

UV- VISIBLE INTRODUCTION

Principle

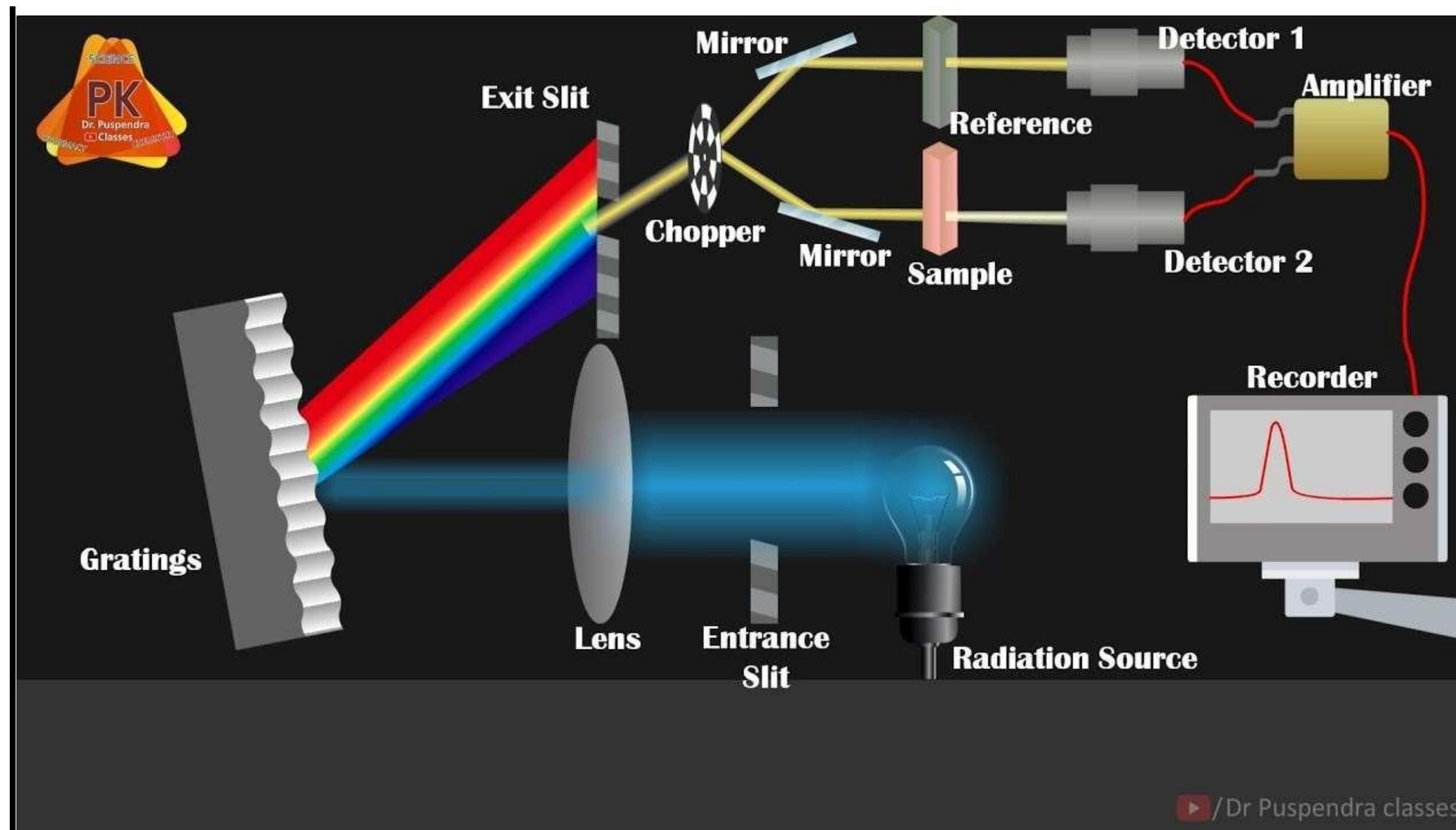
Ultraviolet (UV) & visible spectra arises from the transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state E₀) to higher electronic energy level (excited state E₁).

This transition occurs due to the absorption of UV (wavelength 100-400 nm) or visible (wave length 400-750 nm) region of the electronic spectrum by a molecule (or) ion.

The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons.

$$E_1 - E_0 = h\nu.$$

SCHEMATIC REPRESENTATION UV SPECTR



Types of electrons

| S. No | Electrons | Examples | Energy required to excite electrons | Present in |
|----------|---------------------|---|--|--|
| 1. | σ -electrons | Saturated long chain hydrocarbons. (Paraffins) $(\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3)$ | | |
| 2. | π -electrons | Unsaturated hydrocarbons like trienes and aromatic compounds. | UV (or) visible light | Double bond and triple bonds. (unsaturated bond) |

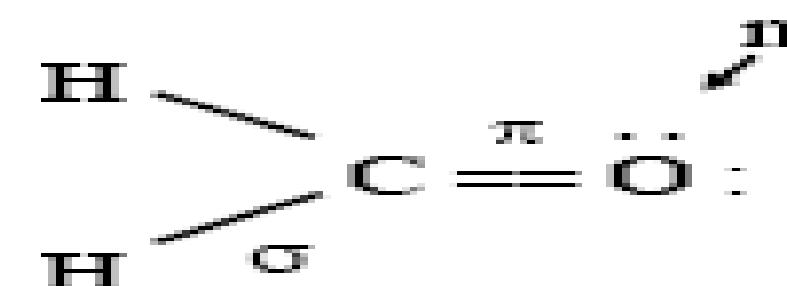
Types of electrons

| | | | | |
|----|-------------|--|--------------|-------------------------------------|
| 3. | n-electrons | Organic compounds containing N, O (or) halogens. | UV radiation | Unshared (or) non bonded electrons. |
|----|-------------|--|--------------|-------------------------------------|

Thus, the unsaturated hydrocarbons and compounds containing N, O, S may absorb visible (or) UV radiations.

Example

The three types of electrons are shown in the molecule (HCHO).



Electronic transitions

$$\pi \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* \ll \sigma \rightarrow \sigma^*$$

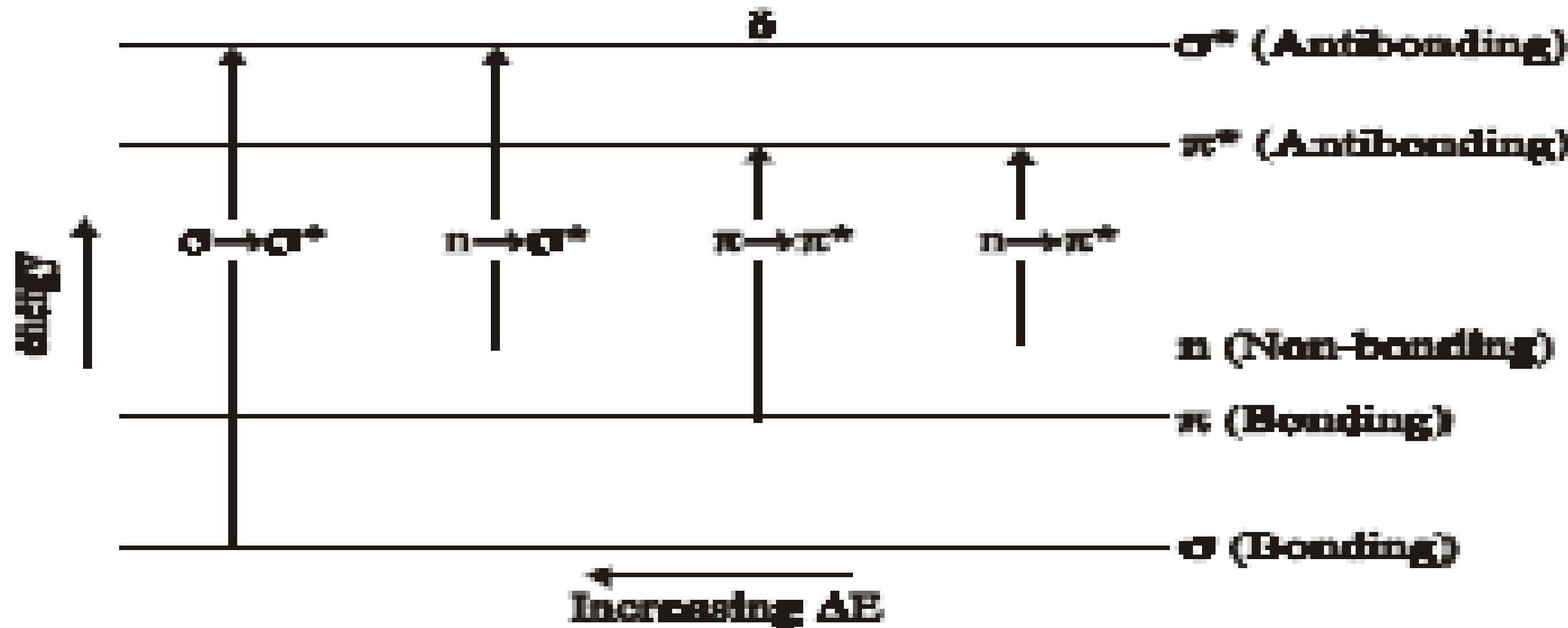


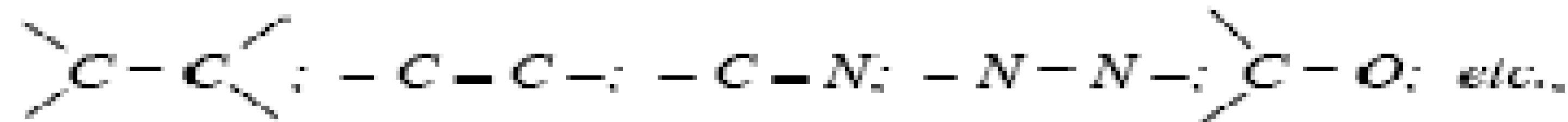
Fig. 5.8 Energy level diagram

8.7.5 Important terms used in UV-visible Spectroscopy

1. Chromophores (Colour producing groups)

The presence of one or more unsaturated linkages (π electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores.

Example



Chromophores undergo $\pi \rightarrow \pi^*$ transitions in the short wavelength regions of UV-radiations.

2. Auxochrome (Colour intensifying groups)

It refers to an atom or a group of atoms which does not give rise to absorption band on its own, but when conjugate to chromophore will cause a red shift.

Example

-OH, -NH₂, -Cl, -Br, -I, etc.,

3. Some important definitions related to change in wavelength and intensity

| | | |
|----|--|--|
| 1 | Bathochromic shift. (red shift) | Shift to higher wavelength (lower frequencies). |
| 2. | Hypsochromic shift. (blue shift) | Shift to lower wavelength (higher frequencies). |
| 3. | Hyperchromic effect. | An increase in intensity. |
| 4. | Hypo chromic effect. | A decrease in intensity. |

Illustration

In chloroethylene, $\text{CH}_2 = \text{CHCl}$,