Topics

- Molecular species that absorb UV/VIS radiation
- Absorption process in UV/VIS region in terms of its electronic transitions
- Important terminologies in UV/VIS spectroscopy

Organic compounds

Inorganic compounds

MOLECULAR SPECIES THAT ABSORB UV/VISIBLE RADIATION

Charge transfer complex

Definitions:

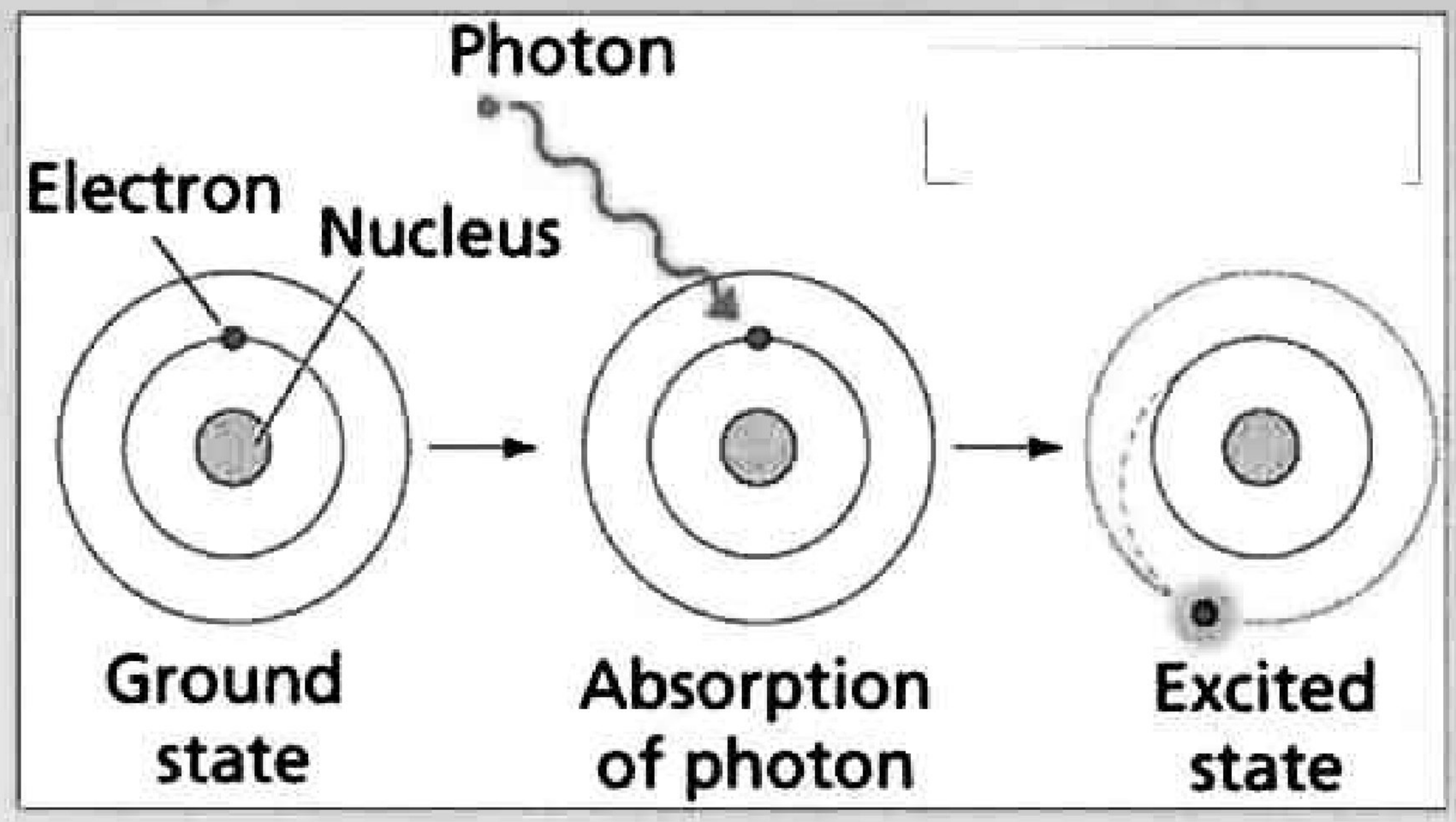
- Organic compound
  - Chemical compound whose molecule contain one or more atoms of carbon.

- Inorganic compound
  - Chemical compound that does not contain carbon.

- Charge transfer (CT) complex
  - A complex where one species is an electron donor and the other is an electron acceptor.

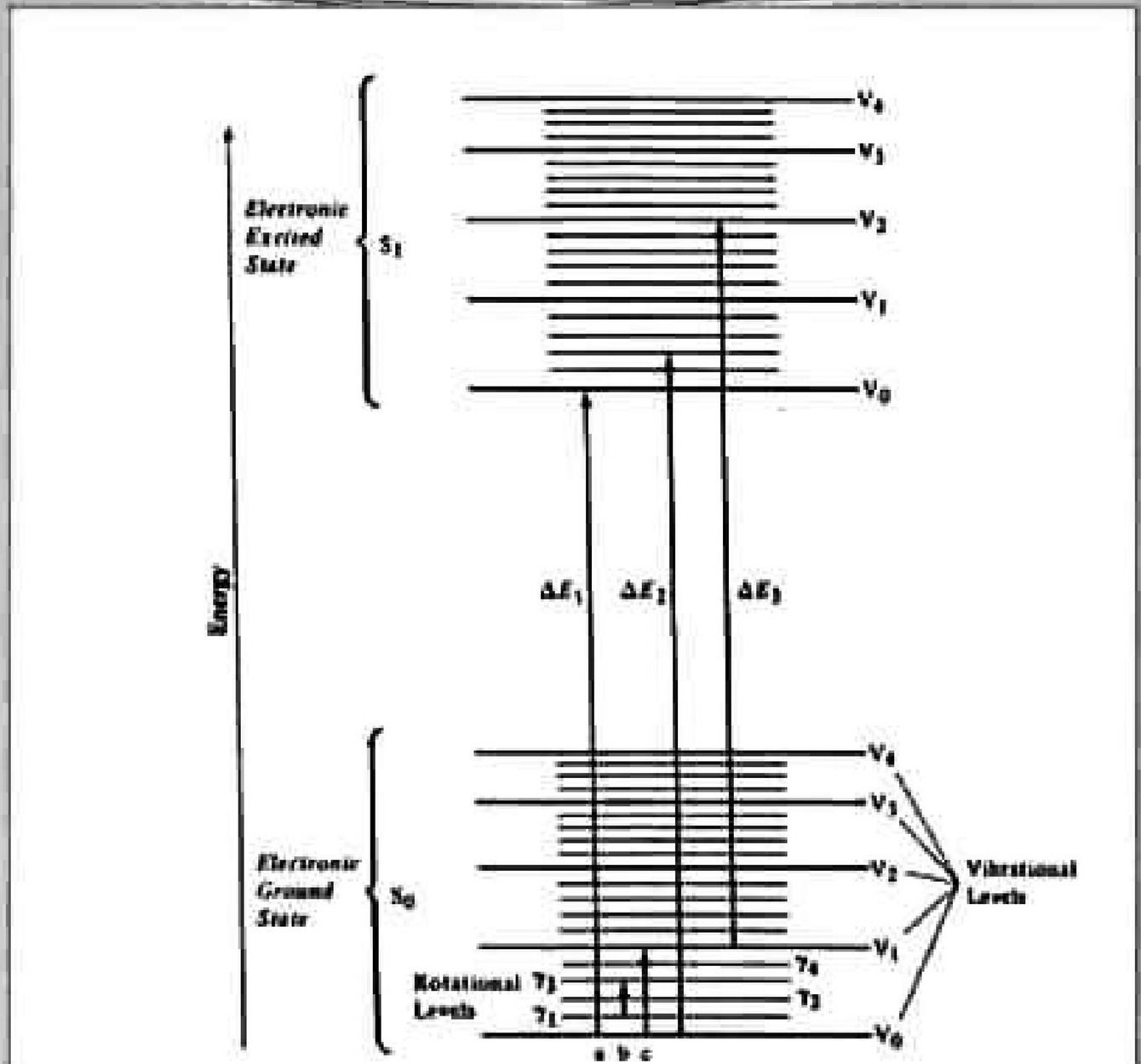
UV-VIS ABSORPTION

In UV/VIS spectroscopy, the transitions which result in the absorption of electromagnetic radiation in this region are transitions between electronic energy levels.



Molecular Absorption

- In molecules, not only have electronic level but also consist of vibrational and rotational sub-levels.
- This result in *band spectra*.



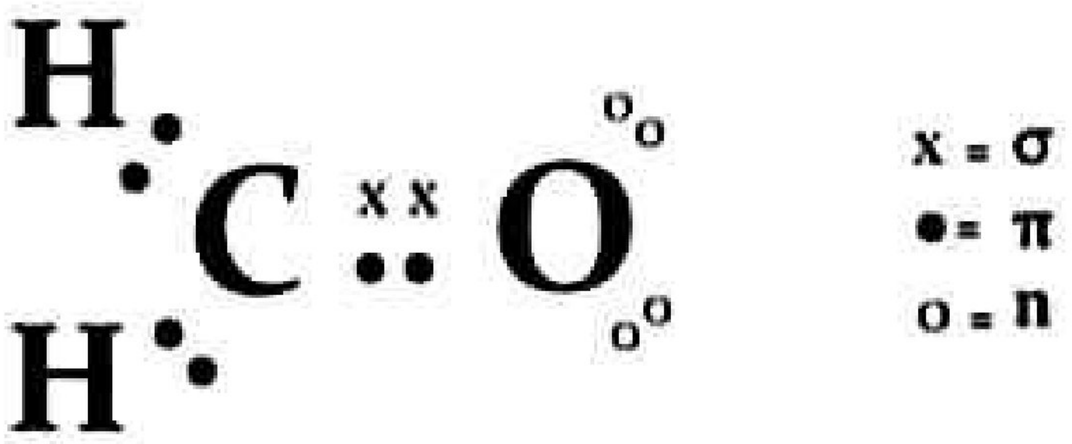
Molecular energy levels and (a) electronic, (b) rotational, and (c) vibrational transitions.

Type of Transitions

3 types of electronic transitions

- σ, π and n electrons
- d and f electrons
- Charge transfer electrons

What is σ, π and n electrons?



Sigma (σ) electron

- Electrons involved in single bonds such as those between carbon and hydrogen in alkanes.
- These bonds are called sigma (σ) bonds.
- The amount of energy required to excite electrons in σ bond is more than UV photons of wavelength. For this reason, alkanes and other saturated compounds (compounds with only single bonds) do not absorb UV radiation and therefore frequently very useful as transparent solvents for the study of other molecules. For example, hexane, C_6H_{14}.

Pi (π) electron

- Electrons involved in double and triple bonds (unsaturated).
- These bonds involve a pi (π) bond.
- For example: alkenes, alkynes, conjugated olefins and aromatic compounds.
- Electrons in π bonds are excited relatively easily; these compounds commonly absorb in the UV or visible region.

Examples of organic molecules containing π bonds.

Ethylbenzene

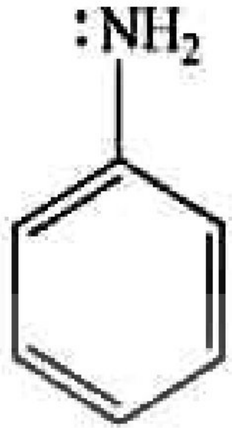
Benzene

1,3-butadiene

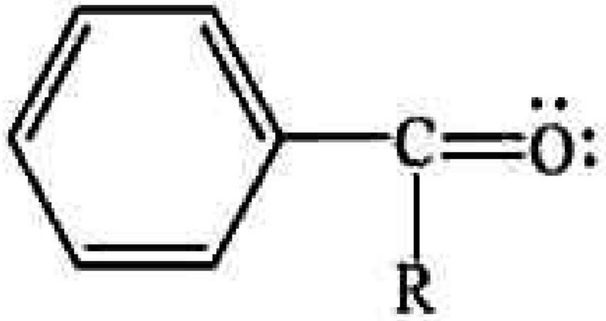
n electron

- Electrons that are not involved in bonding between atoms are called n electrons.
- Organic compounds containing nitrogen, oxygen, sulfur or halogens frequently contain electrons that are nonbonding.
- Compounds that contain n electrons absorb UV/VIS radiation.

Examples of organic molecules with non-bonding electrons.



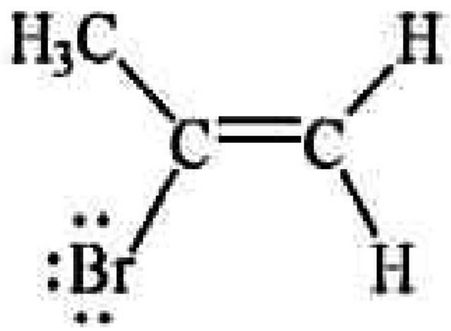
Aminobenzene



Carbonyl compound

R = H ⟶ aldehyde

R = alkyl/aryl ⟶ ketone



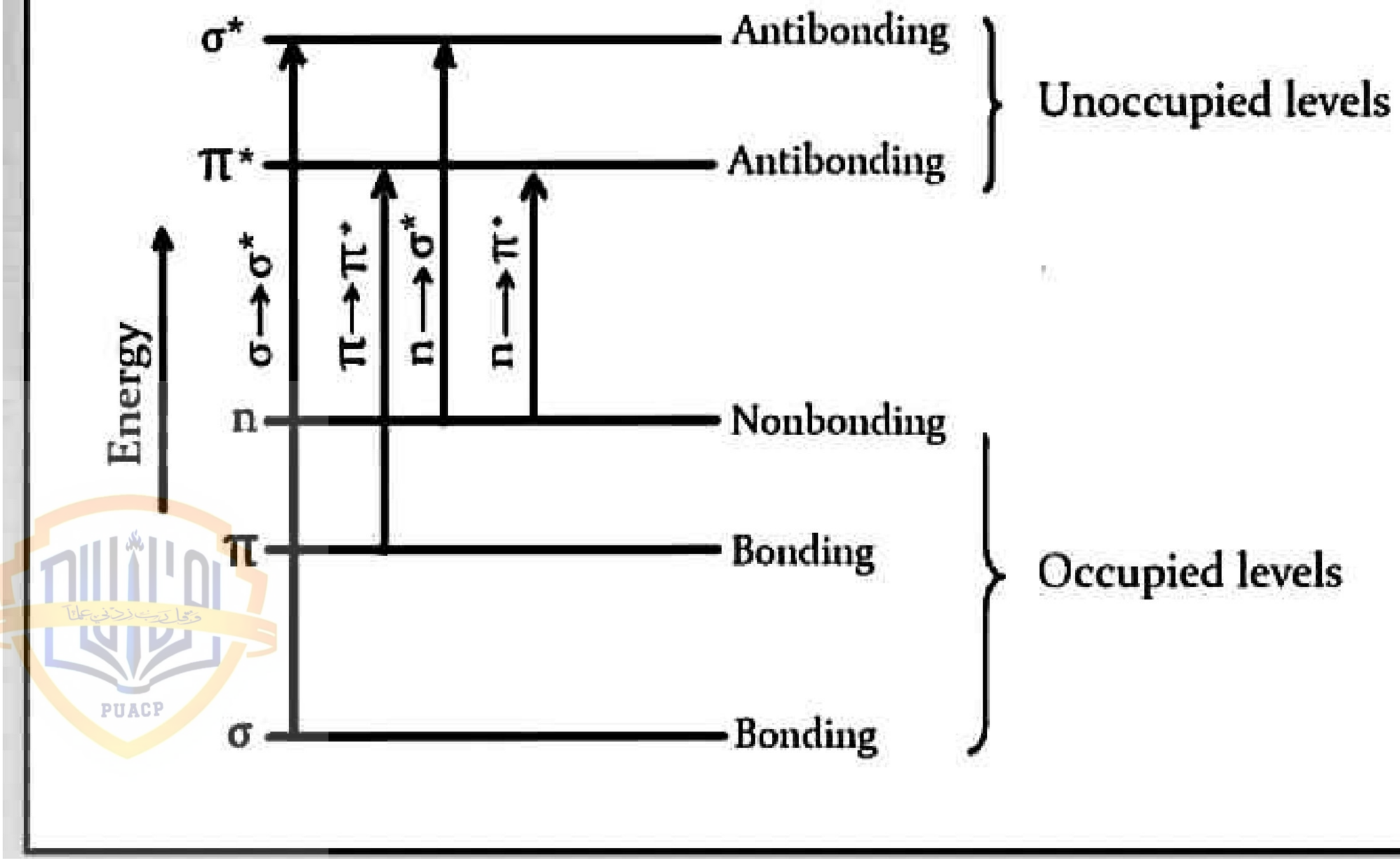
2-bromopropene

Absorption by Organic Compounds

- UV/Vis absorption by organic compounds requires that the energy absorbed corresponds to a jump from occupied orbital to unoccupied orbital.

- Generally, the most probable transition is from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).

Electronic Energy Levels Diagram



$\sigma \rightarrow \sigma^*$ transitions

- Never observed in normal UV/Vis work.
- $\sigma \rightarrow \sigma^*$ in vacuum UV region
- The absorption maxima are < 150 nm.
- The energy required to induce a $\sigma \rightarrow \sigma^*$ transition is too great (see the arrow in energy level diagram)
- This type of absorption corresponds to breaking of C-C, C-H, C-O, C-X, ...bonds

$n \rightarrow \sigma^*$ transitions

- Saturated compounds must contain atoms with unshared electron pairs.
- Compounds containing O, S, N and halogens can absorb via this type of transition.
- Absorptions are typically in the 150 -250 nm region and are not very intense.
- ε range: 100 – 3000 $Lcm^{-1}mol^{-1}$

Some examples of absorption due to n⟶ σ* transitions

Compound	λ_{max} (nm)	ε_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600

$n \rightarrow \pi^*$ transitions

- Unsaturated compounds containing atoms with unshared electron pairs
- These result in some of the most intense absorption in 200 – 700 nm region.
- ε range: 10 – 100 $Lcm^{-1}mol^{-1}$

$\pi \rightarrow \pi^*$ transitions

- Unsaturated compounds to provide the π orbitals.
- These result in some of the most intense absorption in 200 – 700 nm region.
- ε range: 1000 – 10000 $Lcm^{-1}mol^{-1}$