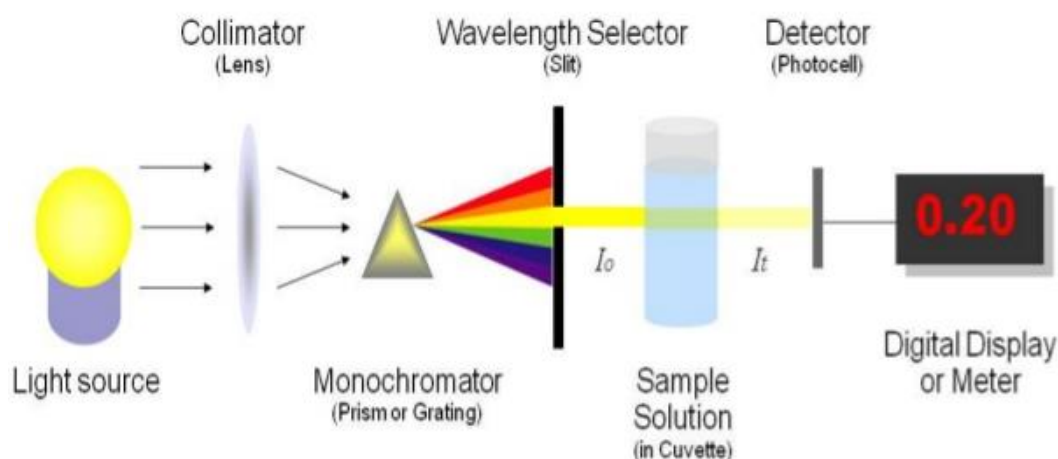
$I$  = Intensity of Incident light

$I_a$  = Intensity of absorbed light

$I_t$  = Intensity of transmitted light

$c$  = molar concentration of sample

$b$  = Length or thickness of the sample cell (cm)



**Mathematically,**

$$\log \frac{I_0}{I} = abc$$

Where, 'a' is a constant called absorptivity, 'b' is the thickness of the absorbing medium, and 'c' is the concentration of the absorbing species.

If the concentration is expressed in terms of  $\text{g cm}^{-3}$  and b in cm; a has the units of  $\text{cm}^{-1}\text{g}^{-1}\text{dm}^3$ .

If the concentrations is expressed in terms of  $\text{mol dm}^{-3}$  and b in cm

The absorptivity is called molar absorptivity and is expressed as  $\epsilon$  and has the units of  $\text{cm}^{-1}\text{mol}^{-1}\text{dm}^3$ .

The Beer-Lambert's law expression becomes

$$\log \frac{I_0}{I} = \epsilon bc$$

### **Limitations of Beer-Lambert's law**

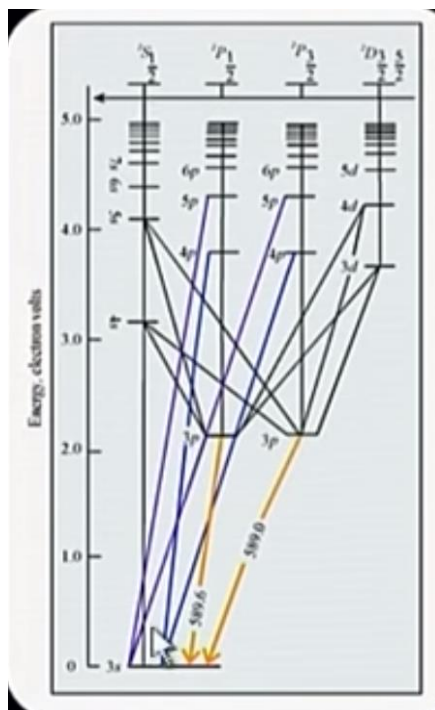
The law is not valid

- When non-monochromatic radiation is used.
- If temperature changes during measurements.
- The law is applicable only to dilute solutions.

- Absorption of radiation by atoms.
- Absorption of radiation by molecules.

## Absorption of radiation by atoms

Absorption of radiation by atoms leads to the transition amongst the electronic energy levels.



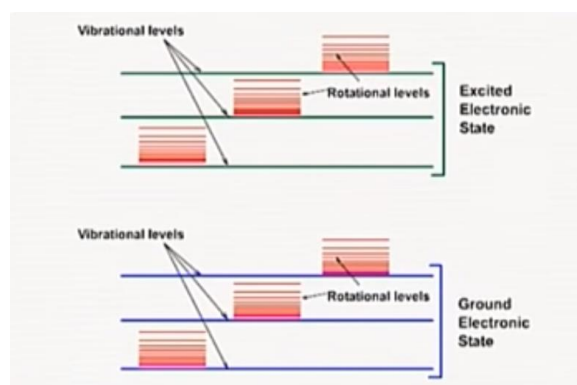
## Grotrain diagrams of sodium

## Absorption of radiation by molecules

The molecular energy has four components

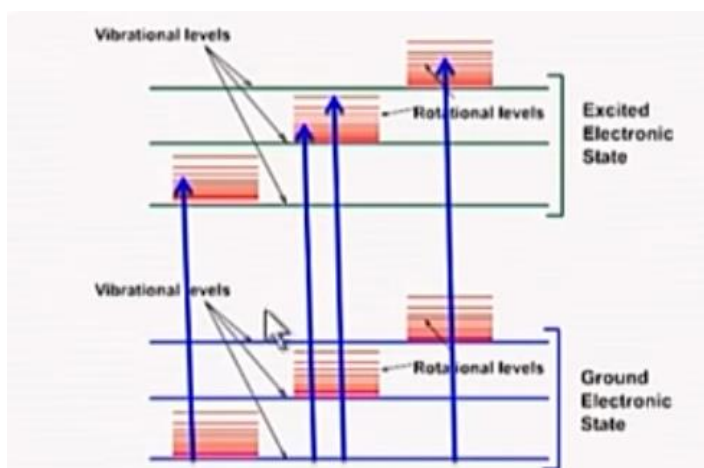
$$E_{TOTAL} = E_{trans} + E_{rot} + E_{vib} + E_{elect}$$

Of these, the rotational, vibrational and electronic energies are quantised



The translation energy is not quantised

Absorption of UV-Vis radiation causes transition among the quantised electronic energy levels



These are accompanied by vibrational and rotational transitions

$$E_{\text{TOTAL}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elect}}$$

$$\Delta E_{\text{TOTAL}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$$

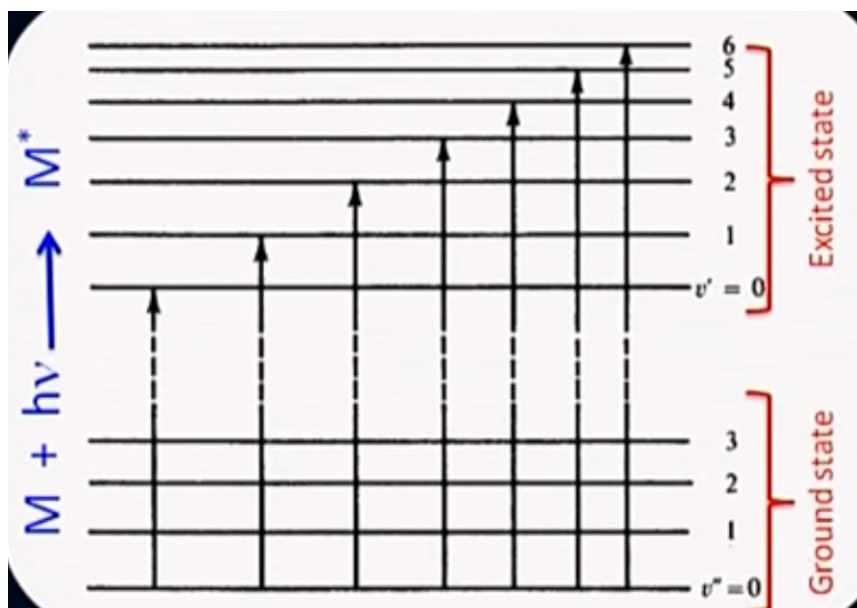
$$\Delta E_{\text{rot}} = \sim 1 \text{ cm}^{-1}$$

$$\Delta E_{\text{vib}} = \sim 1,000 \text{ cm}^{-1}$$

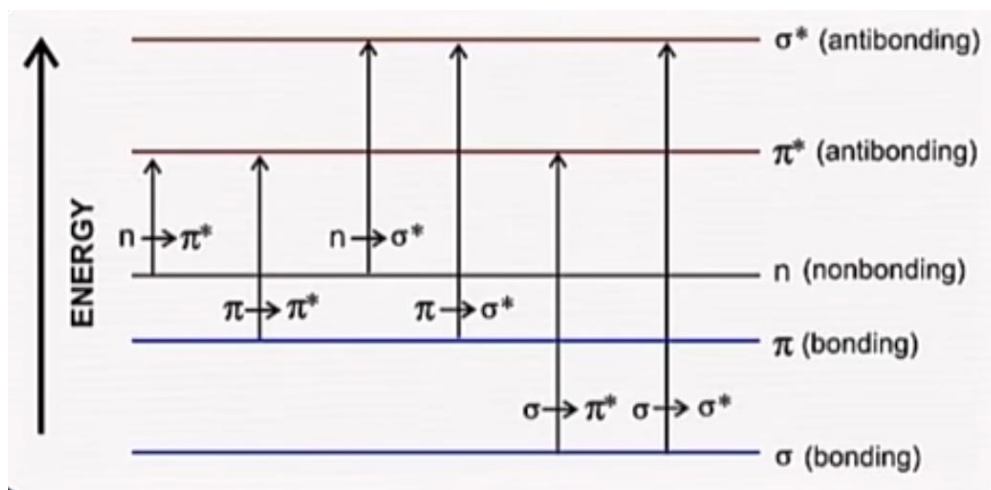
$$\Delta E_{\text{elec}} = \sim 10,000 \text{ to } 100,000 \text{ cm}^{-1}$$

$$\Delta E_{\text{electronic}} = 1000 * \Delta E_{\text{vibration}} = 100000 * \Delta E_{\text{rotation}}$$

While considering electronic transitions, the rotational transition can be ignored. Thus excitation of a molecule on absorption of can be represented as;



Generalized molecular orbital energy level diagram and possible transitions

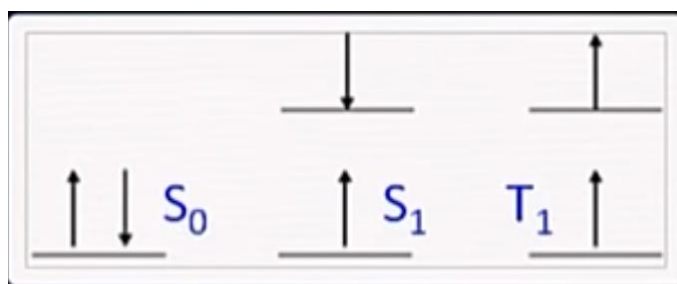


### The electronic transition originates from a singlet state

In the ground state, the molecular orbitals are occupied by two electrons. According to Pauli's principle the spins of these electrons are antiparallel. The total spin,  $S$ , of the molecule in the ground state is zero ( $1/2 + (-1/2)$ ). This energy state is called "singlet state" and is labelled as  $S_0$ .

### **The excited electronic state may be a singlet or a triplet state**

The electron spins in the excited molecule may either be parallel or antiparallel.



The state with parallel spins is called triplet state,  $T_1$  and the one with antiparallel spins is termed a singlet state,  $S_1$ .

### **Characteristics of Singlet and Triplet states**

The life time of the excited singlet state is of the order of  $10^{-9}$  to  $10^{-6}$  s whereas, for the triplet state it is about  $10^{-5}$  to  $10^{-3}$  s

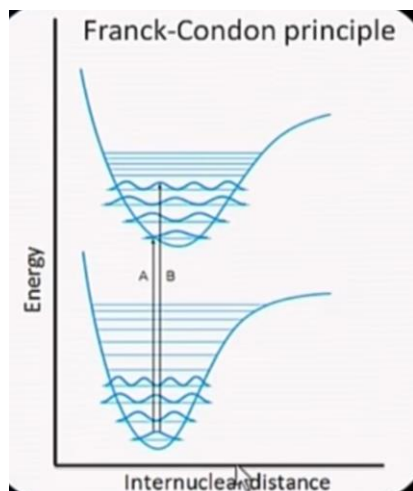
The energy of triplet excited state is lower than that of the singlet excited state. The singlet excited state is usually more reactive.

### **Electronic excitation or activation is governed by Franck-Condon principle.**

According to it the electronic transition is so fast ( $\sim 10^{-15}$  s) that the molecule does not get an opportunity to execute a vibration. i.e., when the electrons are excited the internuclear distance does not

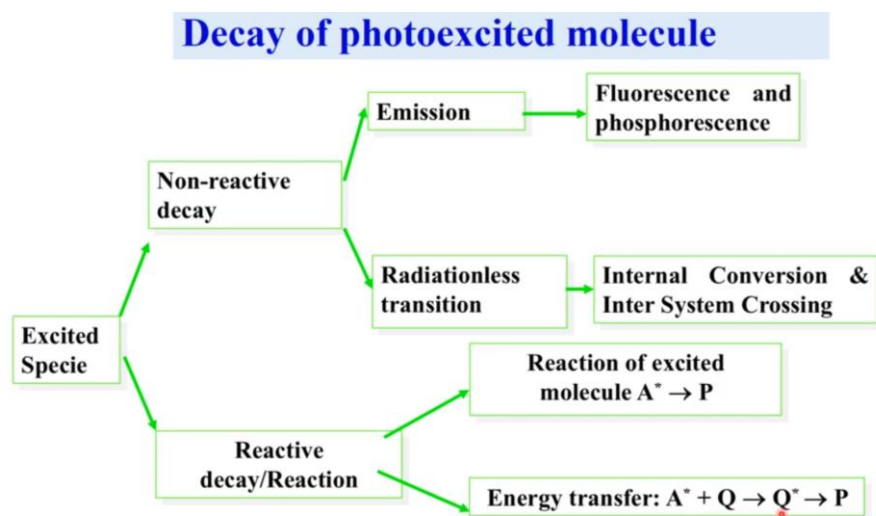


change. The electronic excitation can be represented in terms of a vertical arrow in an energy level diagram.

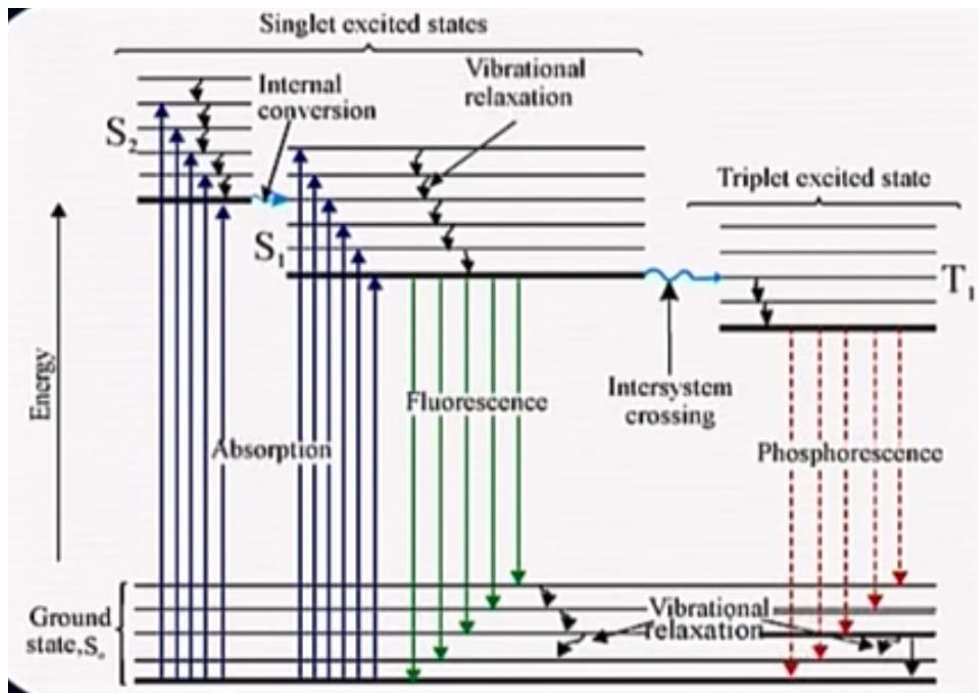


**What is the fate of the excited state?**

Relax back to the ground state by using different processes. The absorbed energy is given off as heat to the surroundings ( non-radiative relaxation). The absorbed energy is emitted as radiation ( radiation relaxation). A radiative relaxation of excited state is called **luminescence** or **photoluminescence**.



The processes of electronic excitation and relaxation can be represented in terms of a **Jablonski diagram**



## Activation

The molecule in the singlet ground state, so gets excited to any of the possible singlet states ( $S_1$  or  $S_2$ ).

## Deactivation

**Two types of processes:**

**Radiative processes:** accompanied by radiation emission.

**Non-radiative processes:** not accompanied radiation emission.

### Non-radiative processes

- Vibrational relaxation
- Internal conversion
- Intersystem crossing

## Vibrational relaxation

The excited molecule, in the higher vibrational levels of the excited state, undergoes collision with other molecules. It rapidly loses (in  $< 10^{-12}$  s) its excess vibrational energy to other molecules and falls to the lowest vibrational level of the excited state. The energy lost is dissipated as heat to the surroundings.

## Internal Conversion

The molecules excited to a higher state (say  $S_2$ ) when reach the vibrational ground state in the electronic level, these can pass to a higher vibrational level of a lower excited state ( $S_1$ ) having the same energy. The molecule can continue to lose energy in this state in a nonradiative way (vibrational relaxation) until it reaches the lowest vibrational level in this excited state.

## Intersystem Crossing

Some times, the molecule in the vibrational states of a singlet excited state may cross over to a vibrational level of a triplet state if the two have same energy this process is called intersystem crossing. This spin-exchange mechanism may also lead, though very rarely, to the crossing over a triplet state to a singlet state.

## Radiative Deactivation

Two deactivation processes are radiative in nature

- Fluorescence
- Phosphorescence

Radiative deactivation or relaxation is also called **luminescence**.

As the excitation of the molecule is due to the absorption of a photon (light), such a luminescence is called **photoluminescence**.

## Radiative Deactivation

### Fluorescence

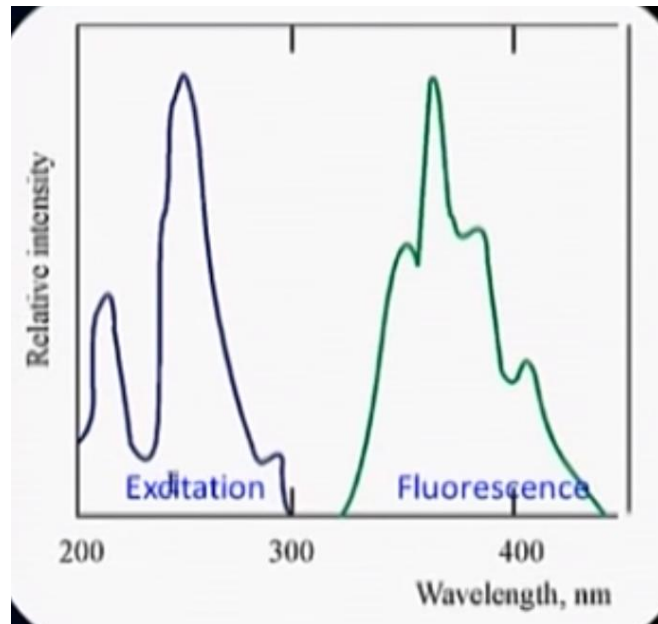
When the molecule in the excited state ( $S_1$ ) relaxes down to the lowest vibrational level it may emit a photon and come down to the electronic ground state ( $S_0$ ). This process is called fluorescence. The fluorescence emissions occur in about  $10^{-9}$  s.

### **Fluorescence emissions is at wavelength higher than the excitation**

The fluorescence emission takes place only after the excited molecule has relaxed to the vibrational ground state of the  $S_1$  state. The molecule has lost part of its energy in the process. The energy of the emitted photon is lower than that of the excitation radiation.

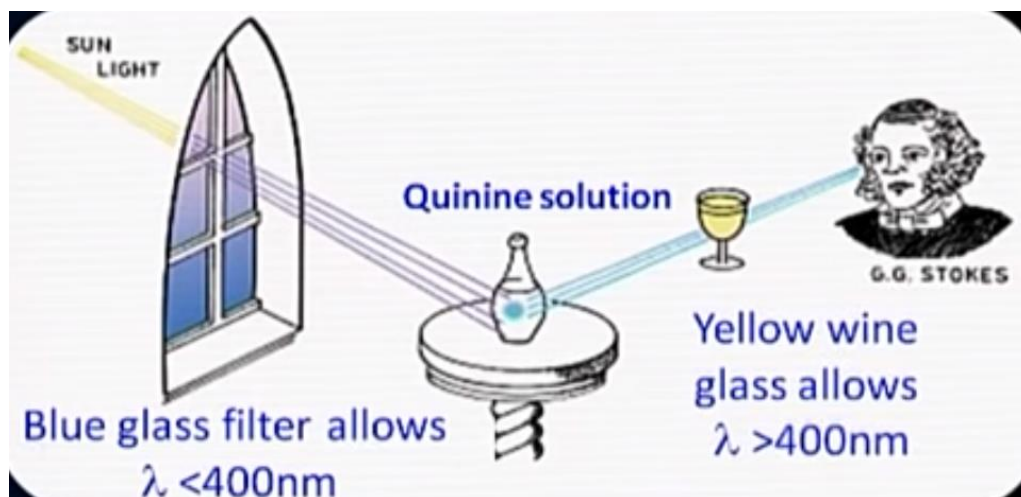
$$\lambda_{\text{emission}} > \lambda_{\text{excitation}}$$

The wavelength of fluorescence emission is greater than the excitation wavelength

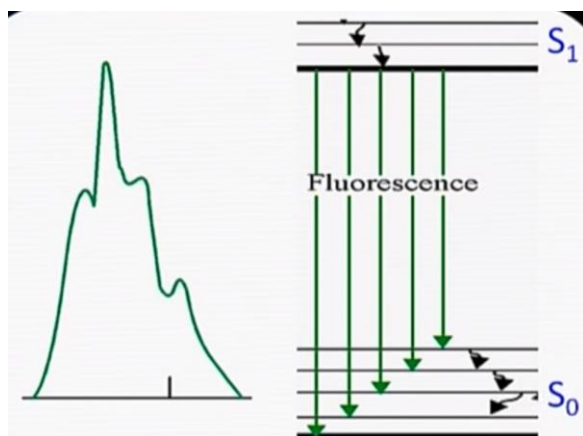


## Stokes Shift

The wavelength difference between the absorption and fluorescence maxima. Observed by Sir.G.G. Stokes in 1852.



The fluorescence spectrum is a band spectrum



## Radiative Deactivation

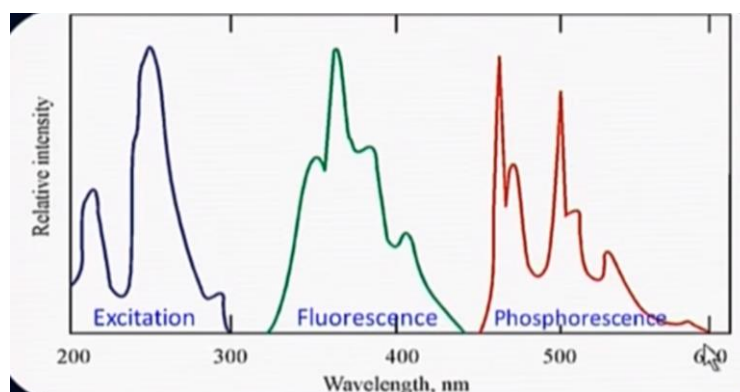
### Phosphorescence

An excited molecule may cross over to the triplet excited state by intersystem crossing. It relaxes to the vibrational ground state in the triplet excited state. This may deactivate to a vibrational mode of the electronic ground state,  $S_0$  accompanied by emission of a photon. This phenomenon is called **phosphorescence**.

### Phosphorescence

The transition from a triplet state to a singlet is theoretically forbidden, it does not take place readily. The transition from an excited triplet state to the ground state in case of phosphorescence requires at least  $10^{-4}$  seconds and may take as long as  $10^2$  seconds.

The energy of the triplet excited state is lower than that of the associated singlet state. The transition to the ground state would have emission of light of lower energy as compared to that of fluorescence. As a consequence, the phosphorescence occurs at even longer wavelengths than fluorescence.



The excitation, fluorescence and phosphorescence spectra of phenanthrene

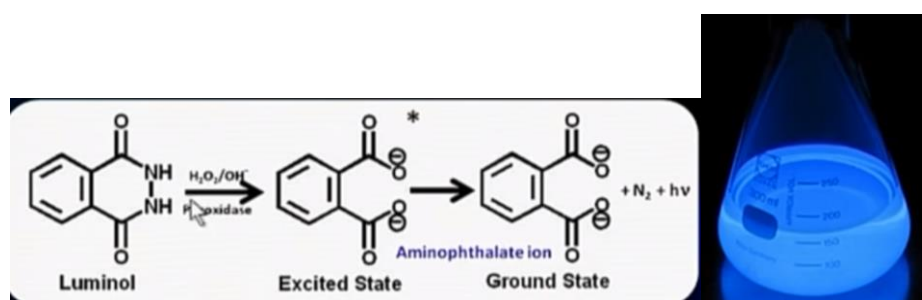
## Phosphorescence is rare at room temperature

The excited molecule spends relatively long time in the triplet state. They may lose their energy by means other than by emission of photon example: by collisions with the solvent molecules. Phosphorescence is rare in solution at room temperature; however, it can be observed by decreasing the temperature of the sample.

## Chemiluminescence and bioluminescence are closely related phenomenon

Chemiluminescence refers to the emission of radiation during a chemical reaction.

Example: oxidation of luminol in an alkaline solution



**Bioluminescence** refers to the phenomenon of luminescence occurring in living systems or the compounds extracted from the living systems.

**Examples:** light emitted by firefly, flashing fish, glinting glows worms, etc.



The light emission by firefly is due to enzymatic oxidation of luciferin by the enzyme luciferase.

## Determination of gaseous pollutants NO-NO<sub>2</sub>

Uses phenomenon of chemiluminescence. To determine the amount of NO, the gas is passed through the reactor in which it reacts with ozone to give NO<sub>2</sub>\*



The activated NO<sub>2</sub>\* gives Chemiluminescence in the visible to infrared range ( 600-2800nm).



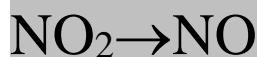
The number of photons emitted is proportional to the amount of NO present measured with the help of photomultiplier tube (PMT).

Concentrations as small as 1 ppb of the gas can be measured by this method.

### **Determination of NO<sub>2</sub>**

To determine the amount of NO<sub>2</sub> present in a sample, this sample having no nitric oxide (NO).

Hence, NO<sub>2</sub> is converted to nitric oxide (NO) by passing through a catalytic converter.



Then, it is passed through the reactor for activation of NO by ozone.



The activated NO<sub>2</sub>\* gives Chemiluminescence in the visible to infrared range ( 600-2800nm).



The number of photons emitted is proportional to the concentration of NO which is measure of NO<sub>2</sub> present in the sample.

### **9.Quantum yield**

As per the law of photochemical equivalence, a molecule absorbs a single photon during excitation



If each molecule undergoes photochemical reaction the number of molecules reacting would be equal to the number of photons absorbed.

However, the excited molecule, either forms a photochemical product or decays to ground state by radiative or non radiative processes. The number of molecules reacting may not be equal to the number of photons absorbed.

## Quantum Yield

It is defined as

$$\phi = \frac{\text{Number of molecules undergoing chemical reaction in a given time}}{\text{Number of photons absorbed in the same time}}$$

The number of molecules undergoing chemical reaction per quantum of absorbed energy.

## Quantum yield

1 Einstein = 1 mole of photons

$$\phi = \frac{\text{Number of molecules undergoing chemical reaction in a given time}}{\text{Number of photons absorbed in the same time}}$$

## High (or) Low Quantum Yield:

The quantum efficiency varies from zero to  $10^6$ . If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield  $\phi = 1$ .

**High Quantum Yield:** When two or more molecules are decomposed per photon, the quantum yield  $\phi > 1$  and the reaction has a high quantum yield.

**Low Quantum Yield:** When the number of molecules decomposed is less than one per photon, the quantum yield  $\phi < 1$  and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfil the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.
2. The reactivity of the molecules should be temperature independent.
3. The molecules in the activated state should be largely unstable and decompose to form the products.

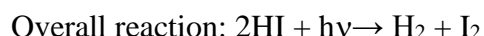
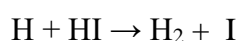


### Causes (or) Reasons for high quantum yield:

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
2. Formation of intermediate products will act as a catalyst.
3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

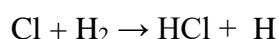
Examples:

**1. Decomposition of HI:** In the primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

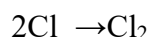


The overall reaction shows that the two HI are decomposed for one photon ( $h\nu$ ). Thus, the quantum yield ( $\phi$ ) = 2

**2. Formation of HCl:** In the primary step, one  $\text{Cl}_2$  molecule absorbs a photon and dissociated into two Cl atoms. This is followed by the secondary reaction as shown below:



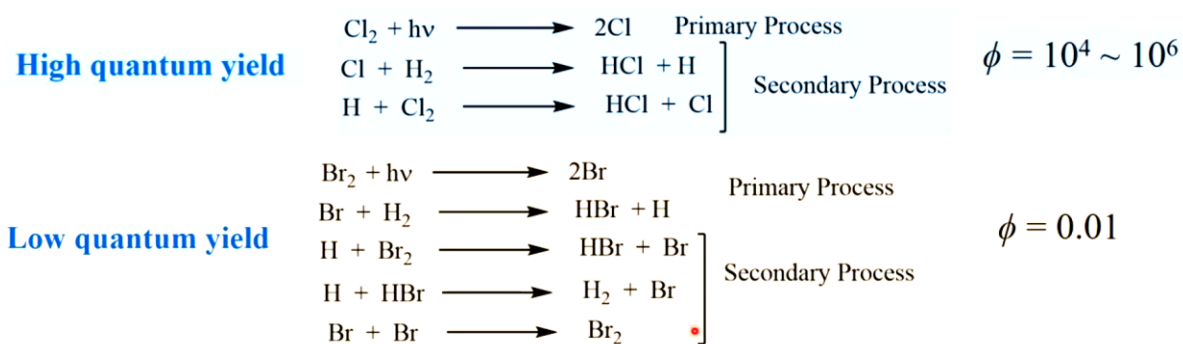
The Cl atom consumed in step 2 is regenerated in step 3, this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.



Thus the quantum yield varies from  $10^4$  to  $10^6$ .

***Causes (or) Reasons for low quantum yield:***

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to enable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.



$\phi > 1$ , initiate chain reaction, free radical reaction

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

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

**Measuring Quantum Yield**

To determine quantum yield we need

To measure the concentration of the product and amount of radiation absorbed

The amount of radiation absorbed can be determined by

The amount of radiation absorbed can be determined by:

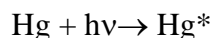
- Photodiode
- Thermocouple
- Chemical actinometer

## **9. Photosensitized reactions**

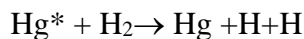
- A photosensitizer is a molecule that produces a chemical change in another molecule in a photochemical process.
- Photosensitizers are commonly used in polymer chemistry in reactions such as photopolymerization, photocrosslinking, and photodegradation.
- Photosensitizers are also used to generate triplet excited states in organic molecules with uses in photocatalysis, photon up conversion and photodynamic therapy.
- Photosensitizers generally act by absorbing ultraviolet or visible region of electromagnetic radiation and transferring it to adjacent molecules.
- Chlorophyll acts as a photosensitizer during the photosynthesis of carbohydrates in plants:  
$$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$
- Photosensitized reactions make positive use of quenching.
- A molecule that does not absorb radiation can be made to undergo photochemical reaction by using a molecule (sensitizer). The sensitizer absorbs that radiation and transfer its energy to the reactant during a collision.

### **Example:**

Photosensitized reaction between  $\text{H}_2$  and  $\text{O}_2$  in presence of mercury vapours. A mixture of hydrogen, oxygen, and mercury vapor is exposed to ultraviolet light. The mercury absorbs 253.7 nm ( $471.5 \text{ kJ mol}^{-1}$ ) to form an excited mercury atom,  $\text{Hg}^*$



The excited mercury atom undergoes collisional quenching with  $\text{H}_2$  molecule and dissociates it



Mercury is called sensitizer

It is important to note that  $\text{H}_2$  does not absorb at 253.7 nm

**Dissociation energies:**

H<sub>2</sub>: 432.0 kJ mol<sup>-1</sup>

O<sub>2</sub>: 490.2 kJ mol<sup>-1</sup>

Only hydrogen dissociates

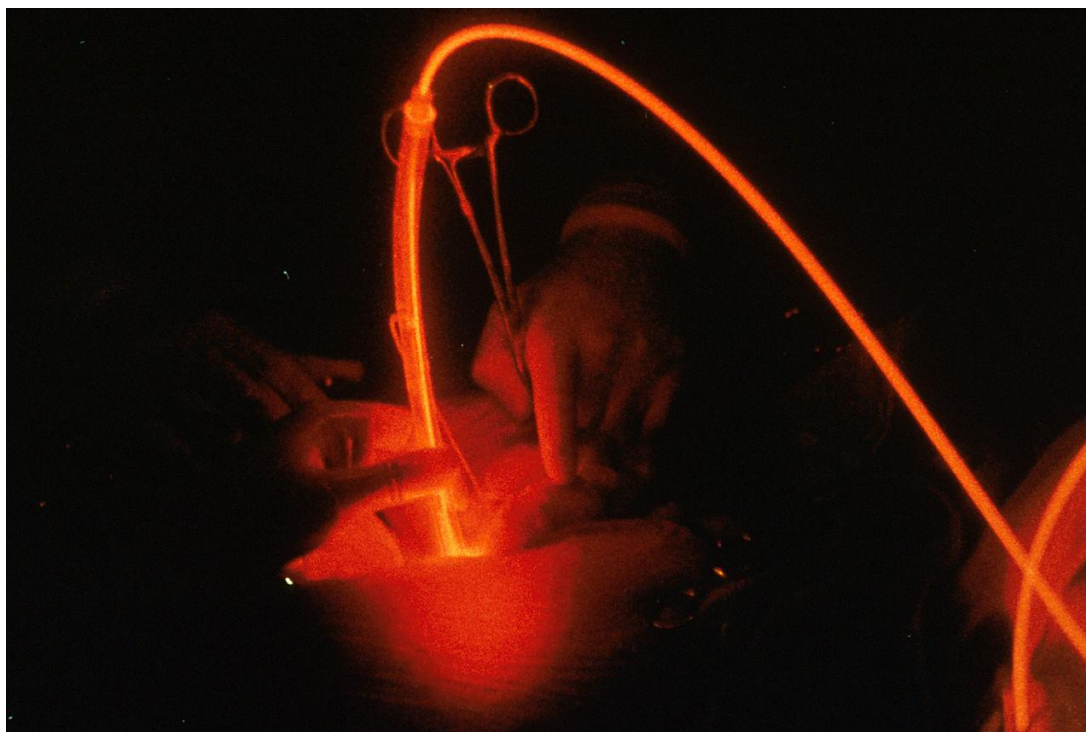
The atomic hydrogen initiates reaction with O<sub>2</sub> to form H<sub>2</sub>O

**10.Applications:**

Medical: Photodynamic therapy and Photosensitizers

Photosensitizers are a part of photodynamic therapy (PDT) which is used to treat some cancers. They help to produce singlet oxygen to damage tumours. They can be divided into porphyrins, chlorophylls and dyes.

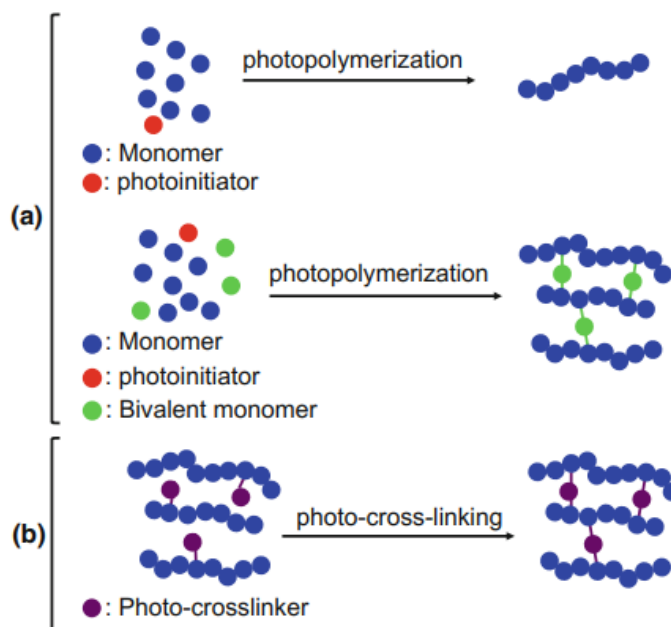
In February 2019, medical scientists announced that iridium attached to albumin, creating a photosensitized molecule, can penetrate cancer cells and, after being irradiated with light (a process called photodynamic therapy), destroy the cancer cells.



A photosensitizer being used in photodynamic therapy.

## Photochemical Processes for Polymeric Materials

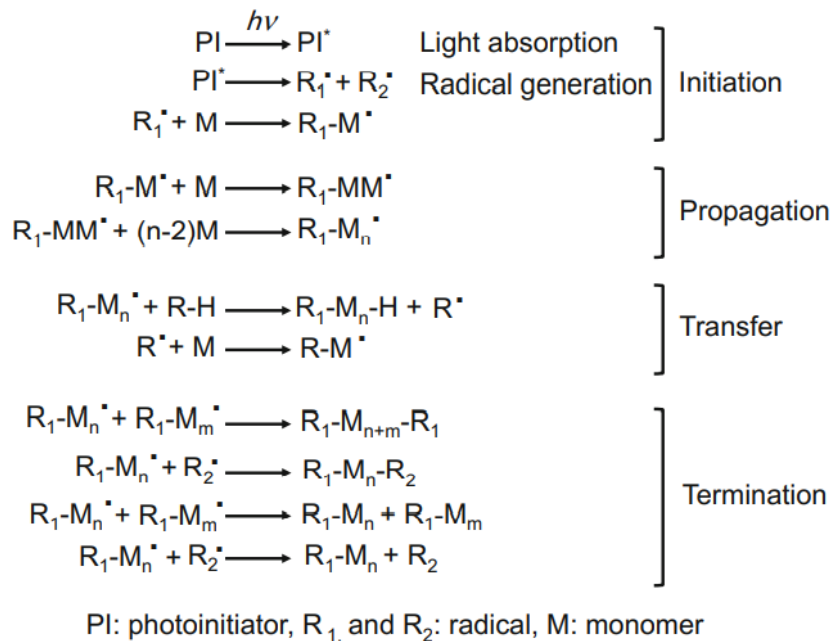
Polymeric (organic) materials are being widely utilized and continuously developed for a variety of biological and medical applications. With advances in organic synthetic chemistry, new functional initiators, monomers, and macromonomers have been developed for use of photochemical processes. The primary advantage is the temporal and spatial control that the process affords, which leads to control over polymerization exotherms at time of gelation and can be used for fabrication of complex structured (via systems of focused lasers or masks). There are two types of photochemical processes of polymeric (organic) materials (Figure). One is photopolymerization and another is photo-crosslinking. When pigmented or colored materials are used, a spectral window must be found to excite photoinitiator. The direct excitation of photoinitiator is inhibited by overlapped absorption spectra. In this case, a photosensitizer should be added. The role of photosensitizer is to absorb the light and to transfer the excess of energy to the photoinitiator through the energy transfer process.



**Photo-chemical process for polymeric materials. Photopolymerization (a) and photo-cross-linkable polymerization (b).**

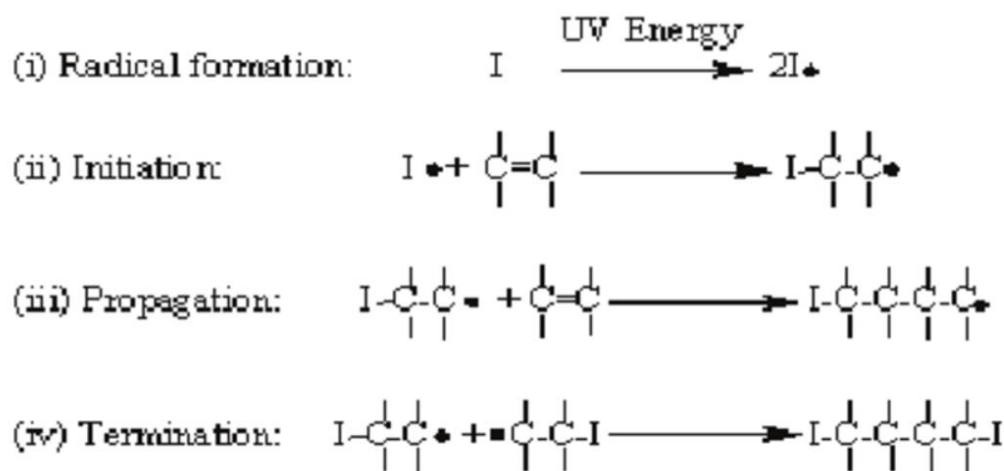
## Photopolymerization

**Polymerization Mechanism:** The reaction mechanism involves initiation, propagation, and termination as shown in Fig. (A). Photo-initiated mechanisms can be used to create radicals from initiator molecules. The rate of initiation is dependent on initiator efficiency, the concentration, and light intensity. During polymerization, the radicals propagate through unreacted double bonds to form long kinetic chains. Chain transfer or radical termination stops the growth.



**Fig.A General photopolymerizations steps**

**Example:** Free Radical Polymerization is when a initiator break down and attacks the pi-bond of a monomer. This initiates a chain reaction where monomers link up (propagation) until a free radical bonds on the other end (Termination). For 3D printing, the initiators are usually photoinitiators, which break down to free radicals in response to certain wavelengths of light.



## 11.Commerical applications of photochemistry

The following objects have proved to be of economic interest:

- (1) Use of light for synthesis,
- (2) Synthesis of photosensitive compounds,
- (3) Development of u.v.-stabilizers,
- (4) Synthesis of compounds with specific spectral properties,
- (5) Contributions to ecology.

**Use of light for synthesis:** The main aim of preparative photochemistry is to reduce manufacturing costs for chemical products by introducing photochemical steps in the syntheses.

**Synthesis of photosensitive compounds:** Light-sensitive compounds have great technical significance in photography, reprography, and printing. Important applications have been also found in u.v.-curable paints, primers, and printing inks.

**Development of u.v.-stabilizers:** Photostabilizers are primarily used in plastics and man-made fibres. Another interesting field of application is sunscreen cosmetics: In the synthesis of compounds

with special spectral properties, attention is focused on lightfast dyes, optical brighteners, fluorescent dyes, and chemiluminescent systems.

**Contributions to ecology:** The main photochemical contributions to ecology are chemical storage of solar energy, investigations on the photodegradation of biologically active ingredients, the investigation of photochemical smog formation, and the development of photodegradable plastics.

Recently, there have been increasing interests in using photochemical reactions in the fields of biomaterials and tissue engineering. This work revisits the components and mechanisms of photochemistry and reviews biomedical applications of photochemistry in various disciplines, including oncology, molecular biology, and biosurgery, with particular emphasis on tissue engineering.

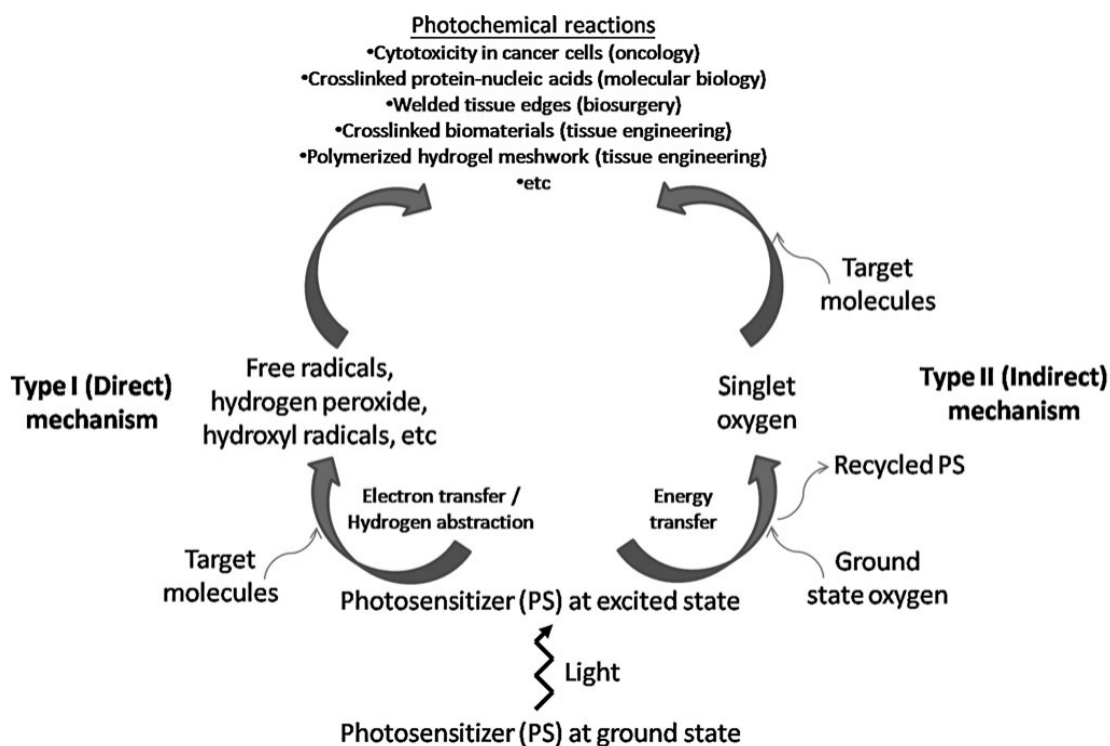


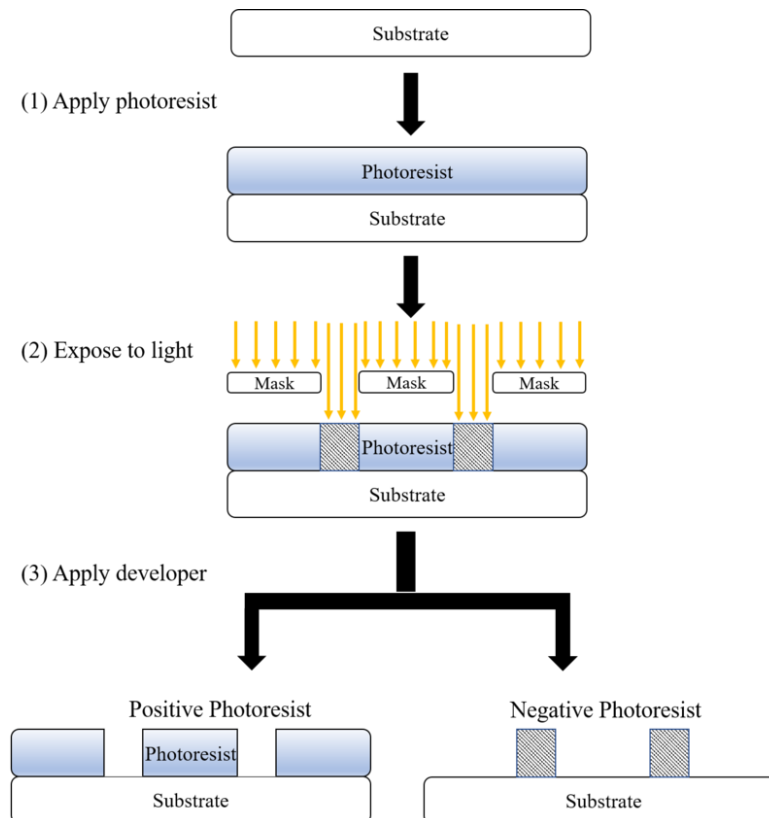
FIG. 3. Type I and type II mechanisms of photochemical reactions.

**Photoresist technology, used in the production of microelectronic components.**

- A **photoresist** (also known simply as a **resist**) is a light-sensitive material used in several processes, such as photolithography and photoengraving, to form a patterned coating on a surface. This process is crucial in the electronic industry.



- The process begins by coating a substrate with a light-sensitive organic material. A patterned mask is then applied to the surface to block light, so that only unmasked regions of the material will be exposed to light.
- A solvent, called a developer, is then applied to the surface. In the case of a positive photoresist, the photo-sensitive material is degraded by light and the developer will dissolve away the regions that were exposed to light, leaving behind a coating where the mask was placed.
- In the case of a negative photoresist, the photosensitive material is strengthened (either polymerized or cross-linked) by light, and the developer will dissolve away only the regions that were not exposed to light, leaving behind a coating in areas where the mask was not placed.



### Model Questions

1. Write the electronic configuration of Carbon and Mo Diagram of Carbon molecule, Nitrogen molecule, Beryllium molecule, calculate Bond Order. (5M)
2. Illustrate the salient features of MOT. 5M
3. Write the Molecular diagram of CO hetero diatomic molecule. 5M
4. Write the electronic configuration of Oxygen and Mo Diagram of Oxygen molecule, calculate Bond Order and comment on Magnetic Properties. (5M)
5. Discuss the Laws of Photochemistry 4M
6. Write the differences between Photochemical and Thermal reactions. 5M
7. Write a Note on Properties of Light -4M
8. Discuss EM spectrum? write a note on Different regions of electromagnetic Radiations. 6M
9. Explain Interaction of Electromagnetic (each region) radiation with Matter -5M
10. List out the Applications of Electromagnetic Radiations 4M
11. State and Explain Beer's Law, Lambert's Law and Beer Lambert's Law 6M
12. Define Quantum Yield? Explain High quantum yield and Low quantum Yield with Example 8M
13. What is work function and explain with example? 3M
14. Write the Applications of Photo chemical reactions? 5M
15. Write a Note on Jablonski Diagram and explain the Terms of photophysical process. 8M
16. Define Fluorescence and Phosphorescence. 4M
17. What is Singlet and Triplet excited states. 2M
18. What is meant by Stokes shift 2M
19. Define Quantum yield? Explain High yield and low yield reactions? 6M
20. Explain Photosensitization and Photopolymerization? 8M
21. Write the Commercial applications of photochemical reactions? 4M