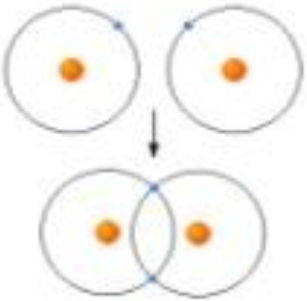
Molecular Orbital Theory

The goal of molecular orbital theory is **to describe molecules** in a similar way to how we **describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations**.

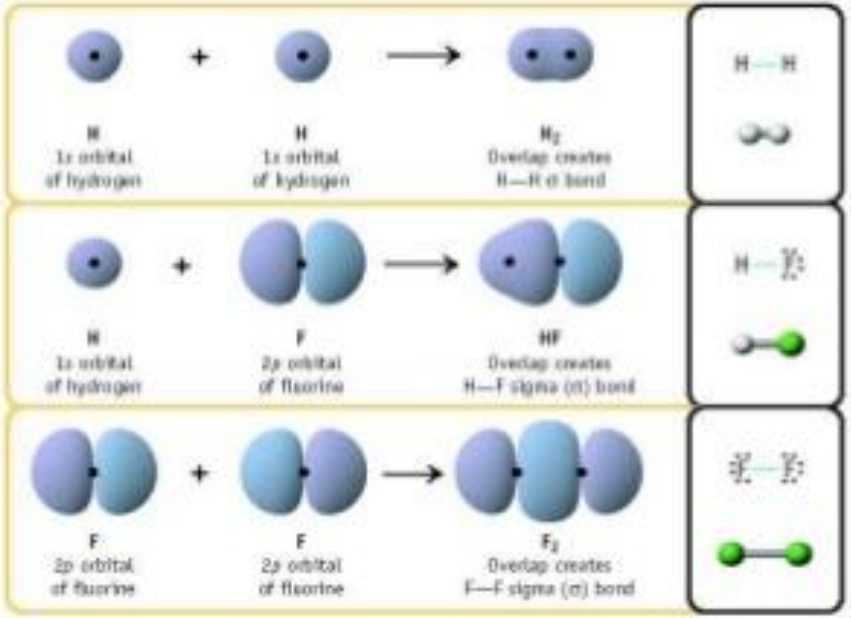
Molecules can form bonds by sharing electron - *Two shared electrons form a single bond*
Atoms can share one, two or three pairs of electrons - *Forming single, double and triple bonds*
Other types of bonds are formed by **charged atoms** (ionic) and **metal atoms** (metallic).

Orbital Mixing: When atoms share electrons to form a bond, their ***atomic orbitals mix*** to form molecular bonds. In order for these orbitals to mix they must:

- ❑ Have similar energy levels.
- ❑ Overlap well.
- ❑ Be close together.



The two atoms share one electron each from there outer shell. In this case both 1s orbitals overlap and share their valence electrons.



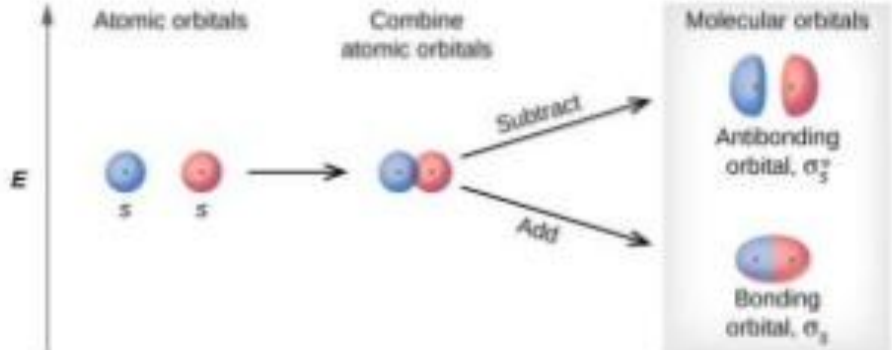
Molecular Orbital Theory

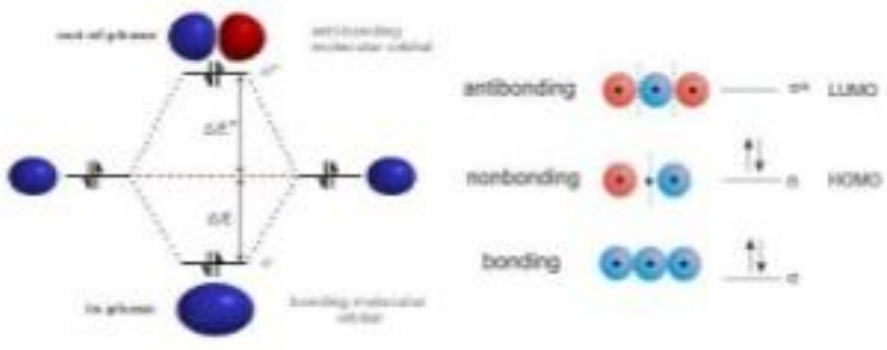
Molecular orbital (MO) theory was developed by F. Hund and R.S. Mullikan in 1932

- In valence bond theory, **orbitals in a molecule are thought to be localized on atoms**, with some overlap of the orbitals between bonded nuclei. In the molecular orbital view, **orbitals in a molecule are thought to be spread out (delocalized) over many atoms.**
- Valence bond theory is often referred to as a **localized bonding theory** while molecular orbital theory is referred to as a **delocalized bonding theory.**
- The molecular orbital theory is used **to predict the shapes and energies of orbitals that contain no electrons.**

Principle of MOT

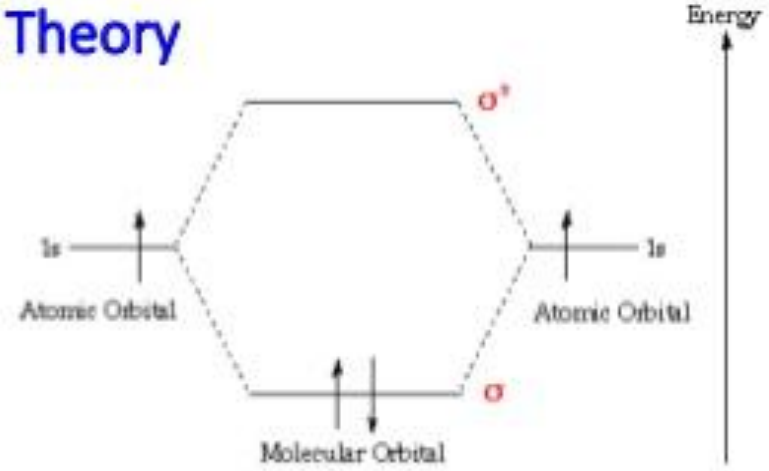
" Any number of atomic orbitals overlaps to form molecular orbitals, an **equal number** of molecular orbitals are formed. When two s orbitals overlap, they form two new orbitals: one at lower energy than the original s orbitals and one at higher energy than the original s orbitals".

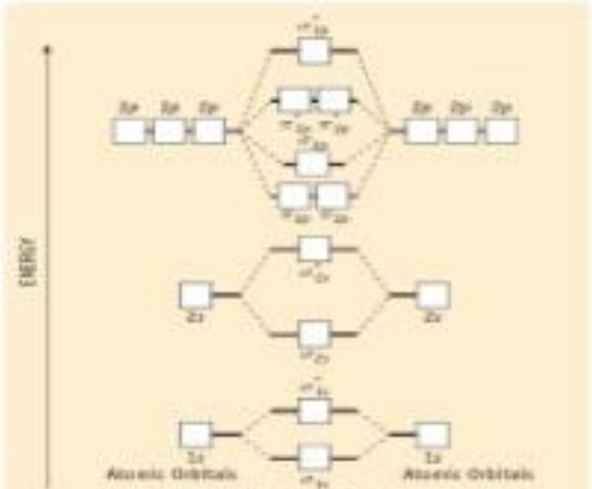


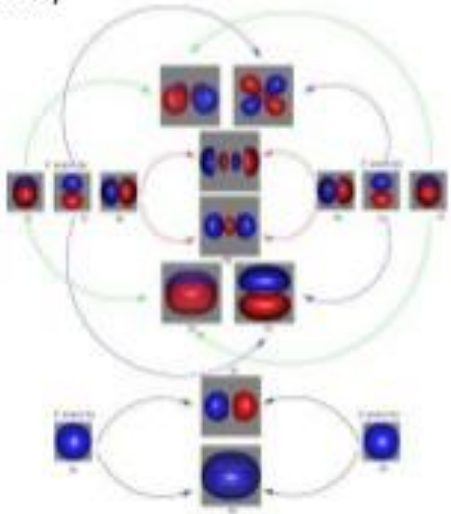


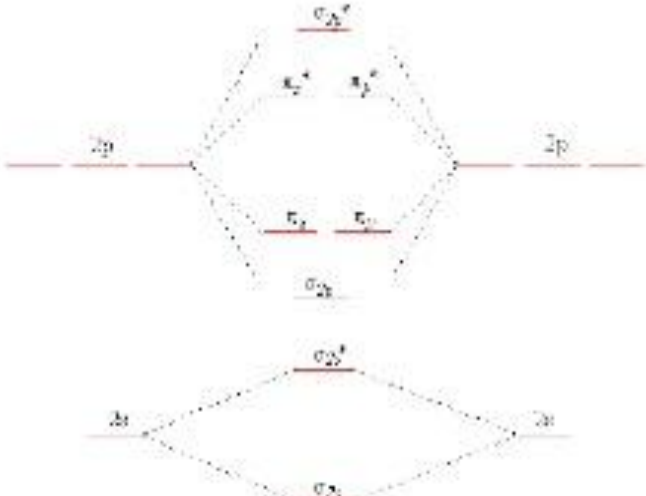
Molecular Orbital Theory

- Each line in the diagram represents an orbital.
- The electrons fill the molecular orbitals of molecules like electrons fill atomic orbitals in atoms
- Electrons go into the lowest energy orbital available to form lowest potential energy for the molecule.
- The maximum number of electrons in each molecular orbital is two. (Pauli exclusion principle)
- One electron goes into orbitals of equal energy, with parallel spin, before they begin to pair up. (Hund's Rule.)





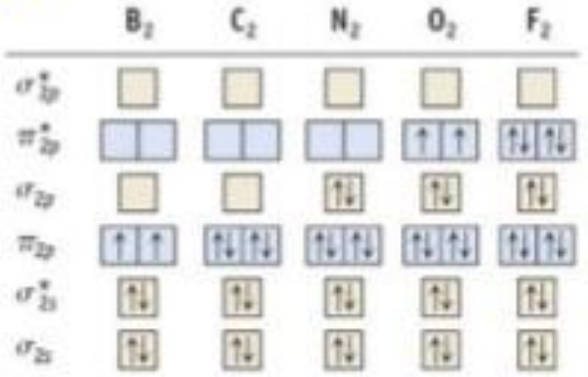


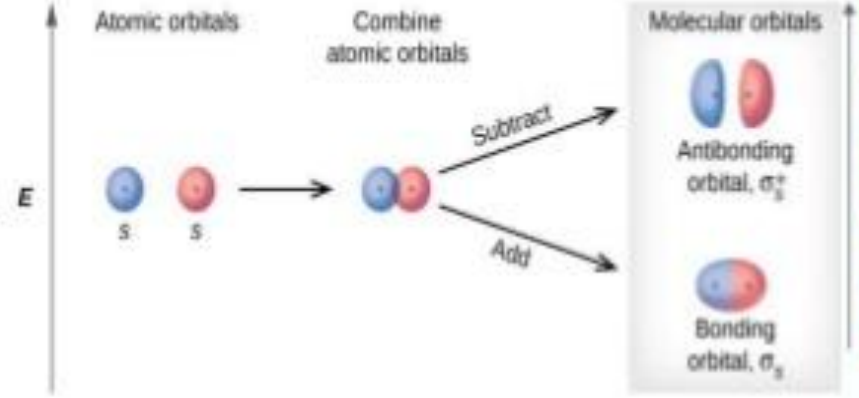


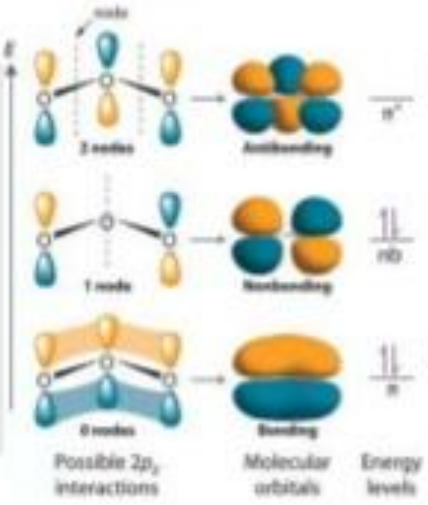
Molecular Orbital Theory

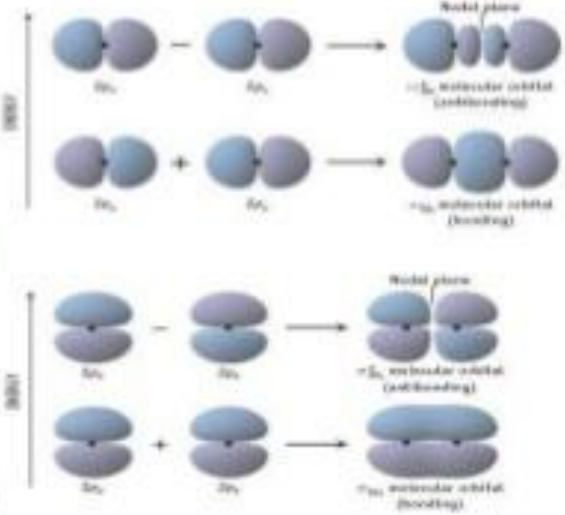
- **Atomic orbitals mix together and make:**
  - **Bonding Orbitals**
    Electrons in these orbitals help hold atoms near each other
  - **Antibonding Orbitals**
    Electrons in these orbitals push atoms apart from each other
  - **Nonbonding Orbitals**
    Electrons in these orbitals have no effect on bonding

- **Molecular Orbitals can:**
  - be **Sigma or Pi**
  - be **spread over multiple atoms**
  - **Paramagnetic**: a compound with any unpaired electrons
  - **Diamagnetic**: no unpaired electrons.







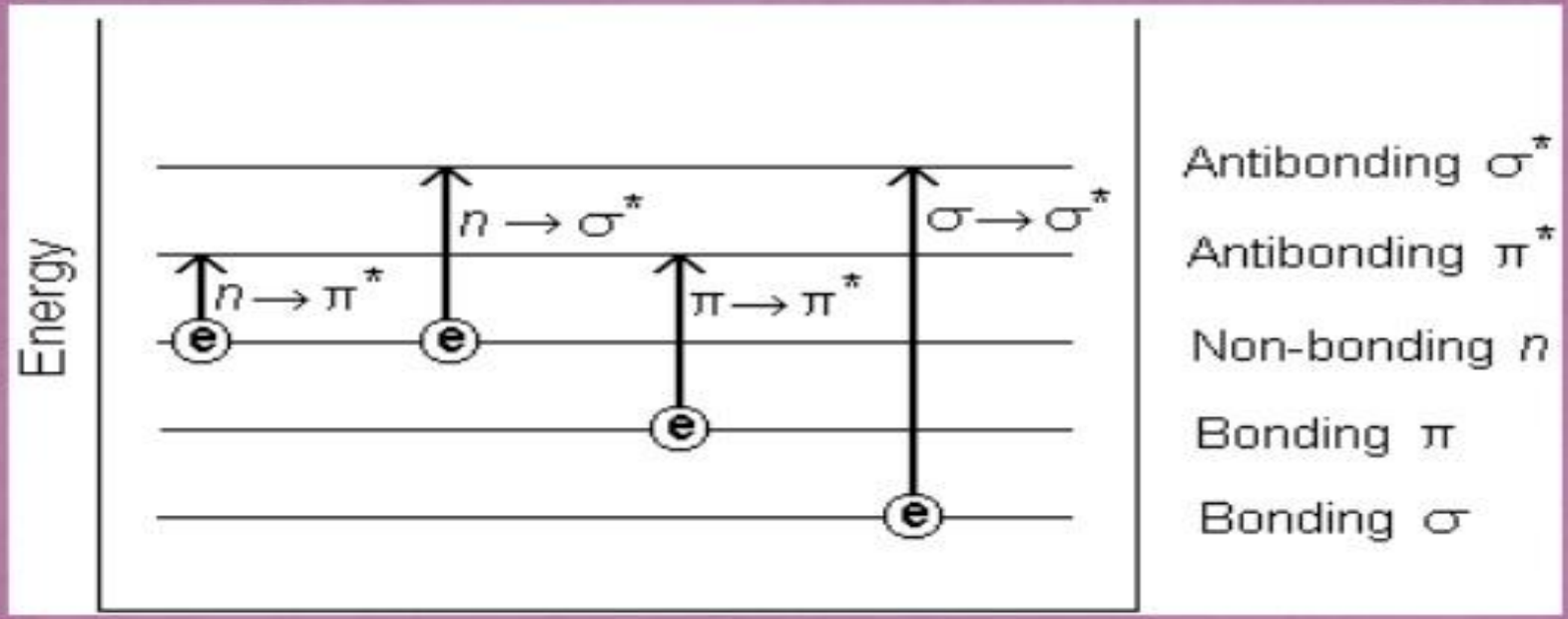


UV SPECTROSCOPY

- UV spectroscopy is concerned with the study of absorption of uv radiation which ranges from 200-400nm.
- Valence electrons absorb the energy thereby molecules undergoes transition from ground state to excited state.
- This absorption is characteristic and depends on the nature of electrons present.
- Types of electrons

σ electrons:	in saturated compounds
π electrons:	in unsaturated compounds
n electrons:	in non bonded electrons

ELECTRONIC TRANSITIONS



1) σ-σ*

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.
- The organic compounds in which all the valence shell electrons are involved in the formation of σ bond do not show absorption in normal uv region (200-400nm)
- This transition is observed with saturated compounds.

- Eg: Methane(CH_4) has C-H bond only and can undergo σ-σ^* transition and shows absorption maxima at 122nm.

- The usual spectroscopic technique cannot be used below 200 nm.

- To study this high energy transition,the entire region should be evacuated (Vacuum uv region)

- Here,the excitation ocuurs with net retention of electronic spin

- This region is less informative

2) π-π^*

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π^*.
- Energy required is less when compared to **n-σ^***
- Compounds containing multiple bonds like alkenes,alkynes,carbonyls,nitriles,aromatic compounds etc undergo π-π^* transition.

Eg:Alkenes generally absorb in the region 170-205nm.

- Absorption usually occurs in the ordinary uv spectrophotometer
- Absorption bands in unconjugated alkenes (170-190nm)
- Absorption bands in carbonyls (180 nm)
- Introduction of alkyl group in olefinic linkage produces bathochromic shift

3) n-σ*

- Saturated compounds containing one hetero atom with unshared pair of electrons(n) like O,N,S and halogens are capable of n-σ* transition.
- These transition require less energy than σ-σ* transition.
- In saturated alkyl halides, the energy required for transition decrease with increase in the size of halogen atom (or decrease in electronegativity)

- Eg:Methyl chloride has a λmax of 173nm.
  Methyl iodide has a λmax of 258nm.

- This type of transition is very sensitive to hydrogen bonding
  Eg: Alcohol & amines

- Hydrogen bonding shift the uv absorptions to shorter wavelength.

4) n-π*

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.
- Compounds containing double bonds involving hetero atoms(C=O,N=O) undergo such type of transitions.
- This transition require minimum energy out of all transitions and shows absorption band at longer wavelength around 300nm.

- Eg:Saturated aldehydes shows both type of transitions ($n-\pi^*$, $\pi-\pi^*$) at {low energy and high energy} around 290 and 180 nm.

TERMS USED IN UV-VISIBLE SPECTROSCOPY

CHROMOPHORE

- Chromophore is defined as the nucleus or any isolated covalently bonded group responsible for the absorption of light radiation.

- Any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region.

  C=C , C=O ,NO_2 etc

- Some of the important chromophores are carbonyls,acids,esters,nitrile,ethylenic groups.

AUXOCHROME

- These are co-ordinatively saturated or un-saturated groups which themselves do not absorb radiations,but when present alongwith a chromophore enhances the absorbing properties of chromophore.

- Also known as colour enhancing group.

- All auxochromes have one or more non-bonding pair of electrons.

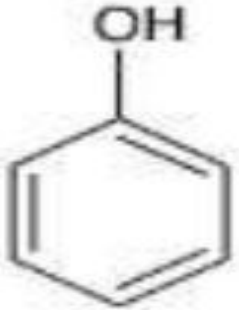
  $-NH_2$,-OH ,-OR,-COOH etc

- It extend the conjugation of a chromophore by sharing the non-bonding electrons.

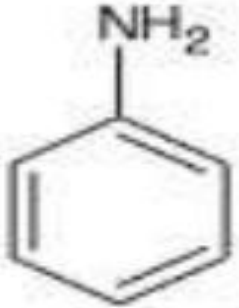
AUXOCHROME

e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



ABSORPTION CHARACTERISTICS OF SOME COMMON CHROMOPHORES

Chromophores: examples

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	Π —> Π*	171	15,000	hexane
C≡C	1-Hexyne	Π —> Π*	180	10,000	hexane
C=O	Ethanal	n —> Π* Π —> Π*	290 180	15 10,000	hexane hexane
N=O	Nitromethane	n —> Π* Π —> Π*	275 200	17 5,000	ethanol ethanol
C-X; X=Br X=I	Methyl bromide Methyl Iodide	n —> σ* n —> σ*	205 255	200 360	hexane hexane

ABSORPTION & INTENSITY SHIFTS

1) Bathochromic shift(red shift)

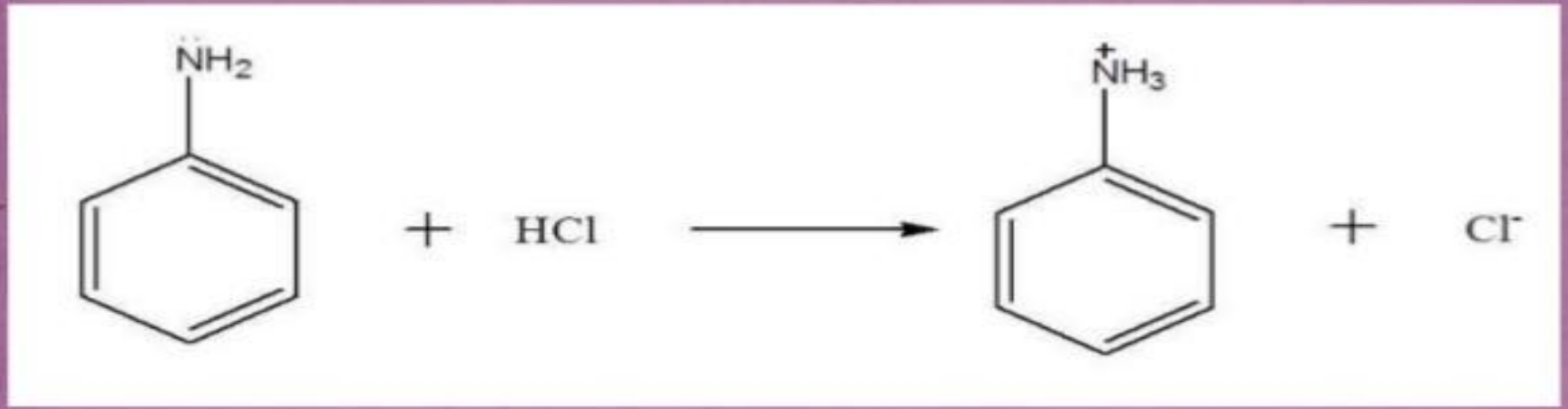
- When the absorption maxima(λmax)of a compound shifts to longer wavelength,it is known as bathochromic shift or red shift.
- The effect is due to the presence of auxochrome or by change of solvent.
- Eg: The **n-π^*** transition for carbonyl compounds experiences bathochromic shift when the polarity of solvent is decreased.

2) Hypsochromic shift(blue shift)

- When the absorption maxima (λmax) of a compound shifts to a shorter wavelength,it is known as hypsochromic shift or blue shift.

- The effect is due to the presence of a group causes removal of conjugation or by change of solvent.

Eg:



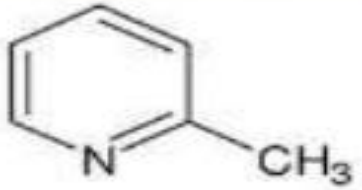
Aniline shows blue shift in acidic medium since it loses conjugation. Aniline(280nm) & Anilinium ion (-203nm).

3) Hyperchromic effect

When the absorption intensity(ε) of a compound is increased,it is known as hyperchromic shift.

The introduction of auxochrome usually increases absorption intensity.

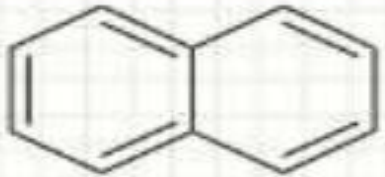
Pyridine
λ_{max} = 257 nm
ε = 2750



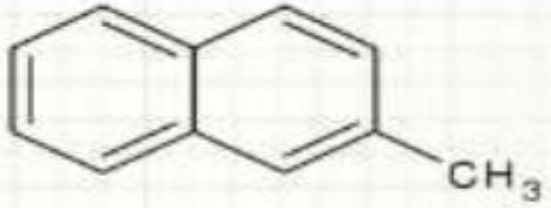
2-methyl pyridine
λ_{max} = 260 nm
ε = 3560

4) Hypochromic effect

When the absorption intensity(ε)of a compound is decreased,it is known as hypochromic shift.
The introduction of a group which distorts the geometry of molecule causes hypochromic effect.

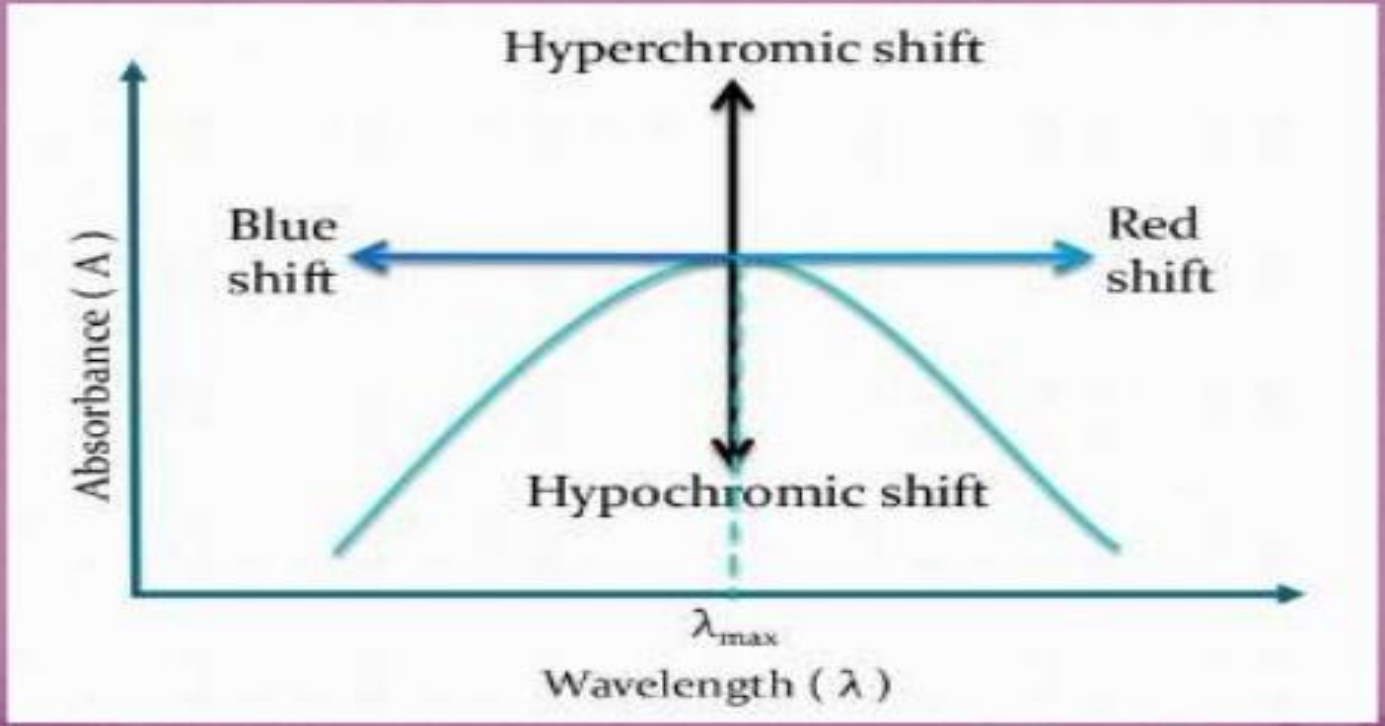


Naphthalene
ε = 19000



2-methyl naphthalene
ε = 10250

SHIFTS & EFFECTS



1. Introduction

In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as Woodward-Fieser Rules. It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore.

Robert Burns Woodward

Louis Frederick Fieser

2. WOODWARD- FIESER RULES

Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

According to Woodward's rules the λ_{max} of the molecule can be calculated using a formula:

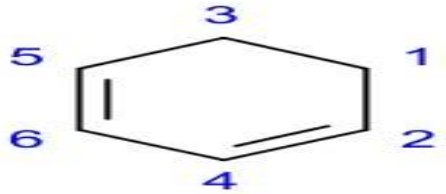
$$\lambda_{max} = \textit{Base value} + \Sigma\ \textit{Substituent Contributions} + \Sigma\ \textit{Other Contributions}$$

There are three sets of rules

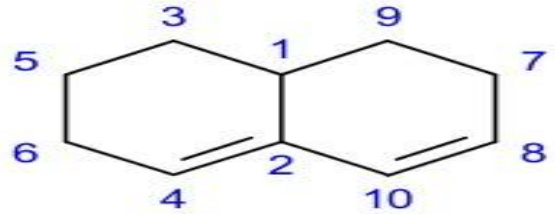
1. Woodward-Fieser rule for Conjugated dienes and polyenes.
2. For - unsaturated Carbonyl compounds.
3. For Aromatic compounds or Benzoyl derivatives.

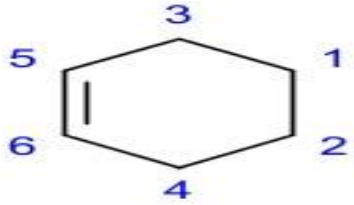
3.1 Woodward Fieser rule for Conjugated Dienes and Polyenes

a. **Homoannular Diene:-** Cyclic diene having conjugated double bonds in same ring.

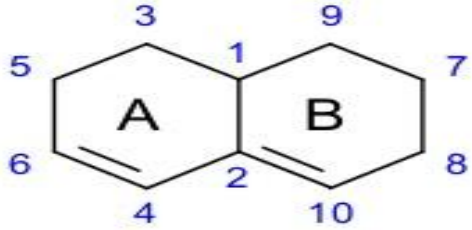


b. **Heteroannular Diene:-** Cyclic diene having conjugated double bonds in different rings.



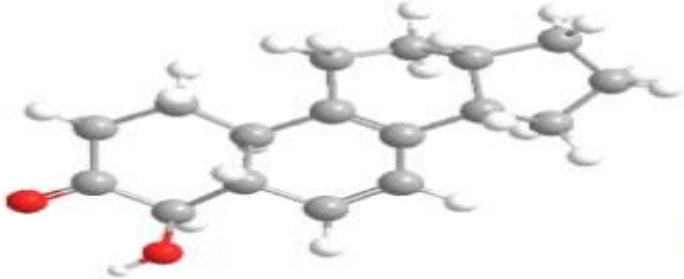


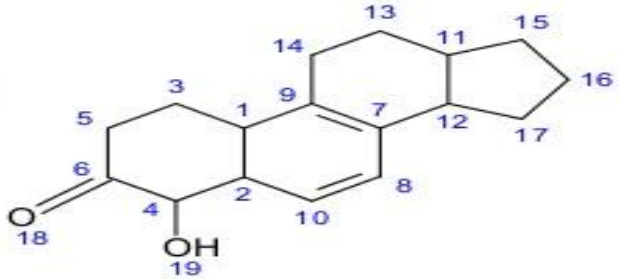
d. **Exocyclic double bond: -** Double bond in which one of the doubly bonded atoms is a part of a ring system.



Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

e. **Double bond extending :-** When more double bonds are present other than conjugations.

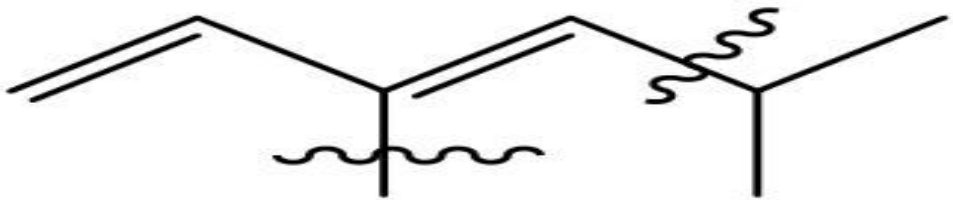




Parent Value	
Acyclic conjugated dienes and Heteroannular conjugated dienes	215 nm
Homoannular conjugated dienes	253 nm
Acyclic trienes	245 nm
Increments	
Each alkyl substitute or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochromes	
-OR	6 nm
-SR	30 nm
-Cl,-Br	5 nm
-NR2	60 nm
-OCOCH3	0 nm

3.3 Example of Woodward Fieser rule for Conjugated Dienes and Polyenes

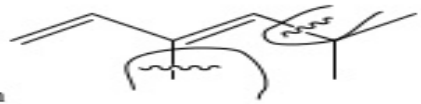
1. Example 1



(3*E*)-3,5-dimethylhexa-1,3-diene—ethane (1/2)

Here,

Parent value for Acyclic conjugated diene = 215 nm

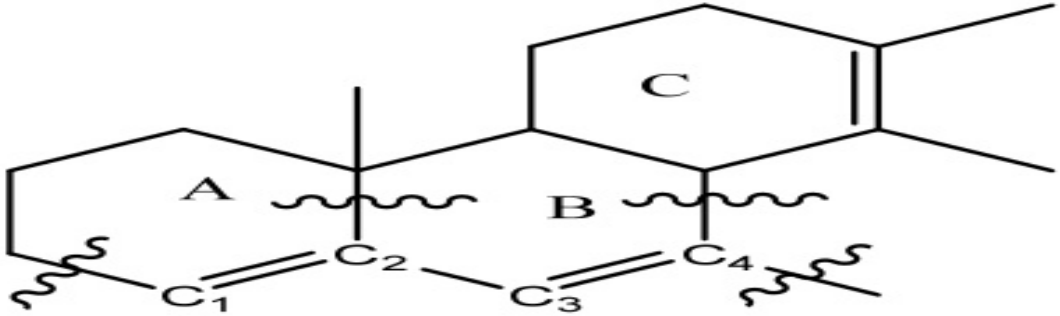


Alkyl Substitute or Ring residue at C-3 and C-5 = 5+5= 10 nm

So, λ_{max} would be = (215+10) nm = 225 nm

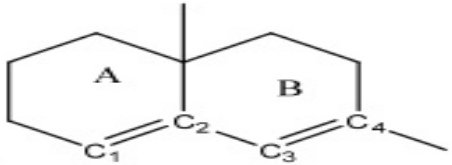
Observed value = 225 + - 5 nm

2. Example 2

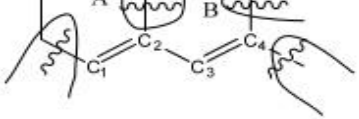


4a,7,8,9-tetramethyl-2,3,4,4a,4b,5,6,8a-octahydrophenanthrene

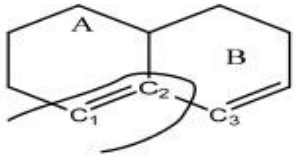
Here,



Parent value for Heteroannular conjugated diene = 215 nm



Alkyl substitute or Ring residue = (5 x 4) nm = 20 nm

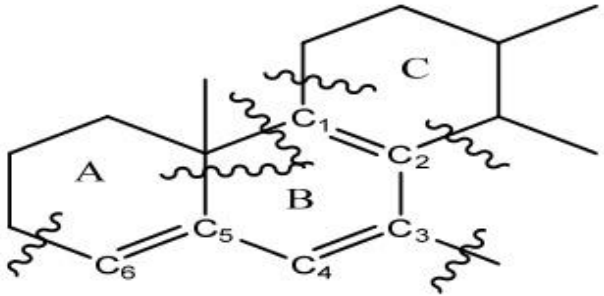


Exocyclic double bond (in respect of B ring) = 5 nm

So, λ_{max} would be = (215+20+5) nm = 240 nm

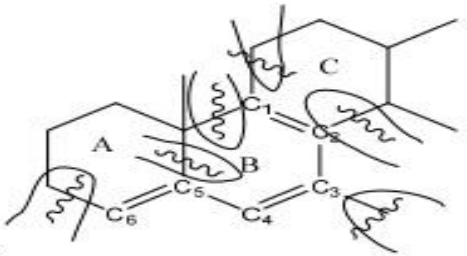
Observed value = 240 + - 5 nm

3. Example 3

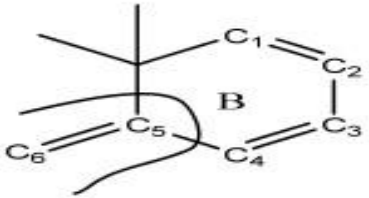


1,2,4b,10-tetramethyl-1,2,3,4,4b,5,6,7-octahydrophenanthrene

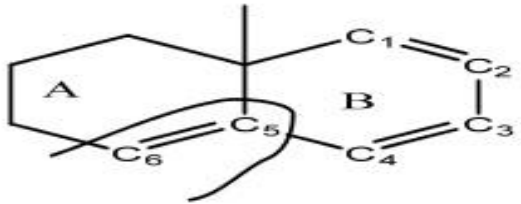
Here, Parent value Homoannular conjugated diene = 253 nm



Alkyl substitute or Ring residue = (5 x 6) nm = 30 nm



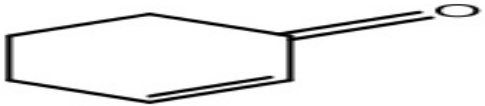
Exocyclic double bond (in respect with ring B) = 5 nm



Double bond extending conjugation = 30 nm

So, λ_{max} would be = (253+30+30+5) nm = 318 nm

Observed value would be = 318 + - 5 nm



6-membered cyclic

4.2 Parent values and increments for different Substituents or Groups

Parent Value			
α,β -unsaturated acyclic or six membered ring ketone	215 nm		
α,β -unsaturated five membered ring ketone	202 nm		
α,β -unsaturated aldehyde	207 nm		
Increments			
Each alkyl substitute or ring residue			
At position α	10 nm		
At position β	12 nm		
At γ position and higher position	18 nm		
Each Exocyclic double bond	5 nm		
Double bond extending conjugation	30 nm		
Homoannular conjugated diene	39 nm		
Auxochromes	**α**	**β**	**γ**
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
-OCOCH3	6	6	6

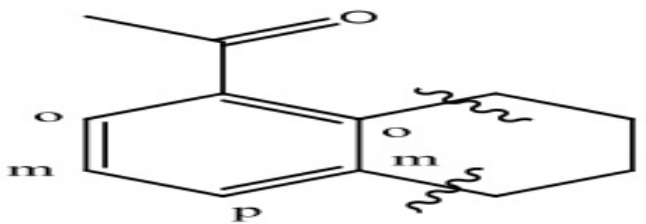
5.1 Woodward Fieser rule for Aromatic compounds or Benzoyl derivatives.

5.2 Parent values and increments for Benzoyl Derivatives

Parent Value	
X = alkyl / ring residue, ArCOR	246 nm
X = H, ArCHO	250 nm
X = OH / O-alkyl, $ArCO_2H$, $ArCO_2R$	230 nm
Increments	
R = alkyl / ring residue	o, m = 3 nm
	p = 10 nm
R = OH / O-alkyl	o, m =7 nm
	p = 25 nm
$R = NH_2$	o, m = 23 nm
	p = 58 nm

5.3 Example of Woodward Fieser rule for Benzoyl derivatives

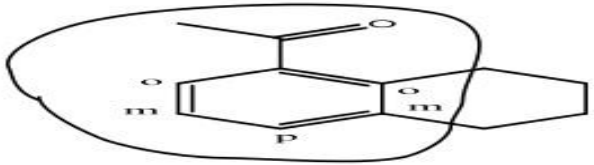
1. Example 1

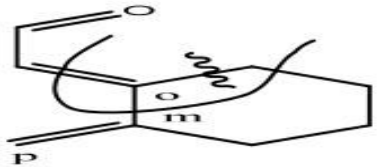


1-(5,6,7,8-tetrahydronaphthalen-1-yl)ethan-1-one

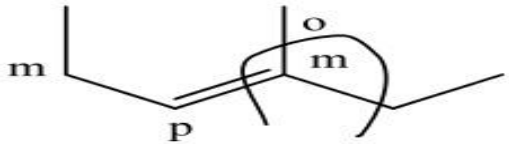
Here,

Parent value for Benzoyl group (aliphatic methyl group) = 246 nm





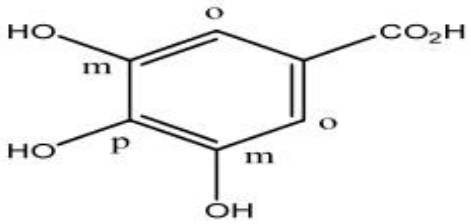
Auxochrome at Ortho Position = 3 nm



Auxochrome at Meta position = 3 nm

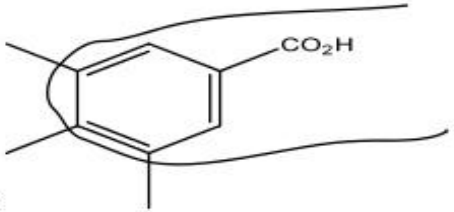
So, λ_{max} would be = (246+3+3) nm = 252 nm

Observed value would be = 252 + - 5 nm

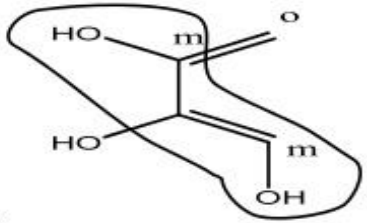


3,4,5-trihydroxybenzoic acid

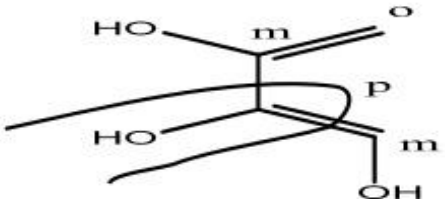
Here,



Parent value for Benzoyl group (o-Alkyl) = 230 nm



Auxochrome –OH at Meta position = (7 x 2) nm = 14 nm

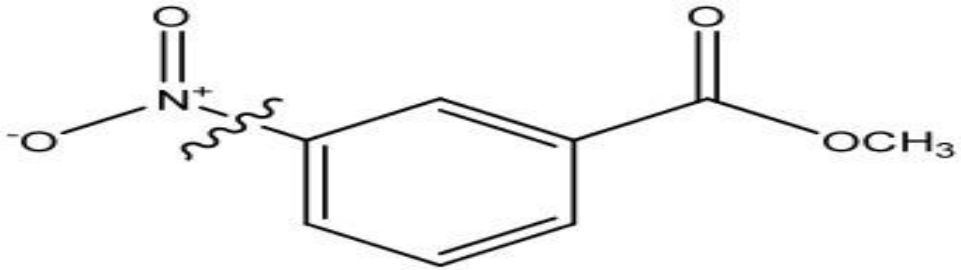


Auxochrome –OH at Para position = 25 nm

So, λ_{max} would be = (230+25+14) nm = 269 nm

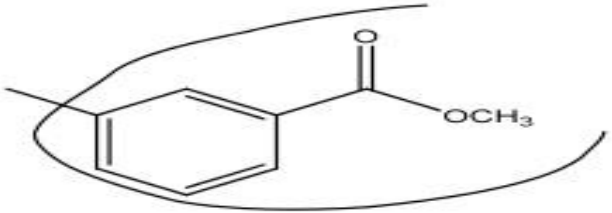
Observed value would be = 269 + - 5 nm

3. Example3

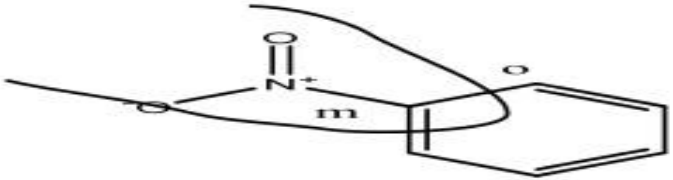


methyl 3-nitrobenzoate

Here,



Parent value for Ester functionality (-OR) = 230 nm



There is no value listed for a Meta nitro group.

So, λ_{max} would be more than 230 nm.