# PHOTOCHEMISTRY

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# Thermal and photochemical reaction

- Thermal reactions: Thermochemistry is the study of the heat and energy associated with chemical reactions. If a reaction releases energy and heat , it is called Exothermic reaction and opposite is the Endothermic reaction , when energy and heat is absorved
- **Photochemical reactions**: Some reactions do not take place in the darkbut take place only in the **presence of light or some other radiation**. Such reaction are known as ‘photochemical reactions’

| Thermochemical reactions | Photochemical reactions |
| --- | --- |
| These reactions involve absorption or evolution of heat. | These reactions involve absorption of light, highly specific, energy absorb depends on type of electronic transition. |
| They can take place even in absence of light i.e. dark. | The presence of light is the primary requisite for the reaction to take place. |
| Temperature has significant effect on the rate of a thermochemical reaction. | Temperature has very little effect on the rate of a photochemical reaction. Instead, the **intensity of light** has a marked effect on the rate of a photochemical reaction. |
| The free energy change $\Delta G$ of a thermochemical reaction is **always negative**. | The free energy change $\Delta G$ of a photochemical reaction **may not be negative**. |
| They are accelerated by the **presence of a catalyst**. | Some of these are initiated by the presence of **a photosensitizer**. However a photosensitizer acts in a different way than a catalyst. |

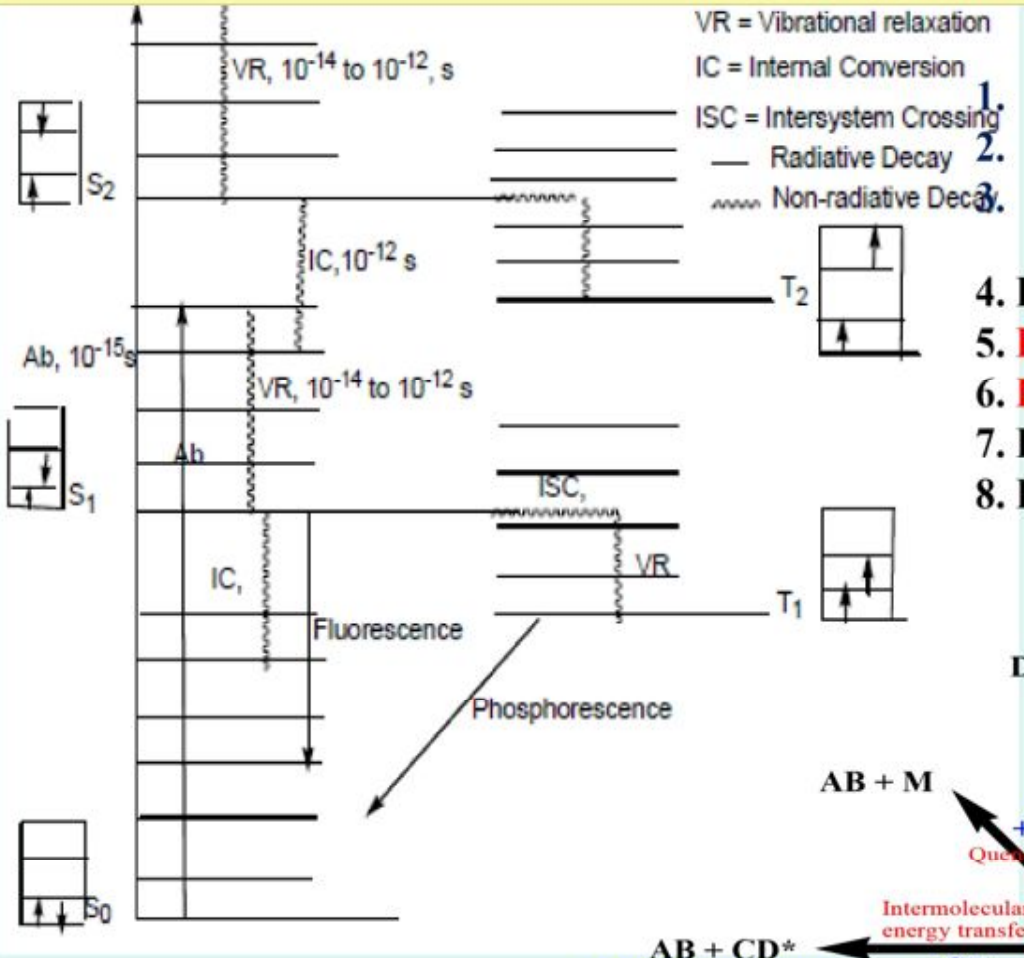
# Photosensitization

The excited molecule present in its $S_1$ or $T_1$ state can transfer its excess energy to another molecule which is then undergoes chemical reaction and first come to ground state is called **photosensitization**. The first molecule is called **photosensitizer**.

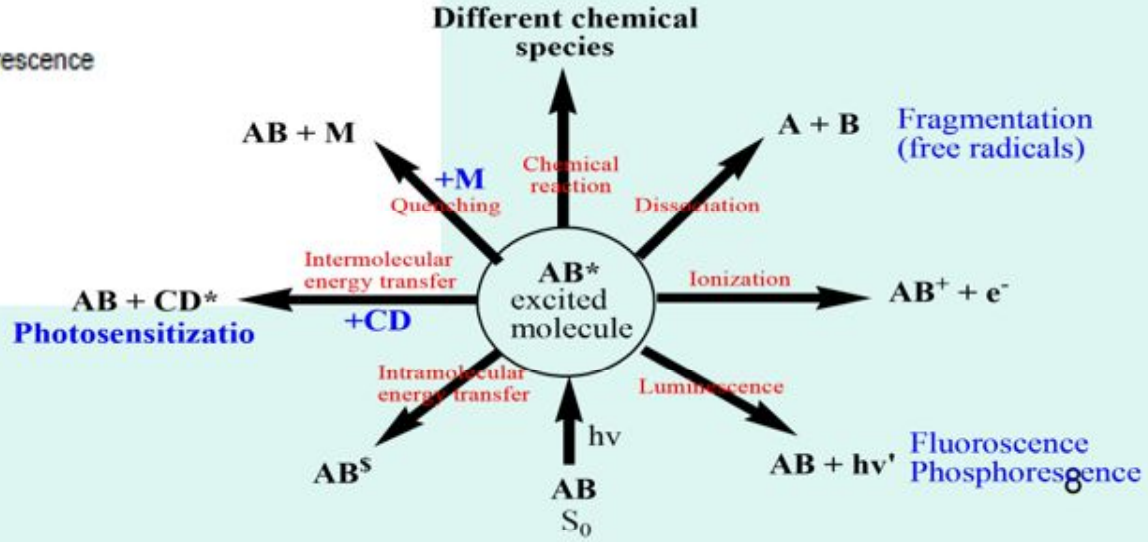
**Chemical reaction**

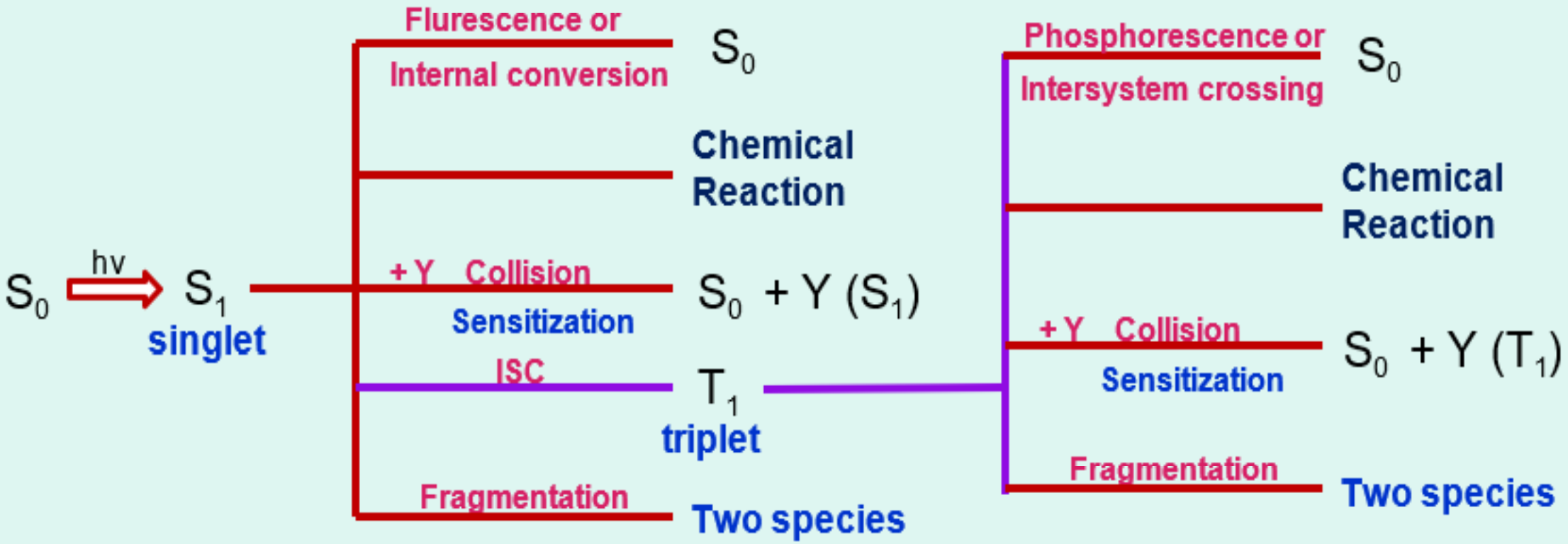
**Acceptor**

**Donor**




1. **Excitation or absorption**
2. **Vibrational relaxation**
3. **Internal conversion** (come to Lower energy state without emission of light)
4. **Inter system crossing (ISC)**
5. **Fluorescence**
6. **Phosphorescence**
7. **Photosensitization**
8. **Photochemical reaction**






The **life time of excited singlets are very short ($10^{-6}$ to $10^{-9}$)** so that chemical reactions occurs via these species is very uncommon due to their high energy.

Therefore it is converted to its triplet state which is **more stable having life time ($> 10^{-4}$)** so that the **probability of the triplet state taking part in the reaction is much higher than for a singlet state.**