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Established as per the Section 2(f) of the UGC Act, 1956
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QS I·GAUGE INDIAN UNIVERSITY RATING GOLD

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MHRD'S INNOVATION CELL (GOVERNMENT OF INDIA)

INSTITUTION'S INNOVATION COUNCIL (Ministry of HRD Initiative)

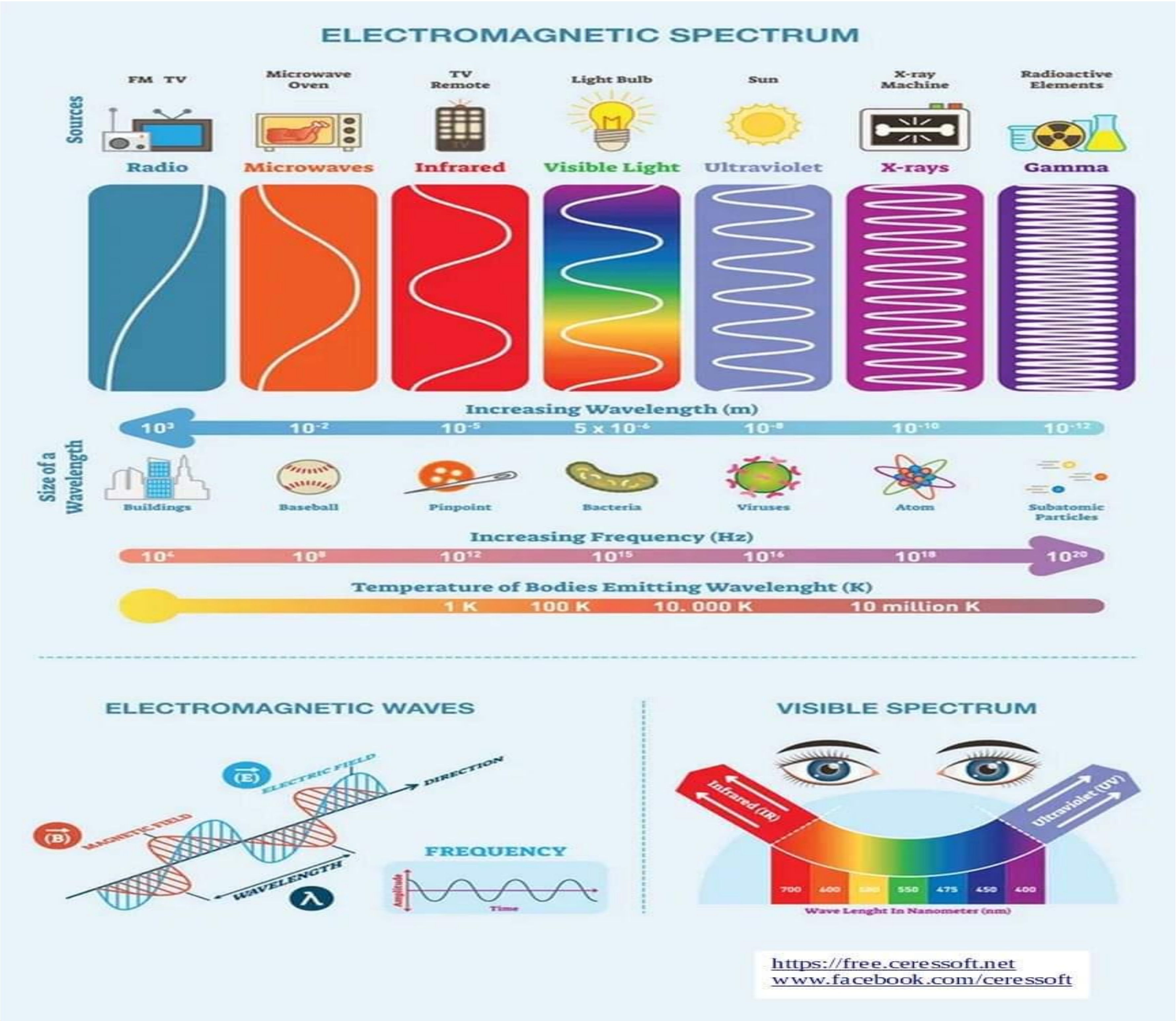
LIGHT AND MATTER IN ENGINEERING

1. Mention applications of EM waves in engineering

Answer:

- 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)

2. Explain EMS, and their application



- The electromagnetic spectrum is continuous
- As the wavelengths grow smaller in size, their frequency increases, along with their energy.
- Radiations interact with matter that is of a similar size.

Explain light and matter interaction

- Radiations interact with matter that is of a similar size.

- For wavelengths larger than UVC, there are four processes of interaction: transmission, reflection, scattering and absorption.
- Wavelengths from UVC onwards can directly interact with matter at an atomic level.
- Ionisation happens when electromagnetic radiation knocks an electron out of an atom.

Discuss 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.**	**Thermal activation leads to increase in the number of collisions between molecules of reactants or reactants and walls of container.** **The thermal energy gets distributed mainly amongst different translational, rotational, and vibrational excitations; very small fraction leads to electronic excitations followed by a reaction.**
5.	The thermal reactions are accompanied by decrease in free energy; i.e., these are spontaneous. i.e. ΔG for thermochemical reaction reaction is always -ve.	In case of photo-exictation even the reaction accompanied by increase in free energy (non-spontaneous) may also occur. i.e ΔG for photochemical spontaneous reaction +ve.

6.	**Photochemical activation is highly selective.**	**Thermochemical activation is not selective in nature.**
7.	$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} C_6H_{12}O_6 + 6O_2$$	Formation of CO_2, NH_3, thermal decomposition reaction etc.
8	In case of photochemical reactions, the rate of reaction is independent of temperature but depends on the intensity of radiation. 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.	The rate of thermal reactions depends on temperature.

Laws of photochemistry

Two laws

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

Explain Grotthus-Drapper 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.

Discuss 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

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

However, exception have been observed (intense lasers)

$$M + 2h\nu \longrightarrow M^{**}$$

- 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 does not mean that one molecule would react per photon absorbed

Explain Lambert’s Law , Beer’s Law and Beer’s and Lamberts Law and their limitation

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.

Explian Beer-Lambert Law and their limitation

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.

Mathematically,

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

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

Limitations of Beer-Lambert’s law

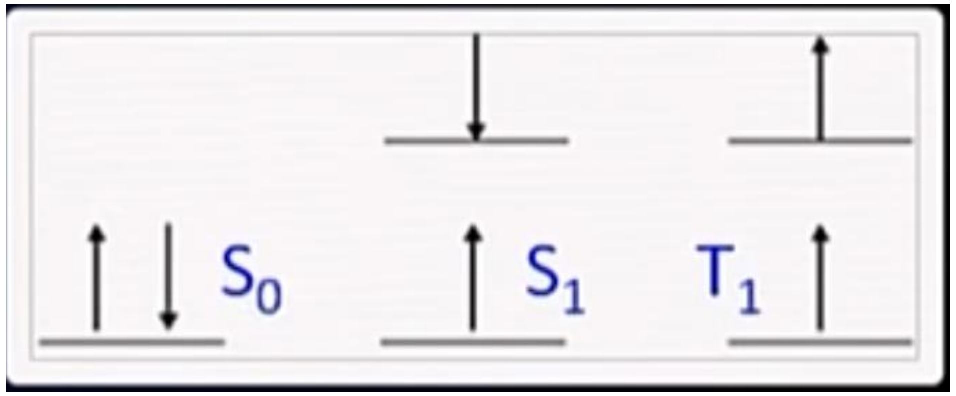
The law is not valid

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

State singlet and triplet state

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.

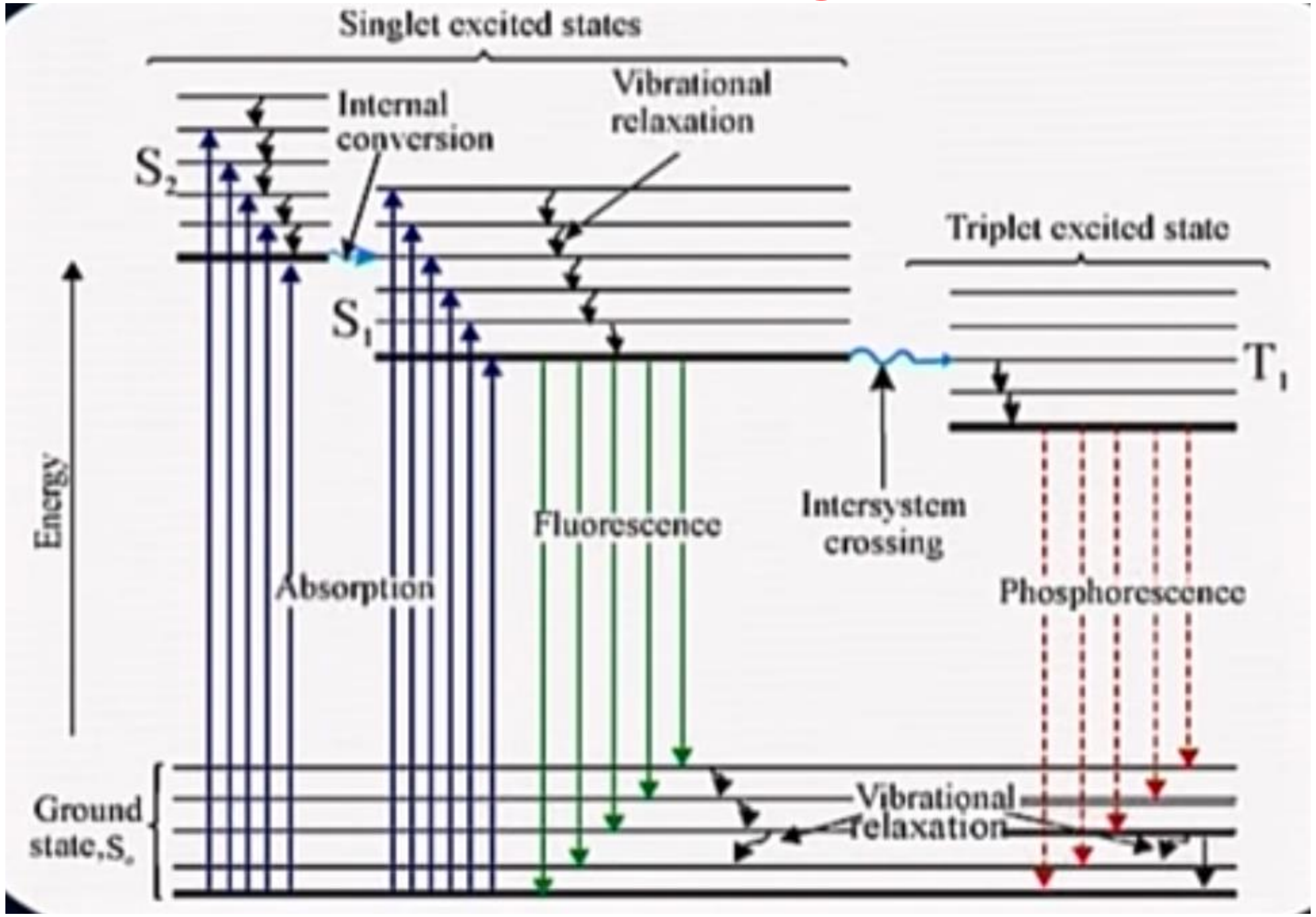
Explain characteristics of singlet and triplet states

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.

Discuss of Jablonski diagram



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

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Deactivation

Two types of processes:

Radiative processes: accompanied by radiation emission.

Non-radiative processes: not accompanied radiation emission.

Non-radiative processes

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 sate.

Intersystem Crossing

Sometimes, 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 sate to a singlet sate.

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

The wavelength of fluorescence emission is greater than the excitation wavelength

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_O accompanied by emission of a photon. This phenomenon is called **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.

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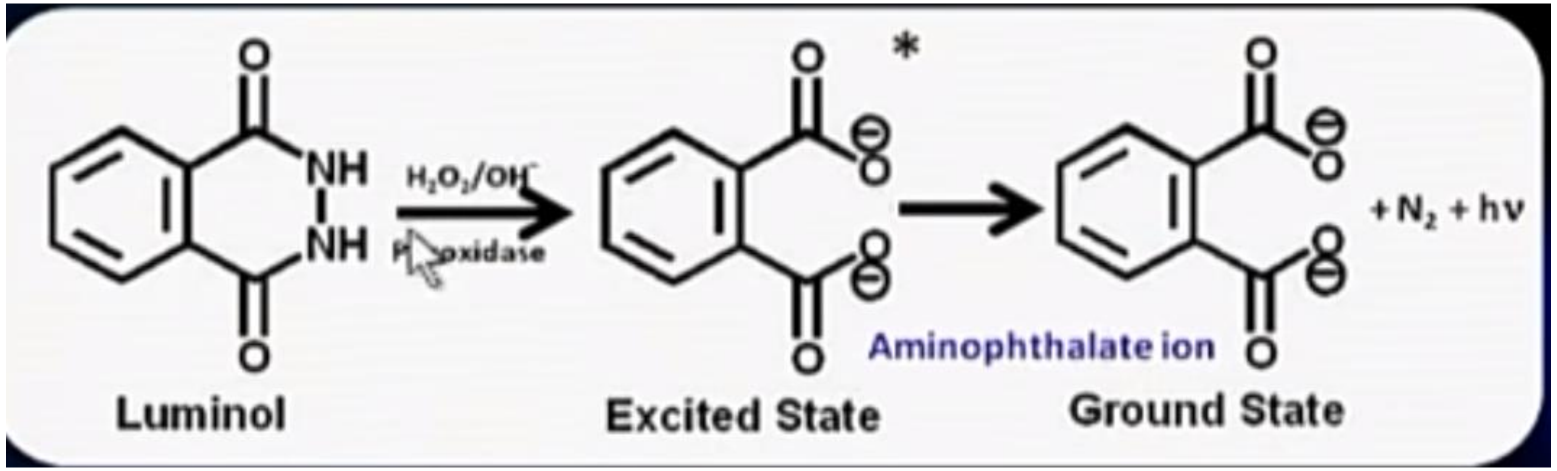
Sate Stokes Shift

The wavelength difference between the absorption and fluorescence maxima.

Explain 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

Leuciferin → oxyluciferrin*

Oxyluciferrin* → Oxyluciferrin + hν

Explain the determination of gaseous pollutants NO-NO_2

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_2*

$$NO + O_3 \rightleftharpoons NO_2^*$$

The activated NO_2* gives Chemiluminescence in the visible to infrared range (600-2800nm).

$$NO_2^* \rightarrow NO_2 + h\nu$$

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.

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Discuss determination of NO_2

To determine the amount of NO_2 present in a sample, this sample has no nitric oxide (NO).
Hence, NO_2 is converted to nitric oxide (NO) by passing through a catalytic converter.
$NO_2 \rightarrow NO$

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

$$NO + O_3 \rightleftharpoons NO_2^*$$

The activated NO_2* gives Chemiluminescence in the visible to infrared range (600-2800nm).

$$NO_2^* \rightarrow NO_2 + h\nu$$

The number of photons emitted is proportional to the concentration of NO which is a measure of NO_2 present in the sample.

Explain Quantum yield

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

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

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.

Explain reasons for low and high quantum yield reactions with examples

High quantum yield

$$Cl_2 + h\nu \longrightarrow 2Cl \quad \text{Primary Process}$$

$$\left.\begin{array}{l} Cl + H_2 \longrightarrow HCl + H \\ H + Cl_2 \longrightarrow HCl + Cl \end{array}\right] \text{Secondary Process}$$

$$\phi = 10^4 \sim 10^6$$

Low quantum yield

$$\left.\begin{array}{l} Br_2 + h\nu \longrightarrow 2Br \\ Br + H_2 \longrightarrow HBr + H \end{array}\right. \quad \text{Primary Process}$$

$$\left.\begin{array}{l} H + Br_2 \longrightarrow HBr + Br \\ H + HBr \longrightarrow H_2 + Br \\ Br + Br \longrightarrow Br_2 \end{array}\right] \text{Secondary Process}$$

$$\phi = 0.01$$

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

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

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

$$6CO_2 + 6H_2O + nh\gamma \rightarrow C_6H_{12}O_6 + 6O_2 \qquad \Delta_r G_m = 2870 \text{ kJ mol}^{-1}$$

In Photosynthesis, one mole of glucose, 48 light quanta needed.

Discuss photosensitized reactions with examples and their applications

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 upconversion 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: $\mathbf{6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2}$

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 H_2 and 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 kJ mol^{-1}) to form an excited mercury atom, Hg*

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

The excited mercury atom undergoes collisional quenching with H_2 molecule and dissociates it

$$Hg^* + H_2 \rightarrow Hg + H + H$$

Mercury is called sensitizer

It is important to note that H_2 does not absorb at 253.7 nm

Dissociation energies:

H_2: 432.0 kJ mol^{-1}

O_2: 490.2 kJ mol^{-1}

Only hydrogen dissociates

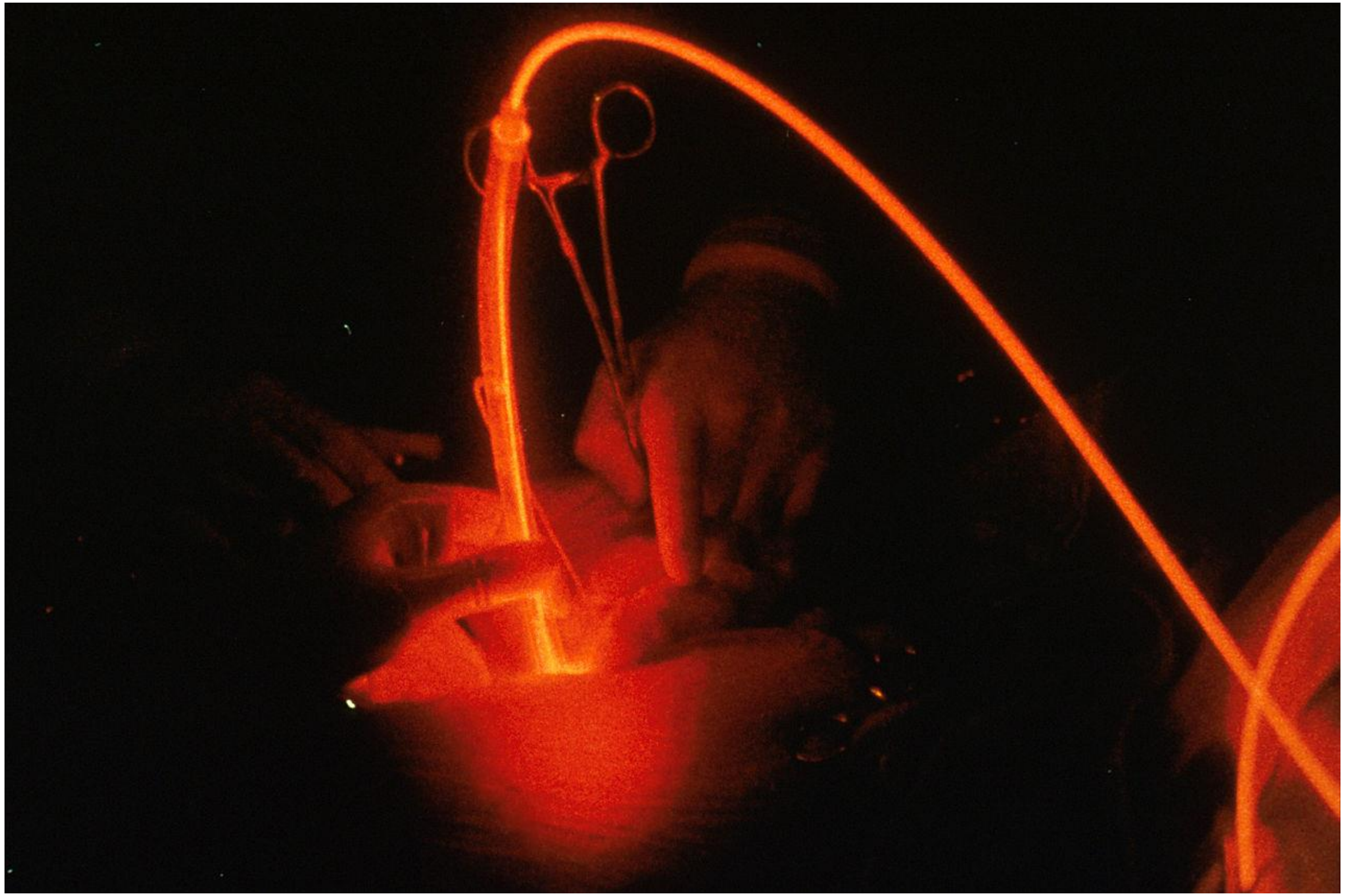
The atomic hydrogen initiates reaction with O_2 to form H_2O

Applications:

Medical: Photodynamic therapy § Photosensitizers

Photosensitisers 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.

Discuss photochemical processes for polymeric materials

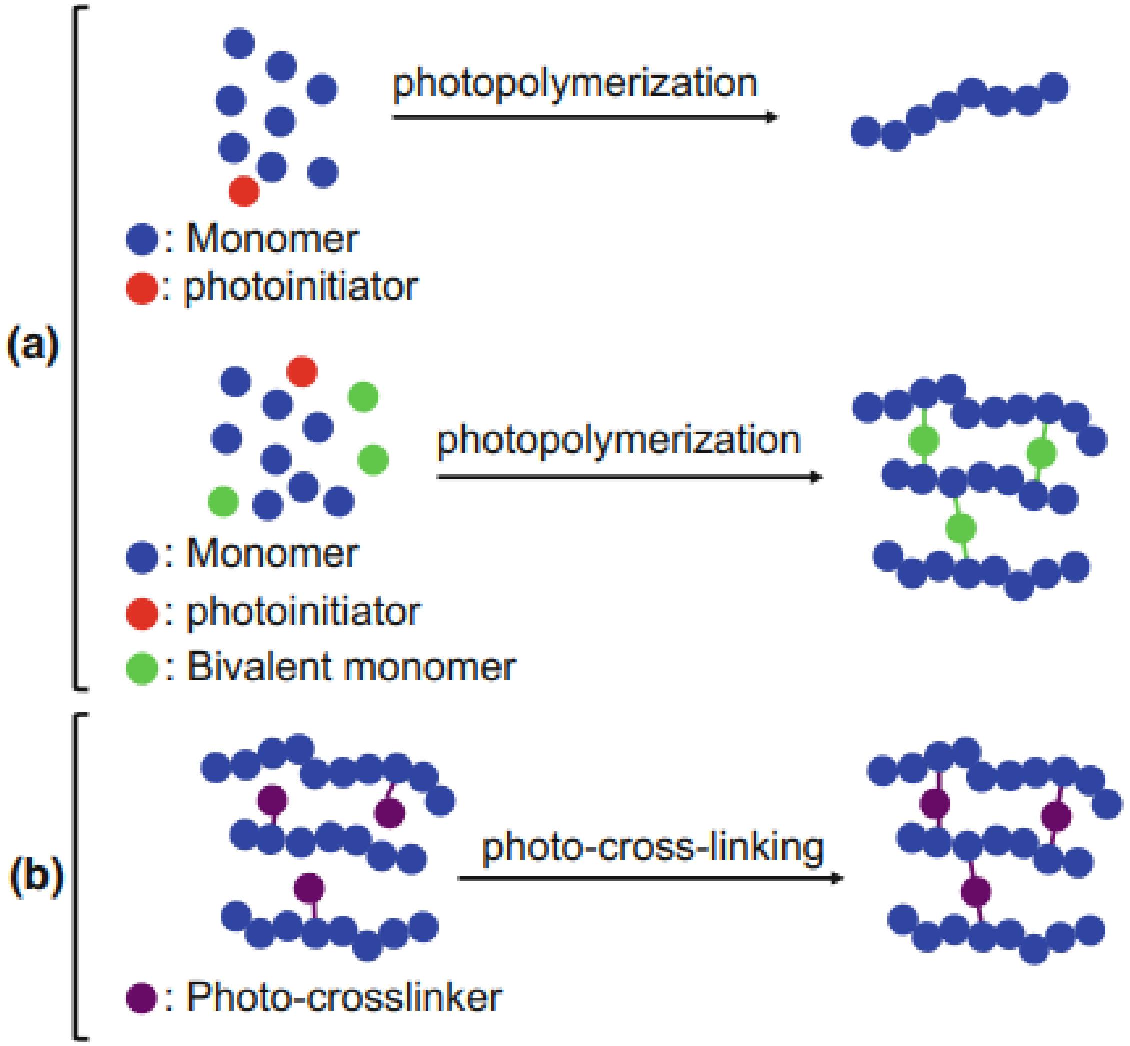
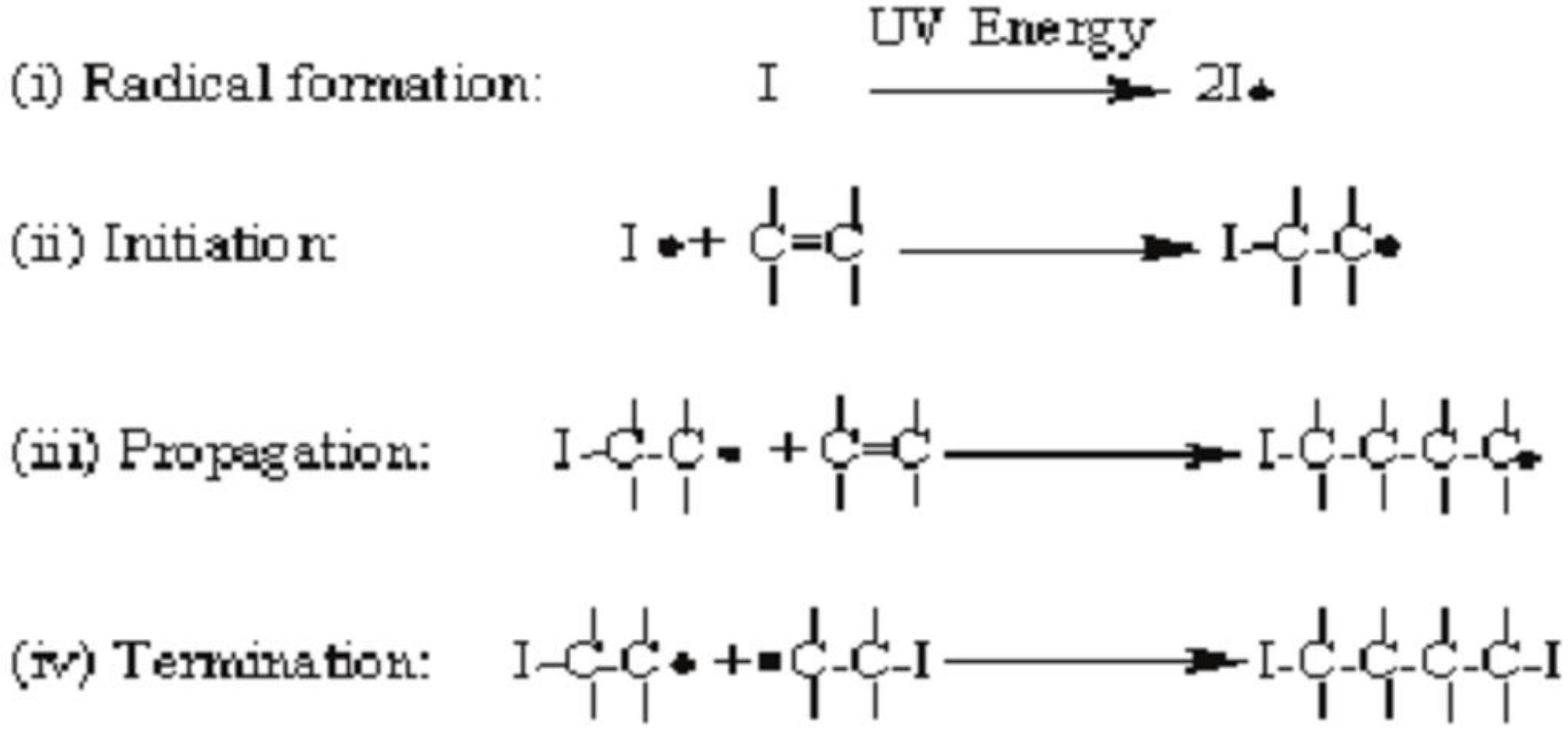


Fig. 2.1 Photo-chemical process for polymeric materials. Photopolymerization (**a**) and photo-cross-linkable polymerization (**b**)

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 photoinitators, which break down to free radicals in response to certain wavelengths of light.



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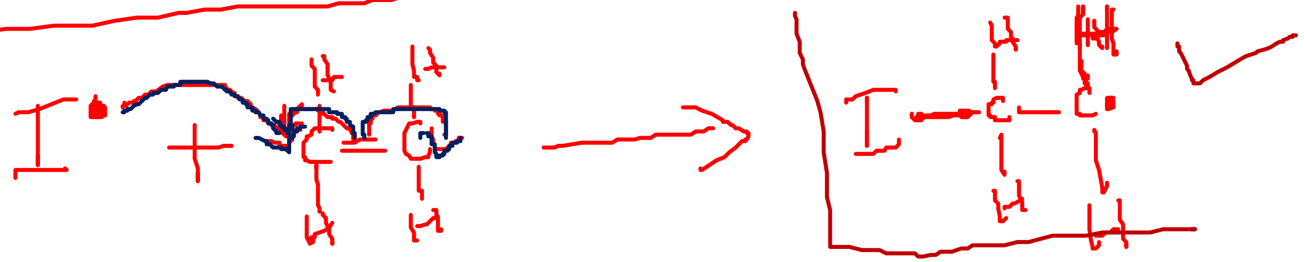
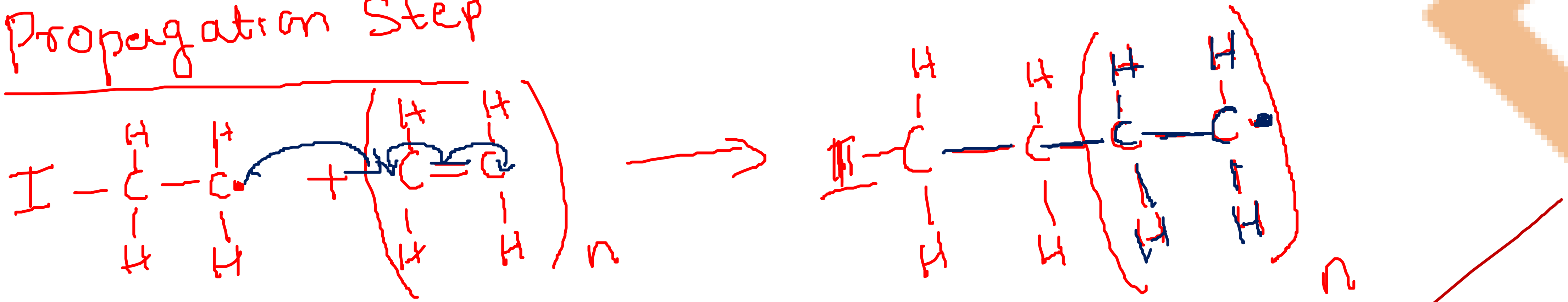
Radical formation

$I_2 \xrightarrow{h\nu} I - I \longrightarrow \boxed{2I^\bullet}$

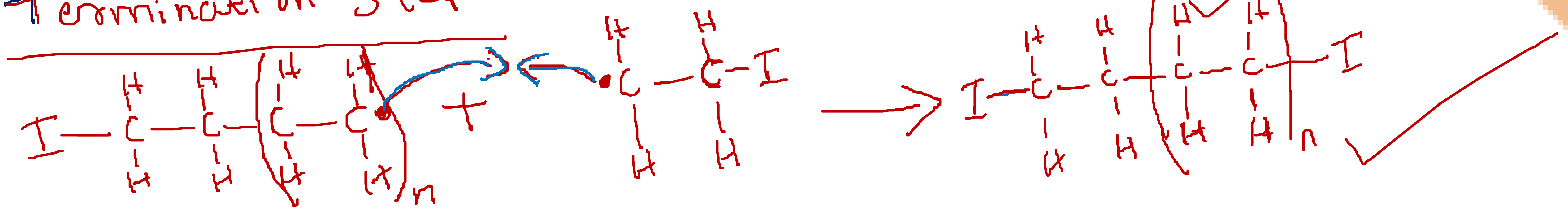
Intiation Step



Propagation Step



Termination Step



Polymerization Mechanism:

Initiation

$$PI \xrightarrow{h\nu} PI^{*} \quad \text{Light absorption}$$

$$PI^{*} \longrightarrow R_1^{\bullet} + R_2^{\bullet} \quad \text{Radical generation}$$

$$R_1^{\bullet} + M \longrightarrow R_1\text{-}M^{\bullet}$$

Propagation

$$R_1\text{-}M^{\bullet} + M \longrightarrow R_1\text{-}MM^{\bullet}$$

$$R_1\text{-}MM^{\bullet} + (n\text{-}2)M \longrightarrow R_1\text{-}M_n^{\bullet}$$

Transfer

$$R_1\text{-}M_n^{\bullet} + R\text{-}H \longrightarrow R_1\text{-}M_n\text{-}H + R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow R\text{-}M^{\bullet}$$

Termination

$$R_1\text{-}M_n^{\bullet} + R_1\text{-}M_m^{\bullet} \longrightarrow R_1\text{-}M_{n+m}\text{-}R_1$$

$$R_1\text{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}M_n\text{-}R_2$$

$$R_1\text{-}M_n^{\bullet} + R_1\text{-}M_m^{\bullet} \longrightarrow R_1\text{-}M_n + R_1\text{-}M_m$$

$$R_1\text{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}M_n + R_2$$

PI: photoinitiator, R_1 and R_2: radical, M: monomer

Mention commericial 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,

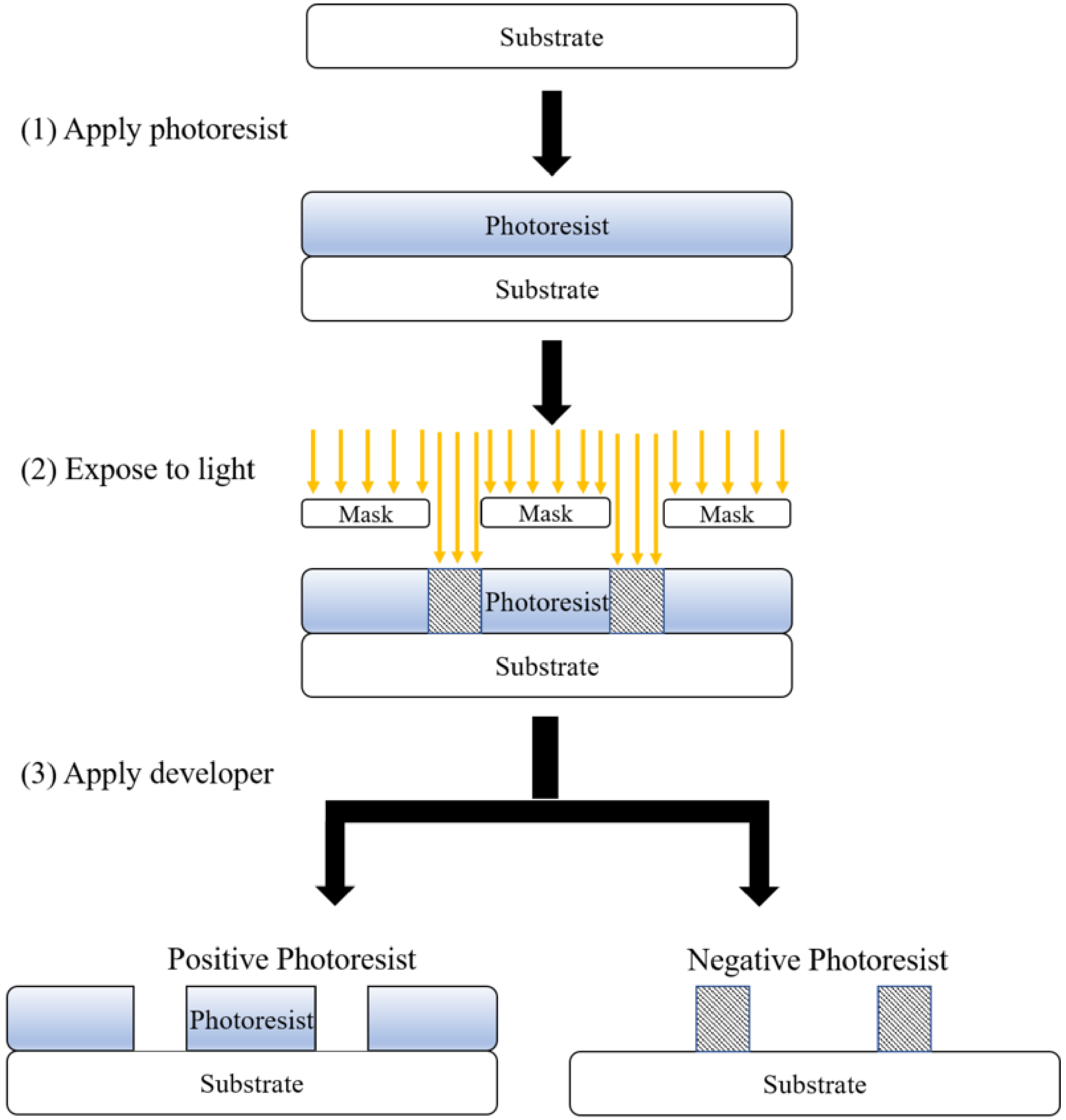
(4)Synthesis of compounds with specific spectral properties,

(5)Contributions to ecology.

Discuss 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.

Photoresist technology, used in the production of microelectronic components.



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THANK YOU