UCB008 - APPLIED CHEMISTRY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

SCBC-TIET

Molecular Spectroscopy Series

Lecture - III

UV-Visible Spectroscopy – Electronic Transitions

by

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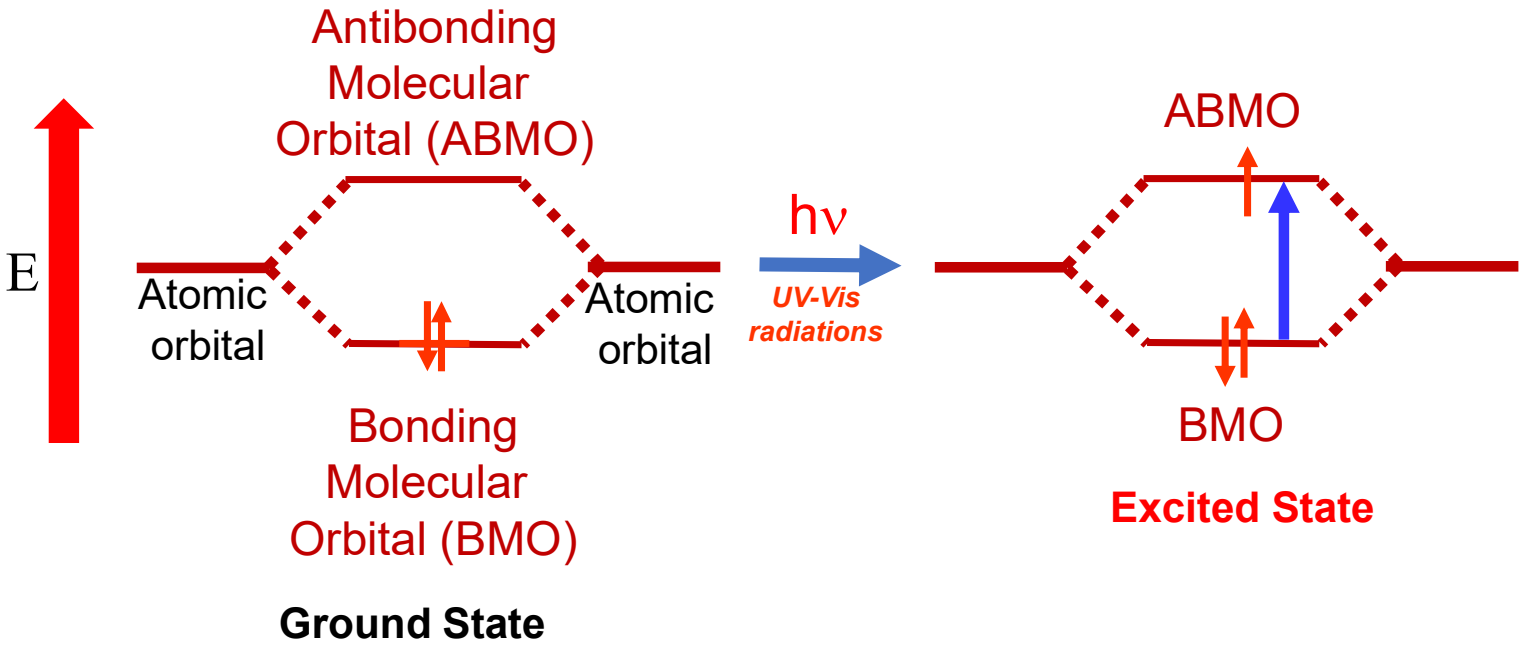
Learning Outcomes

At the end of this session participants should be able to:

- Visualize and illustrate the types of electronic transitions

UV-Visible Spectroscopy (or) Electronic Spectroscopy



UV-Visible Spectroscopy (or) Electronic Spectroscopy

EM Radiations of UV–visible region

+

compound having multiple bond

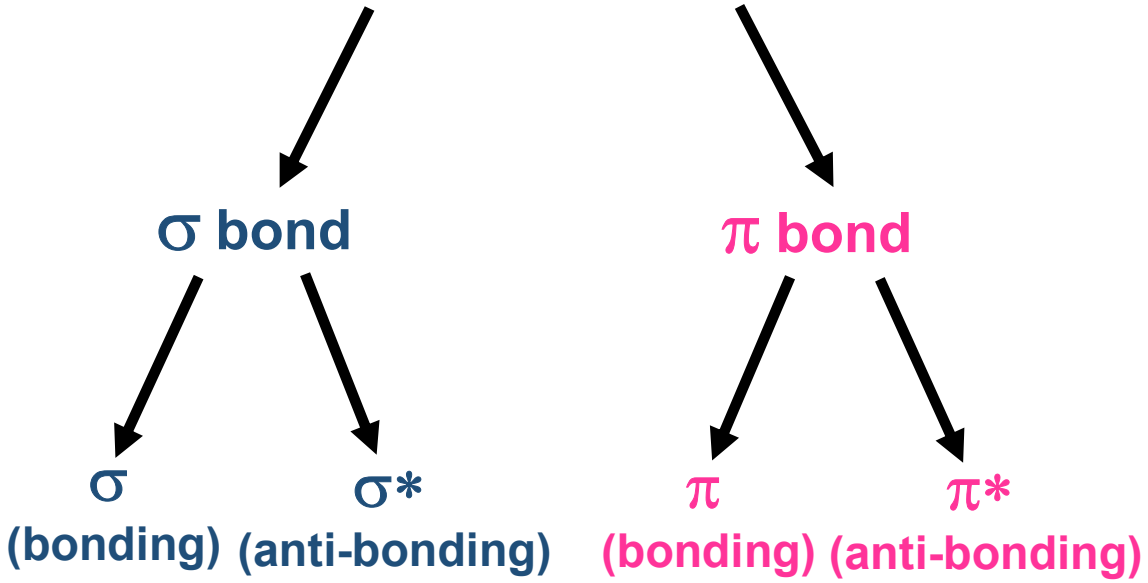
↓

Absorption of radiation

↓

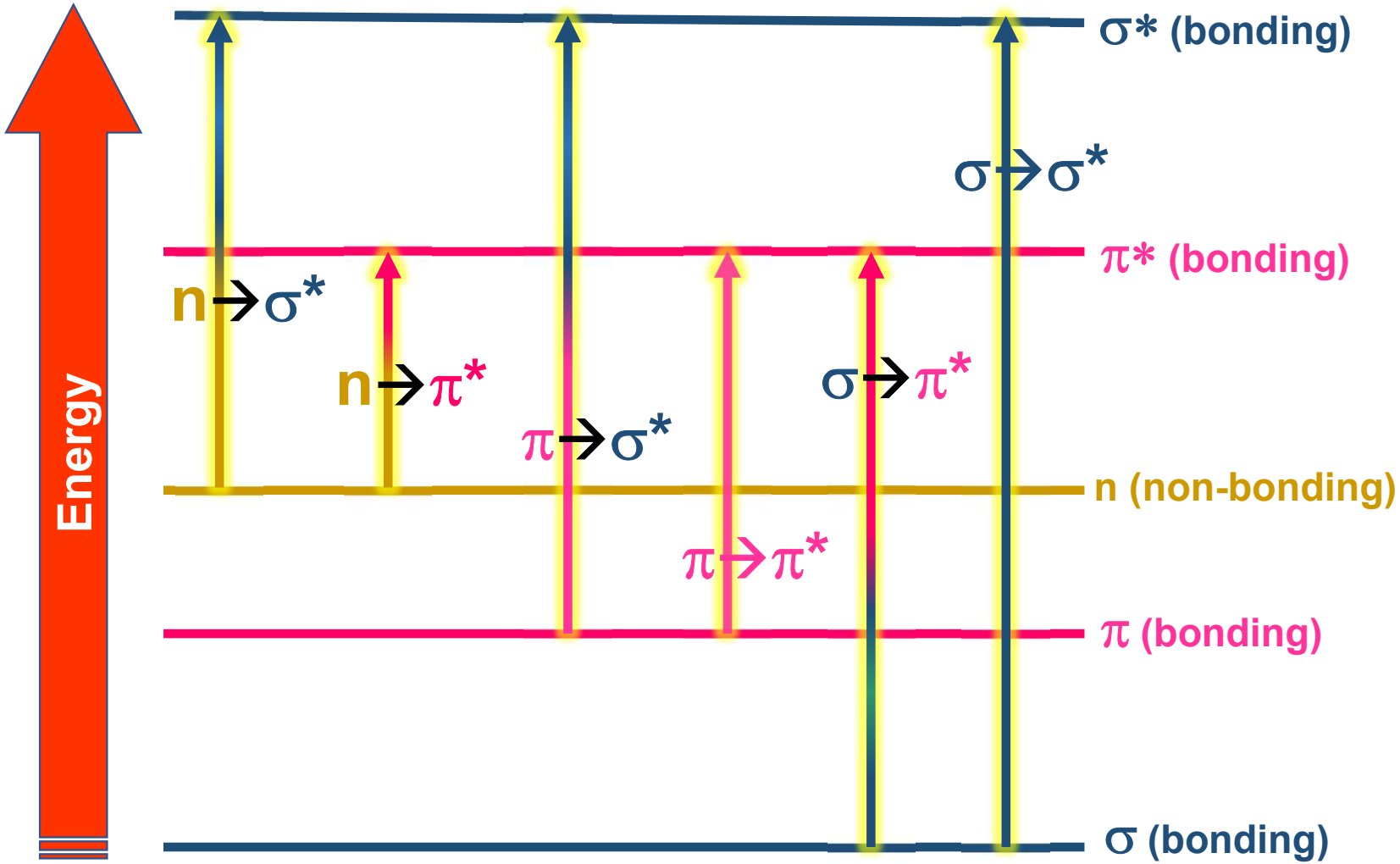
Transition of valence electron from ground to excited state

Covalent bonds in organic molecule



- Compounds containing hetero atom have non-bonding electrons
- A electronic transition is always from bonding molecular orbital (BMO) to anti-bonding molecular orbital (ABMO)

Types of Electronic Transitions



Energy Requirement for Electronic Transitions

$$\sigma-\sigma^* > n-\sigma^* \simeq \pi-\pi^* > n-\pi^*$$

~150nm ~170-190nm 280nm

$\sigma-\sigma^*$ - saturated hydrocarbons e.g. ethane

$n-\sigma^*$ - saturated compounds containing hetro atom having unshared pair of electrons. e.g. saturated halides, alcohols, ethers, aldehydes, amines, etc.

$\pi-\pi^*$ - compounds having double or triple bond and aromatics e.g. butadiene, benzene, etc.

$n-\pi^*$ - unsaturated compounds containing hetro atom having unshared pair of electrons e.g. carboxylic acids, aldehydes, ketones, etc.

Electronic Transitions

- An allowed electronic transition involves orbitals having same symmetry e.g., $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions.

- Allowed transitions have higher extinction coefficient (ε_{max}) values of greater than 10^4.
  - e.g., $\pi \rightarrow \pi^*$ transition of 1-3 butadiene absorbs at 270 nm (ε_{max} : 21000)

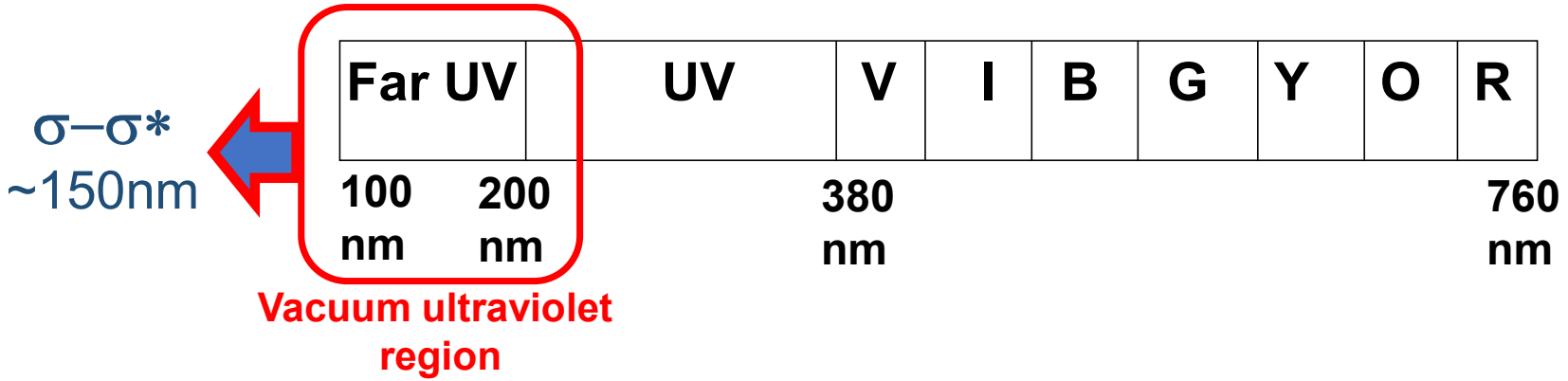
- Transitions between orbitals having different symmetry are classified as **symmetry forbidden transitions.**
  - e.g., $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions are possible only theoretically .

- The forbidden transition namely **n** $\rightarrow \pi^*$ have very low extinction coefficient (ε_{max}) values.
  - e.g., **n** $\rightarrow \pi^*$ transition of carbonyl compounds, at 280 nm, has ε_{max} 15.

Electronic Transitions

Chromophore	Example	Excitation	λ_{max} (nm)	ε
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000
C-X X=Br; X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360

σ–σ* transitions



- σ–σ* requires photons of 150 nm.
- Conventional UV-visible spectrophotometer works in the range of 200 nm to 760 nm.
- This instrument cannot be used below 200 nm as oxygen in air strongly absorbs in far UV region.
- Thus, σ–σ* transitions cannot be observed using conventional UV-visible spectrophotometer.

σ–σ* transitions

- Analysis in far UV region requires vacuum ultraviolet spectrophotometer which is cost intensive.
- Vacuum UV spectrophotometer is used mainly for determining bond energies.
- This equipment is not used for organic structural determination.

In the next session.....

- Terms used in the UV-visible spectroscopy