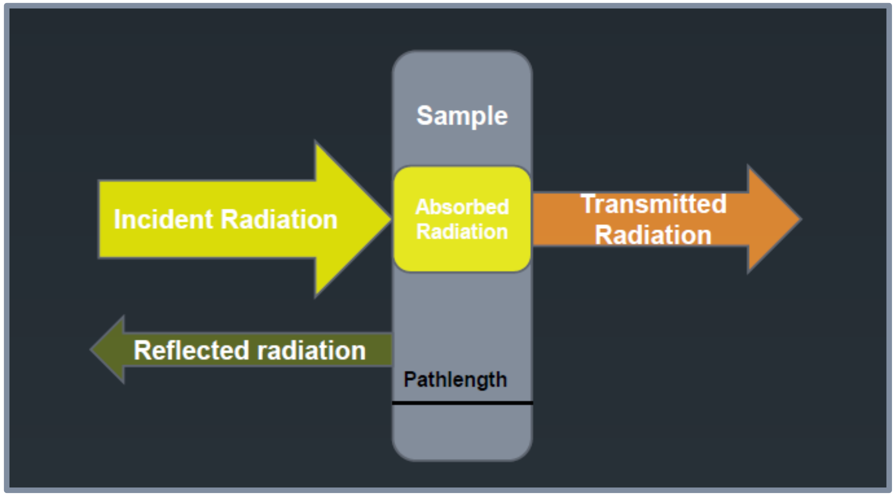
APPLICATIONS OF SPECTROSCOPY
(UV-VISIBLE SPECTROSCOPY)

Ankita Ojha
Assistant Professor
Department of Chemistry
Maharaja College, Arrah

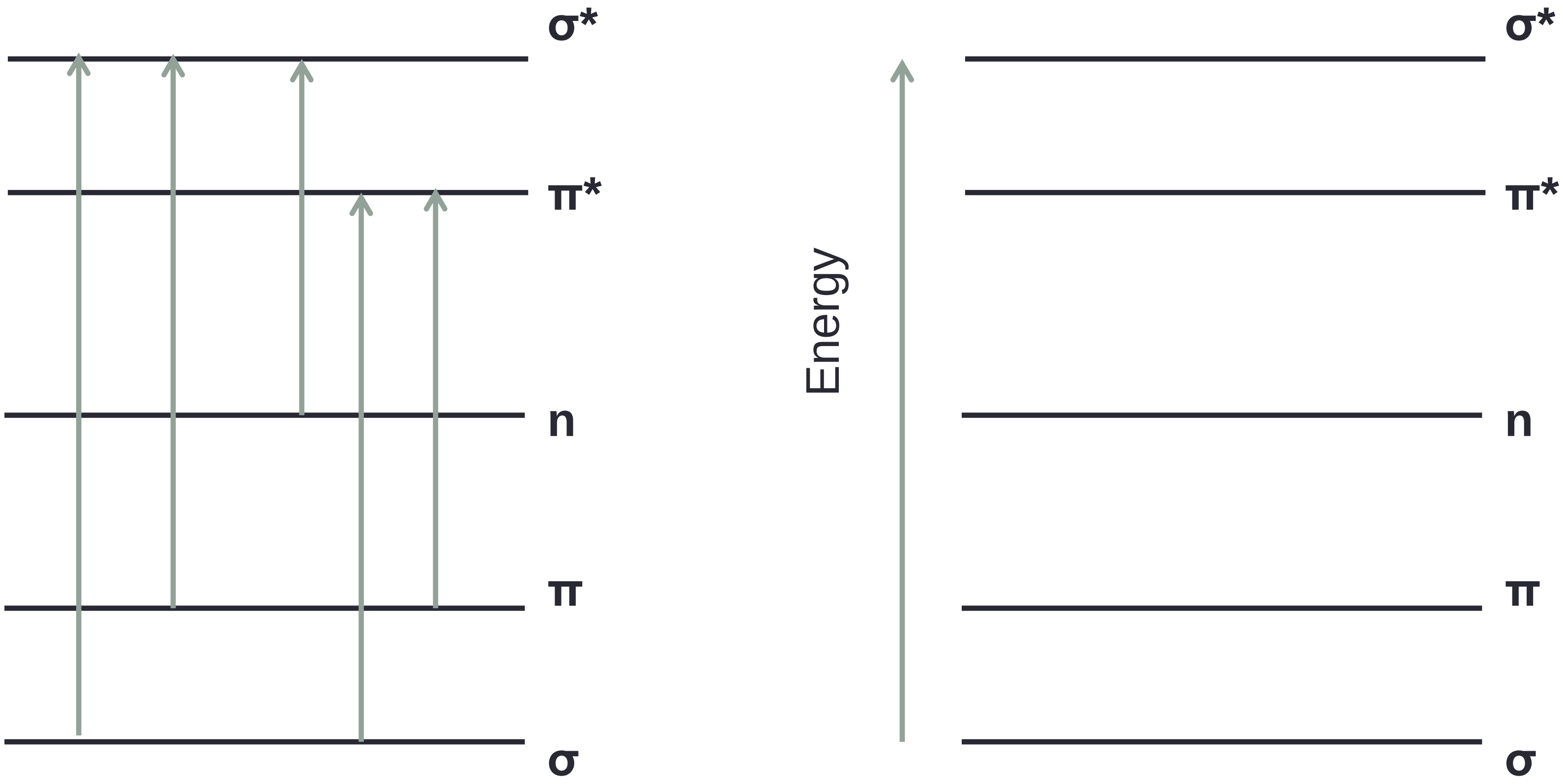
- **Most of the organic molecules are transparent in UV and visible range of radiation i.e. between 190-800 nm. This limits the application of this technique. However some molecules show absorption in this region. The result obtained can be combined with IR and NMR data to get the structural data about the organic compounds.**
- **When a radiation of UV-Visible range passes through a sample in cuvette it either absorbs or transmits the radiation. Also some part of radiation is reflected. The major importance of analysis is about the transmitted and absorbed radiation range.**



- **As a result of electronic excitation the electron in molecules gets excited from low energy ground state to high energy excited state.**
- **The spectrum obtained is known as absorption spectrum which is plotted for the absorbance or transmittance vs. wavelength in nm.**
- **The transitions of electrons is between electronic energy levels. The electrons in *HIGHEST OCCUPIED MOLECULAR ORBITAL (HOMO) and LOWEST UNOCCUPIED MOLECULAR ORBITAL (LUMO).***
- **The difference between electronic energy levels mostly lie between 125 to 650 kJ/mole.**
- **The energy for various electronic levels can be given as**

$$\sigma < \pi < n$$

The value of $\sigma * or\ \pi$*orbitals are higher than these and vary according to the molecular structure.



There are five types of possible transitions:

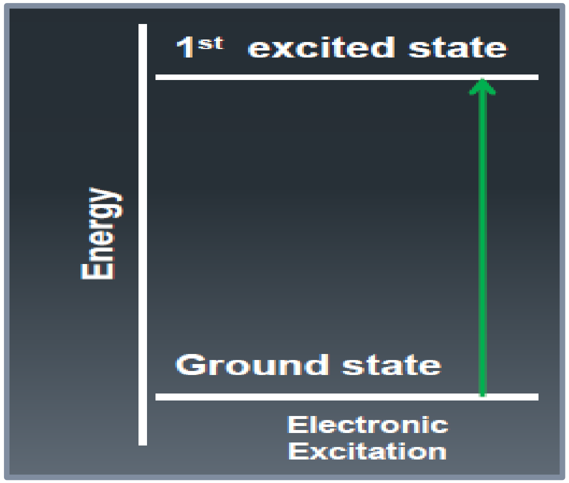
$$\sigma \rightarrow \pi *$$

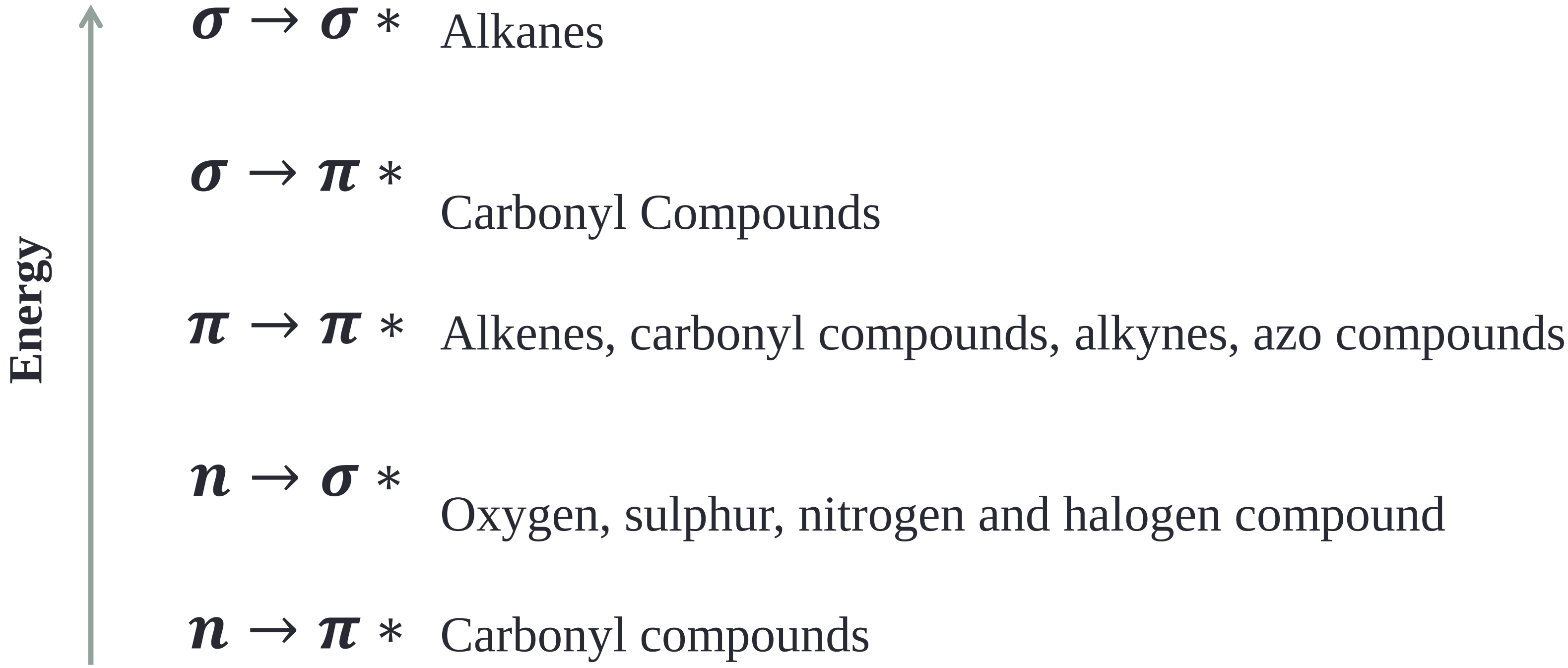
$$\pi \rightarrow \pi *$$

$$\sigma \rightarrow \sigma *$$

$$n \rightarrow \pi *$$

$$n \rightarrow \sigma *$$



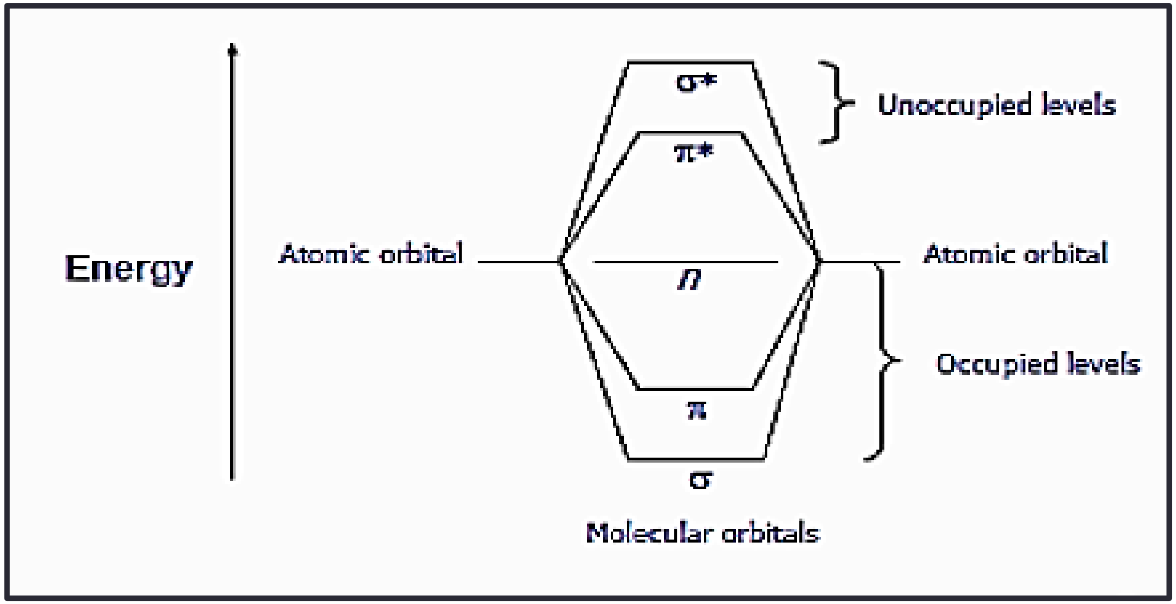


$\sigma \rightarrow \sigma *$	Alkanes
$\sigma \rightarrow \pi *$	Carbonyl Compounds
$\pi \rightarrow \pi *$	Alkenes, carbonyl compounds, alkynes, azo compounds
$n \rightarrow \sigma *$	Oxygen, sulphur, nitrogen and halogen compound
$n \rightarrow \pi *$	Carbonyl compounds

- **Transitions of lowest energy is the most important transition.**
- **However, not all transitions are possible. The transitions that are not allowed are known as “Forbidden transitions”.**
- **There are certain restrictions that have been imposed on the systems for transitions. These are called “Selection Rules.”**

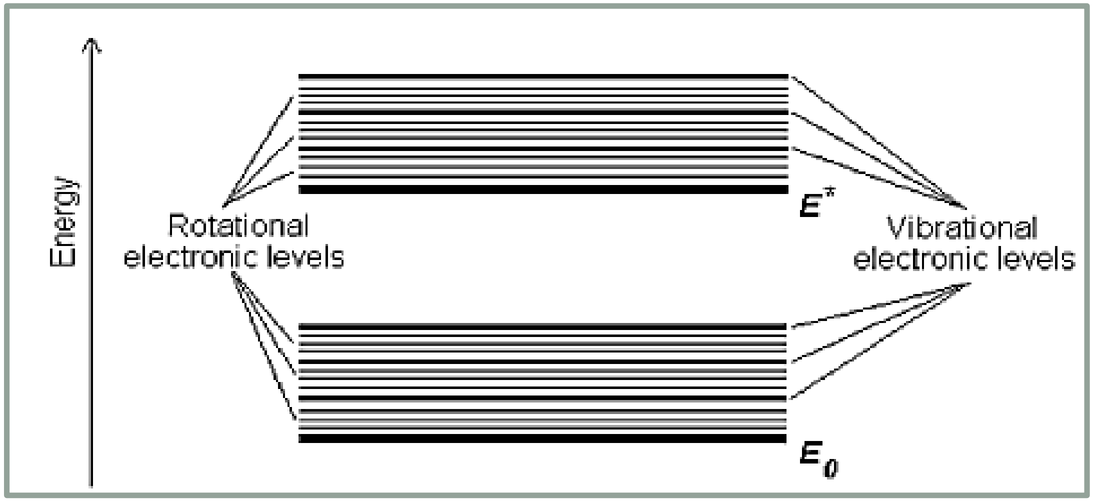
Selection Rule in UV-Vis spectroscopy

- **According to first rule: The transitions that leads to the change in spin quantum number of the electrons are not allowed and are forbidden.**
- **The change in the energy level must be ± 1. The $n \rightarrow \pi *$ transition is however one such example where it is forbidden theoretically but is an observable entity.**



The Origin of UV band structure

Due to the quantization of energy level the UV –vis absorption band shows a sharp spectrum in the case of atoms. Things slightly change when we talk about molecules. In case of molecules the absorption spectrum shows a range of wavelength due to the excited rotational and vibrational modes of transitions ate room temperature. This molecular vibration can not be frozen even when we try at absolute zero. The rotational and vibrational are thus *superimposed* on the electronic level.



Principle of absorption spectroscopy

- The amount of radiation absorbed is directly proportional to the number of molecules that absorbs radiation. This relation has been explained in the terms of Lambert-Beer Law which is shown as

$$A = \varepsilon c l = \log \frac{I_o}{I}$$

Where A = absorbance of the radiation by the sample

Io = Intensity of incident radiation

I= Intensity of light leaving the sample

c=molar concentration of the sample

ε=molar absorptivity of the sample

l=length of the sample cuvette in cm

Deviations of Lambert-Beer Law

- **This law is only observed for the system having single absorbing species. In case sample consists of many species, this law does not prove that effective**
- **This law does not hold good for the systems which have solute-solvent interaction. In case of some metal complexes, the metal ion forms coordinate bonds even with the solvent molecule.**
- **The law fails miserably for very concentrated samples and holds no importance for such samples.**
- **Sometimes there exists a thermal equilibrium between HOMO and LUMO which may fail the law.**
- **Fluorescent samples also deviate from the equation.**

Video lecture is going to be updated soon