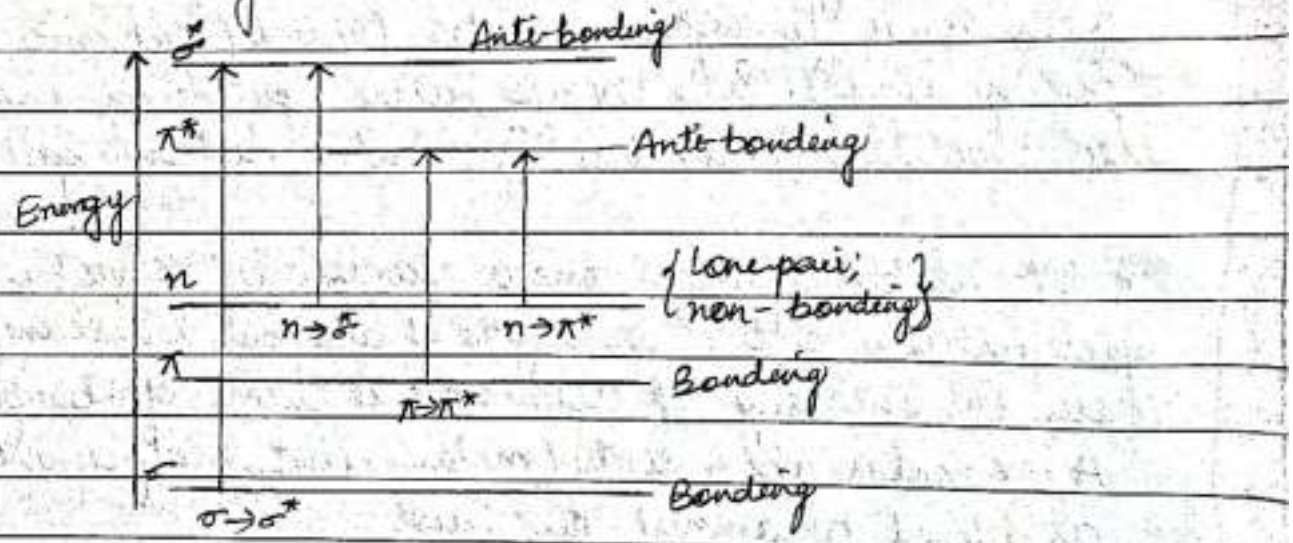
Electronic transitions

The excitation of a molecule by absorption of radiation in the UV-visible region involves promotion of its electrons from a bonding or non-bonding (n) orbital to an antibonding orbital. There are σ & π bonding orbitals associated with σ^* & π^* antibonding orbitals respectively. Non-bonding (n or p) orbitals are not associated with antibonding orbitals because non-bonding or lone pair of electrons present in them do not form bonds.

Following electronic transitions are involved in UV-visible region



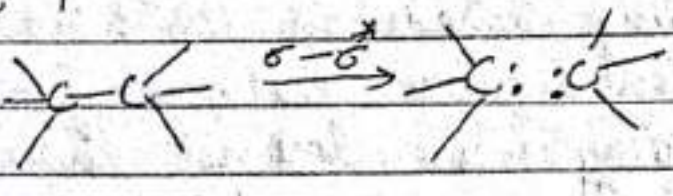
Usual order of energy required for various transition is

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

(1) $\sigma \rightarrow \sigma^*$ Transitions

A transition of a electron from bonding Sigma orbital to the associated antibonding Sigma orbital is $\sigma \rightarrow \sigma^*$. It is a high energy process because σ bonds are generally very strong

These three transition occurs in (200-800nm). In alkanes, e.g., this is the only transition available they absorb high energy UV radiation around 150nm; ethane shows λmax 135nm. The region below 200nm is called Vacuum-UV region, since oxygen present in air absorbs strongly at ~200nm and below



(2) $n \rightarrow \sigma^*$ transitions.

The transition or promotion of an electron from a non-bonding orbital to an antibonding sigma orbital is designated as $n \rightarrow \sigma^*$ transition

Compounds containing non-bonding electrons on a heteroatom are capable of showing absorption due to $n \rightarrow \sigma^*$ transitions. These transitions require lower energy than $\sigma \rightarrow \sigma^*$

This transition involves saturated compounds with one hetero atom with unshared pair of electron i.e saturated, halide, alcohols, ethers aldehyde etc.

CH_3Cl	λmax 173nm
CH_3OH	λmax 183nm
H_2O	λmax 167nm
CH_3I	λmax 258nm

In saturated alkyl halides, the energy required for this transition decrease with increase in size of halogen atom (or decrease in electronegativity of the atom). Due to the greater electronegativity of chlorine than iodine the n electrons on Chlorine atom are comparitively difficult to excite. The n electrons on iodine atom

are loosely bound. Since this transition is more probable in case of methyl iodide its molar extinction coefficient is also higher than CH_3Cl.

$n \rightarrow \sigma^*$ transitions are sensitive to hydrogen bonding. Alcohols e.g. form hydrogen bonds with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus this transition requires greater energy.

Protonated trimethylamine does not show absorption due to $n \rightarrow \sigma^*$ transitions, because it has no non-bonded electrons.

(3) $\pi \rightarrow \pi^*$ Transitions

This type of transition occurs in compounds containing one or more covalently unsaturated groups like $C=C$, $C=O$, NO_2 etc. $\pi \rightarrow \pi^*$ transition require lower energy than $n \rightarrow \sigma^*$ transitions.

In unconjugated alkenes, this transition occurs in the range 170-190nm; ethylene shows λ_{max} 171nm.

Similarly unconjugated carbonyl compounds show $\pi \rightarrow \pi^*$ transition in the range 180-190nm.

Acetone shows λ_{max} 188nm

(4) $n \rightarrow \pi^*$ transitions

In this transition, an electron of unshared electron pair on a hetero atom is excited to π^* anti-bonding orbital.

These transition occurs with compound containing double bonds involving hetero atom bearing unshared pair of electrons ($C=O$, $C=S$, $N=O$)

This transition requires lowest energy, therefore this transition give rise to an absorption band at long

wavelength. Saturated aldehydes and Ketones show both types of transitions i.e low energy $n \rightarrow \pi^*$ high energy $\pi - \pi^*$ occuring in the regions 270-300nm and 180-190nm.
Acetone shows $n \rightarrow \pi^*$ at λmax 279nm
The band due to $\pi \rightarrow \pi^*$ transitions is more intense i.e it has high value of ϵ than less intense $n \rightarrow \pi^*$ transitions.
In addition, Carbonyl Compounds also exhibit high energy $n \rightarrow \sigma^*$ transitions around 160nm; acetone show λmax 166nm
* This $n \rightarrow \pi^*$ transitions is forbidden by Symmetry Considerations, thus the intensity of the band due to this transition is low, although the wavelength is long.

Transition Probability: Allowed and Forbidden Transitions

It is not always necessary that excitation of an electron takes place from a bonding orbital or lone pair to an antibonding or non-bonding orbital. When a compound is exposed to UV or Visible light.
Depending upon the Symmetry and the value of ϵmax the transitions can be Classified as
(a) Allowed Transitions
(b) Forbidden Transitions
(1) The geometry of the molecular orbital in the ground state
(2) The geometry of the molecular orbital in excited state
(3) The orientation of electric dipole of incident light that might induce transition

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The transitions will be allowed transition if the above three factors have appropreate symmetry relationship.

$E_{max} = 0.87 \times 10^{20} P.a.$

where P = transition probability with value 0 to 1
a = Target area of absorbing system (Chromophore)

The value of E_{max} is found to be around 10^5 when chromphore has length of order 10 A° or 10^{-7} cm.
A chromophore with low transition probability will have $E_{max} < 1000$
Thus there is a direct relationship between the area of chromophore and the absorption intensity.
E_{max}
Transitions with E_{max} values $> 10^4$ are called allowed transitions and are generally caused by $\pi \rightarrow \pi^*$ transition
Ex 1,3 butadiene λ_{max} 217 E_{max} 21000 results from allowed transition
Transitions with E_{max} values $< 10^4$ are called forbidden transitions. These are generally caused by $n \rightarrow \pi^*$ transitions e.g., in Carbonyl Compounds, the absorption near 300nm with E_{max} 10-100 results from forbidden transitions.

The allowedness of electronic transitions is related not only with the geometries of the lower & high energy molecular orbitals but also with the symmetry of molecule as a whole. Symmetrical molecules, (eg: benzene is highly symmetrical), have more restrictions on their transitions than comparitively less symmetrical molecules.

Because of this reason the electronic absorption spectrum of benzene molecule is simple as compared to less symmetrical molecules. There are very less symmetry restrictions for a highly unsymmetrical molecule, thus it will exhibit a complex electronic spectrum.

Chromophore

A Chromophore is a covalently unsaturated group responsible for electronic transition (absorption in the UV or visible region) e.g., C=C, C=O, C≡O, NO_2 C≡N etc.
If a Compound absorbs light in the visible region (400-800nm), only then it appears Coloured. Thus, a Chromophore may or may not impart Colour to a Compound depending on whether the chromophore absorbs radiation in the visible or U.V region.

Chromophores like C=C or C≡C having π-electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π & non-bonding electrons like C=O, C≡N, N=N, undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ & $n \rightarrow \sigma^*$ transitions. Since the wavelength & intensity of absorption depend on a number of factors, there are not set rules for the identification of Chromophore.

Auxochrome

A covalently satured group which when attached to a chromophore, changes both wavelength and the intensity of the absorption maximum is known as auxochrome. e.g., NH_2, OH, SH halogen etc.
Auxochrome generally increase the value of λ_{max} as

well as ε_{max} by extending the Conjugation through resonance. These are also called Colour enhancing group. An auxochrome itself does not show absorption above 200nm. Actually, the combination of Chromophore and auxochrome behaves as a new Chromphore having different Values of λ_{max} and ε_{max}.

Ex Benzene shows λ_{max} 256nm ε_{max} 200
Aniline shows λ_{max} 280nm ε_{max} 1430

Hence NH_2 group is an auxochrome which extends the Conjugation involving the lone pair of electrons on the nitrogen atom resulting in the increased value of λ_{max} & ε_{max}.

Bathochromic Shift (Red Shift)

The shift of an absorption maximum to a longer wavelength due to the presence of an auxochrome, or Solvent effect is called Bathochromic Shift or red Shift

Ex- Benzene λ_{max} 256 and aniline λ_{max} 280nm

Thus there is a bathochromic Shift of 24nm in λ_{max} of benzene due to the presence of auxochrome NH_2.

Similarly a bathochromic Shift of $n \rightarrow \pi^*$ band is observed in Carbonyl Compounds on decreasing solvent polarity eg λ_{max} of acetone is at 264.5nm in water as compared to 279nm in hexane

Hypochromic Shift

The shift of an absorption maximum to a shorter wavelength is called hypsochromic or blue shift. This is caused by the removal of Conjugation

or change in the solvent polarity. For example, Aniline shows λmax 280nm, whereas anilinium ion shows λmax 254nm. This hypsochromic shift is due to the removal of n→π conjugation of the lone pair of electrons of the nitrogen atom of aniline with the π-bonded system of the benzene ring on protonation because the protonated aniline has no lone pair of electrons for conjugation.

Similarly, there is a hypsochromic shift of 10-20nm in λmax of π→π* bands of carbonyl compounds on going from ethanol to hexane as solvent i.e decreasing solvent polarity.

Hypsochromic Effect

An effect which leads to a decrease in absorption intensity εmax is called hypsochromic effect. This is caused by introduction of a group which distorts chromophore

Ex- Biphenyl shows λmax 252nm εmax 19000 whereas 2,2'dimethylbiphenyl shows λmax 270nm & εmax 800nm. The decrease of 18200 is in the value of εmax of 2,2'dimethylbiphenyl is due to hypsochromic effects of the methyl groups which distorts chromophore by forcing the rings out of co-planarity resulting in the loss of conjugation.

Hyperchromic Effect

An effect which leads to a increase in absorption intensity εmax is called hyperchromic effect. The introduction of auxochrome usually causes hyperchromic shift.

Ex Benzene shows B-band at 256nm, εmax 200

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Whereas aniline shows B-band at 280nm, ε_{max} 1430. The increase of 1230 in the value ε_{max} of aniline compared to that of Benzene is due to the hyperchromic effect of the auxochrome NH_2.