UCB008 - APPLIED CHEMISTRY

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

SCBC-TIET

Molecular Spectroscopy Series

Lecture - VI

UV-Visible Spectroscopy – λ_{max} and Conjugation

by

Prof. Ranjana Prakash

School of Chemistry and Biochemistry

Thapar Institute of Engineering and Technology

Patiala -147004, India

Ranjana Prakash

Learning Outcomes

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

- Understand the effect of conjugation on λ_{max}

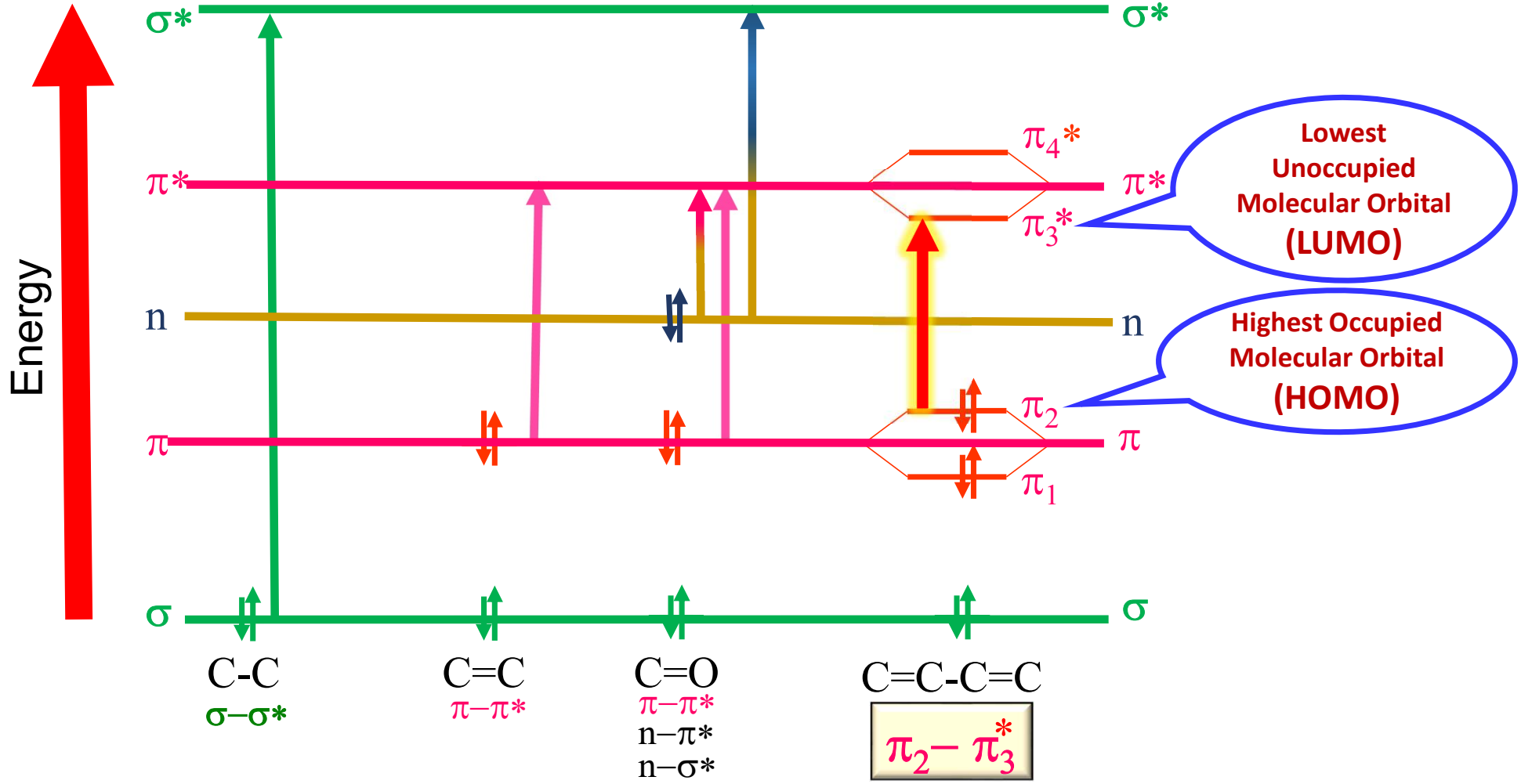
How conjugation causes bathochromic shift….

- More the number of double bonds in conjugation, longer wavelength photon is required for transition.
- Thus, energy requirement for electronic transition decreases.
- Compounds having $\geq$ 8 double bonds in conjugation will appear coloured to human eye.
- Energy requirement for $\pi \rightarrow \pi^*$ transitions decreases as the conjugation increases and can reach the visible region of the spectrum which make the compounds coloured.

How conjugation causes bathochromic shift….

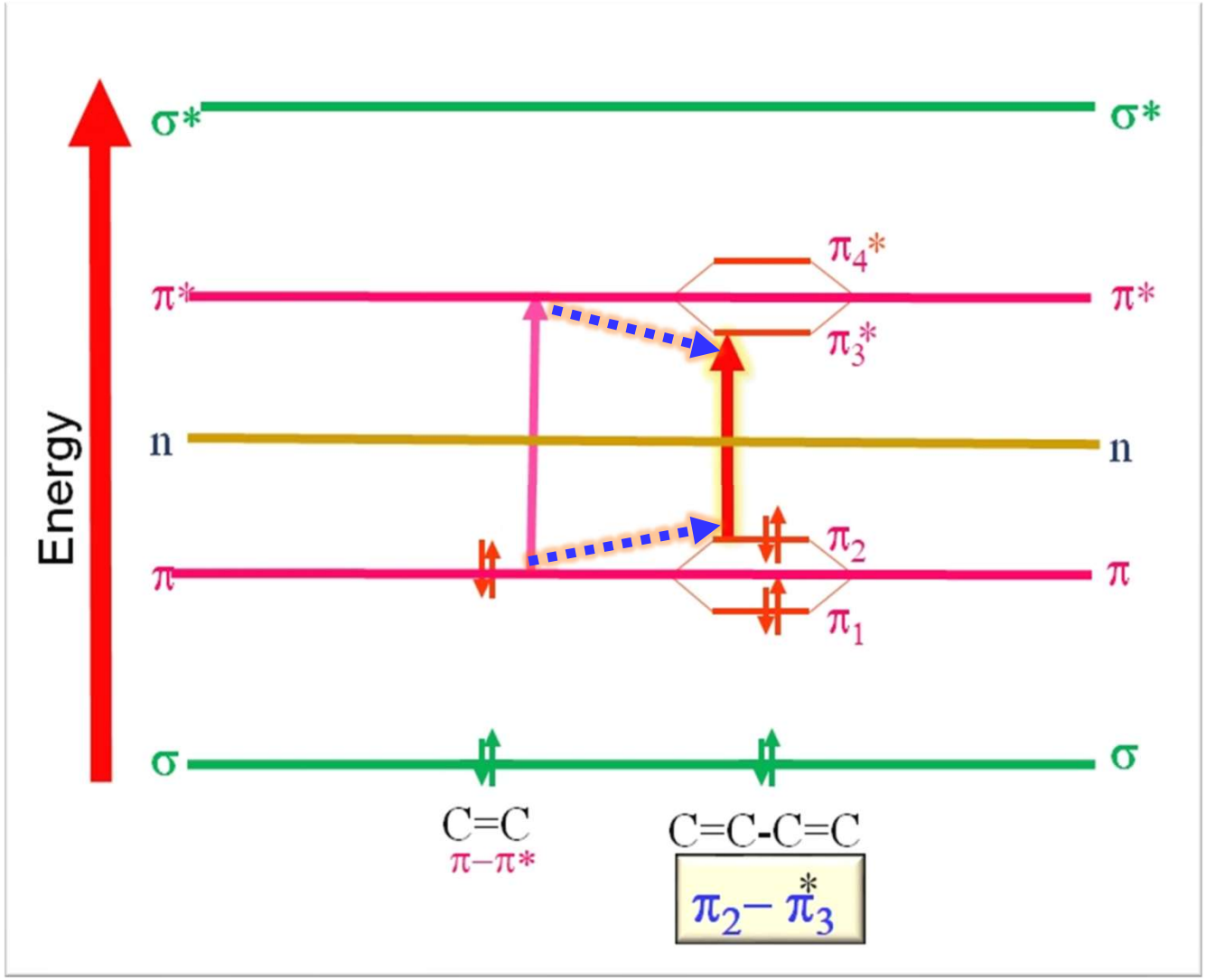
- An electronic transition is from bonding molecular orbital to anti-bonding molecular orbital.
- Energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO).**
- **This results in excited state**.

Relative energies of orbitals - electronic spectroscopy



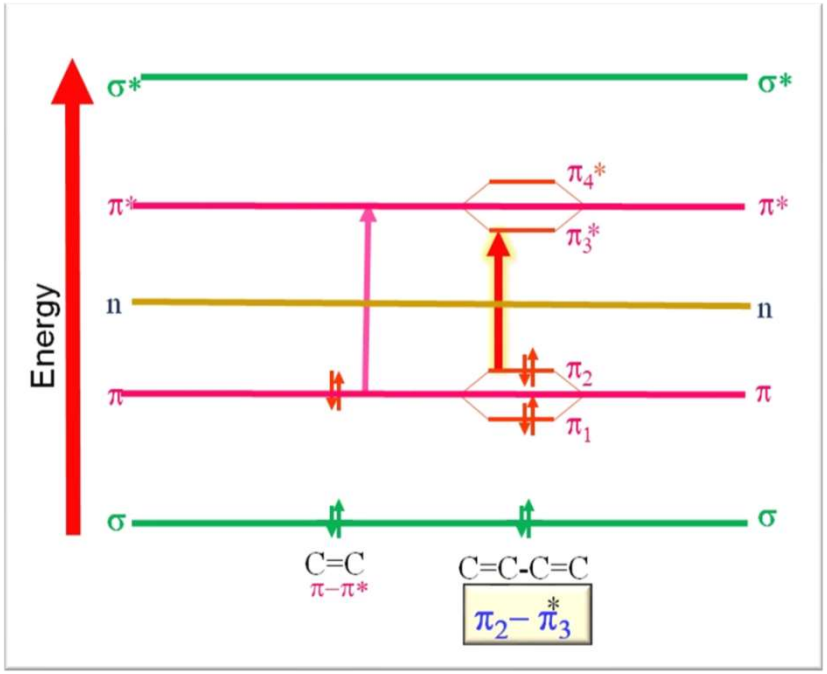
Kemp, W., Organic Spectroscopy, Palgrave Publ.

Effect of conjugation on relative energies of molecular orbitals



How conjugation causes bathochromic shift….

- When two double bonds are conjugated, the four p-atomic orbitals combine to generate four π -molecular orbitals (two are bonding and two are antibonding).
- When two double bonds are in conjugation the energy level of **HOMO** is raised and that of **LUMO** is lowered.
- The energetically most favorable π → π* excitation occurs from the highest energy bonding pi-orbital (**HOMO** – π_2) to the lowest energy antibonding pi-orbital (**LUMO** – π_3^*).
- In a similar manner, the three double bonds of a conjugated triene create six π - molecular orbitals, half bonding and half antibonding.



In the next session.....

- Development of colour in organic compounds