In saturated hydrocarbons & compounds in which all valence shell electrons are involved in single bonds, $\sigma \rightarrow \sigma^*$ transition occurs which require higher energy found in ultraviolet region.

In unsaturated molecules, $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ transitions occur, found in UV or visible region (slightly lower energy).

Some examples:

- For aldehydes & ketones, the more intense band near 1800 Å or 180 nm is due to $\pi \rightarrow \pi^*$ transition & the weaker band at 285 nm is due to $n \rightarrow \pi^*$ transition.
- Olefinic hydrocarbons, show $\pi \rightarrow \pi^*$ transition in the 160-170 nm range.
- Acetylene shows absorption near 180 nm.

Functional groups such as C=C, -N=N-, which absorb at wavelengths longer than 180 nm, are called <u>Chromophores</u>. e.g. nitro, nitroso, carbonyl, thiocarbonyl, sulphoxide groups, aromatic rings.

Molecules like CH_3NH_2 & CH_3I, which do not have π-orbital, show $n \rightarrow \sigma^*$ transitions.

The intensity of an electronic band is determined by the extent of overlap of the wave functions in the ground & excited state.

There is poor overlap of wave functions of n & π^* orbitals in $n \rightarrow \pi^*$ transition & hence are less intense. There is appreciable overlap of wave functions of ground state π & excited state π^* & hence $\pi \rightarrow \pi^*$ transition is more intense & hence has sharp peak.

In strongly acidic media, $n \rightarrow \pi^*$ band disappears protonation of lone pair of electrons. Hence, n-orbital is stabilised & $n \rightarrow \pi^*$ transition requires more excitation energy falling in the UV region & hence may not be observed.

* λ_{max} spectra depends on pH.

Solvent also effects the transitions like $n \rightarrow \pi^*$. in cases where lone pair electrons in O or N-containing systems interact with polar solvents.

The shift in absorption bands & changes in intensity due to various factors (described above) can lead to any of the following:

1. Bathochromic shift (or the red shift):

It involves a shift of λ_{max} to longer wavelengths.

2. Hypsochromic shift (or the blue shift):

It involves a shift of λ_{max} to shorter wavelengths.

3. Hyperchromic shift:

It leads to an increase in the intensity of an absorption band with reference to its molar extinction co-efficient.

4. Hypochromic shift:

It leads to a decrease in the intensity of an absorption band with reference to its molar extinction co-efficient.

Auxochrome: It refers to an atom or a group of atoms which does not give rise to an absorption band on its own but when in conjugation with a Chromophore, causes a bathochromic shift &

& a hyperchromic effect.

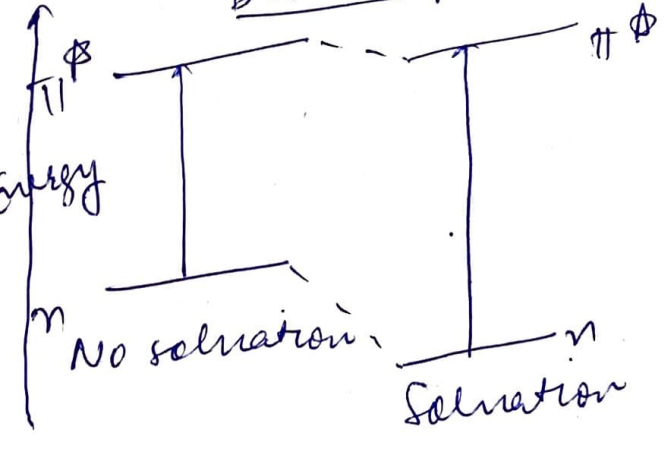
Eg. $-C=C-$ group is a chromophore in ethylene when one of the hydrogens is replaced by a halogen atom, a bathochromic shift & a hyperchromic effect are produced. This is because the lone pair on the halogen atom conjugates with the alkene double bond. So halogen atom acts as an auxochrome.

Solvent effect:

1. Polar solvents stabilize the ground state (n) of $n \rightarrow \pi^*$ transition (by interacting with lone pair of electrons) more than they stabilise the excited state (π^*). It causes an increase in energy & hence, a decrease in wavelength of transition. This is called blue shift.

2. Polar solvents stabilise the excited state (π^*) of $\pi \rightarrow \pi^*$ transition more than the ground state (π) leading to a decrease in energy & hence, increase in wavelength of the transition. This is called red shift.

Blue shift



Red shift