4 ELECTRONIC (UV-VISIBLE) SPECTROSCOPY

It involves the transitions of electron(s) within a molecule or ion from a lower to a higher electronic energy level or vice-versa by the absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum.

While electronic spectra in the visible range span (12,500 – 25,000) cm^{-1}, those in the UV region span (25,000 – 72,000) cm^{-1}.

As the electronic energy levels are quantized, it means a discrete line should appear in the spectra for every transition. But a discrete line is not obtained since electronic transitions are accompanied by vibrational and rotational transitions. This leads to the appearance of bands in the electronic spectra of simple molecules in the gaseous phase.

An important principle for the interpretation of electronic spect

4.1 Classifications of Electronic Transitions

Electronic transitions in molecules can be broadly classified into

(*i*) ($\sigma \rightarrow \sigma^*$) *Transition* : As ($\sigma$) electrons are held more firmly in the molecule, this transition takes place in UV or far UV region.

(*ii*) ($\pi \rightarrow \pi^*$) *Transition* : This transition takes place in the near UV and visible regions.

(*iii*) ($n \rightarrow n^*$) *Transition* : This transitions are generally of weak intensities and lie in the visible region.

The relative energies of the molecular orbitals are illustrated below in Fig. 8 for mostly encountered organic compounds.

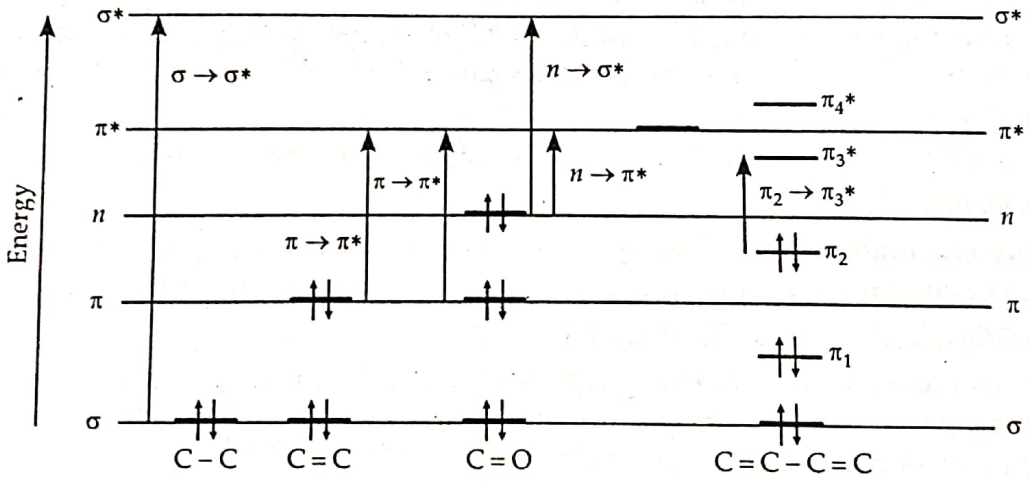

Fig. 8. Electronic Transitions and relative energies of molecular orbitals.

The positions of bands for different electronic transitions are summarized below :

S. No.	*Organic Compound*	*Electronic Transition*	*Position of band and Remarks*
1.	Alkanes	$\sigma \rightarrow \sigma^*$	(~ 150 nm) (Requires high energy which do not lie in UV region.)
2.	Alkenes (simple)	$\pi \rightarrow \pi^*$	(170 nm – 190 nm)
3.	Saturated aliphatic ketones	$n \rightarrow \pi^*$	(~ 280 nm) (Forbidden and hence of low intensity)
		$n \rightarrow \sigma^*$	(~ 185 nm) (Allowed and hence of high intensity)
		$\pi \rightarrow \pi^*$	(~ 160 nm) (Allowed and hence of high intensity)
4.	Conjugated dienes	$\pi \rightarrow \pi^*$	(~ 217 nm) (Transition is of very low energy and is due to conjugation.)