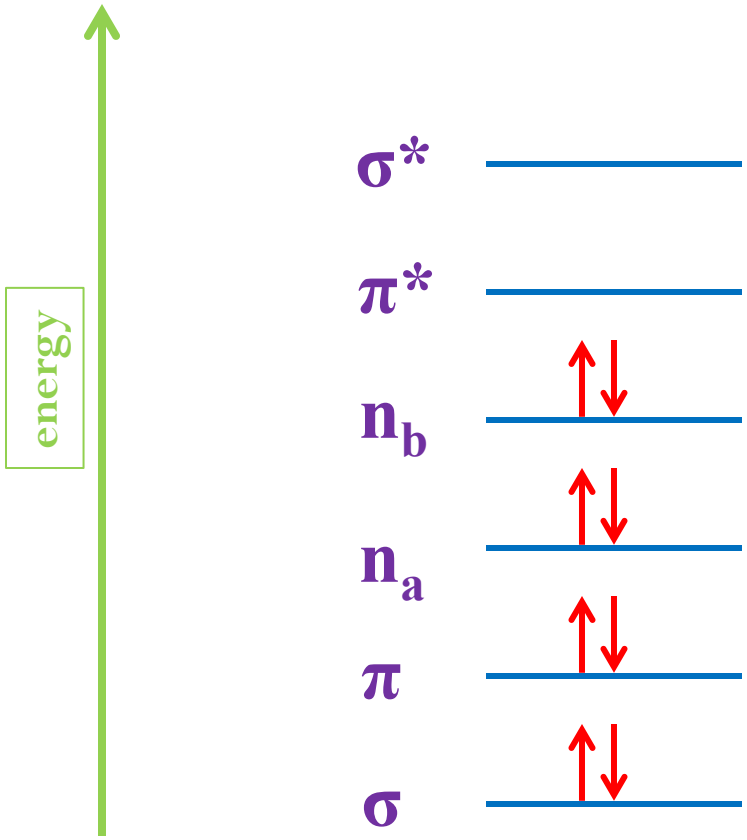
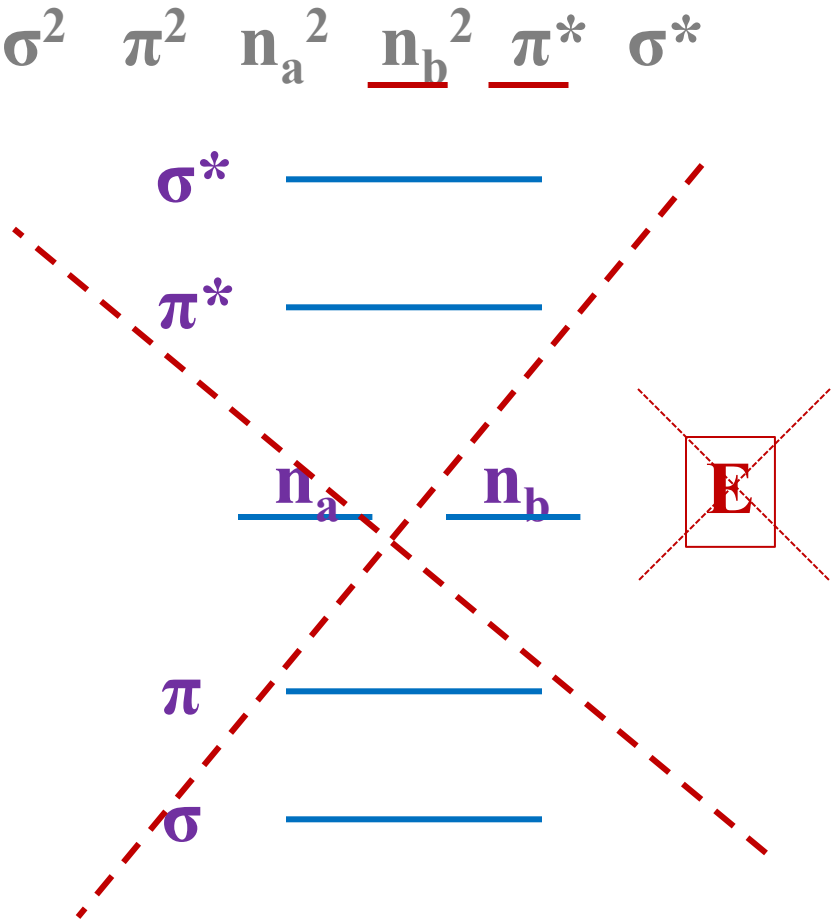
Spectroscopy in Inorganic Chemistry

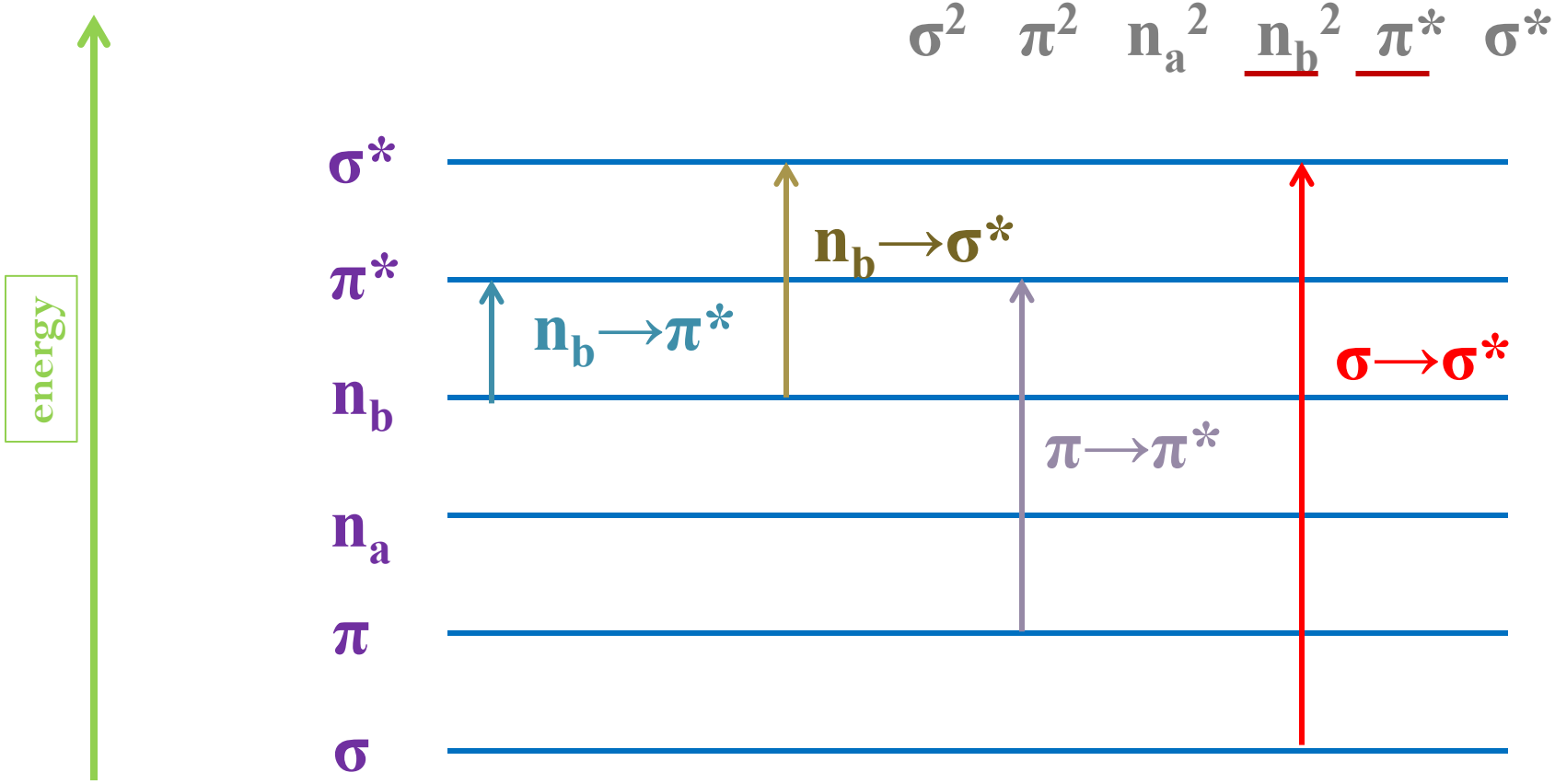
Electronic Absorption Spectroscopy

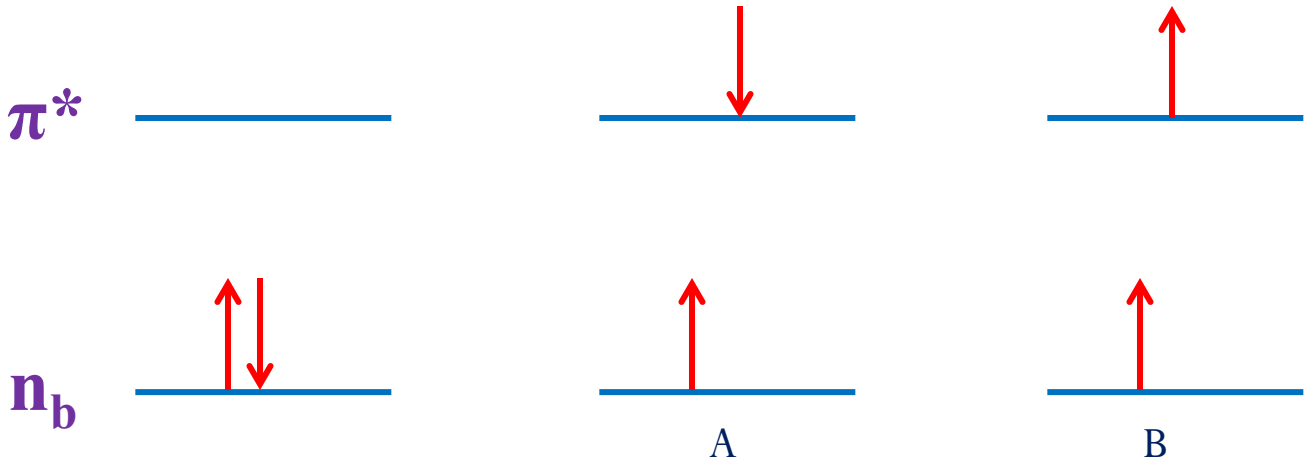
Nomenclature

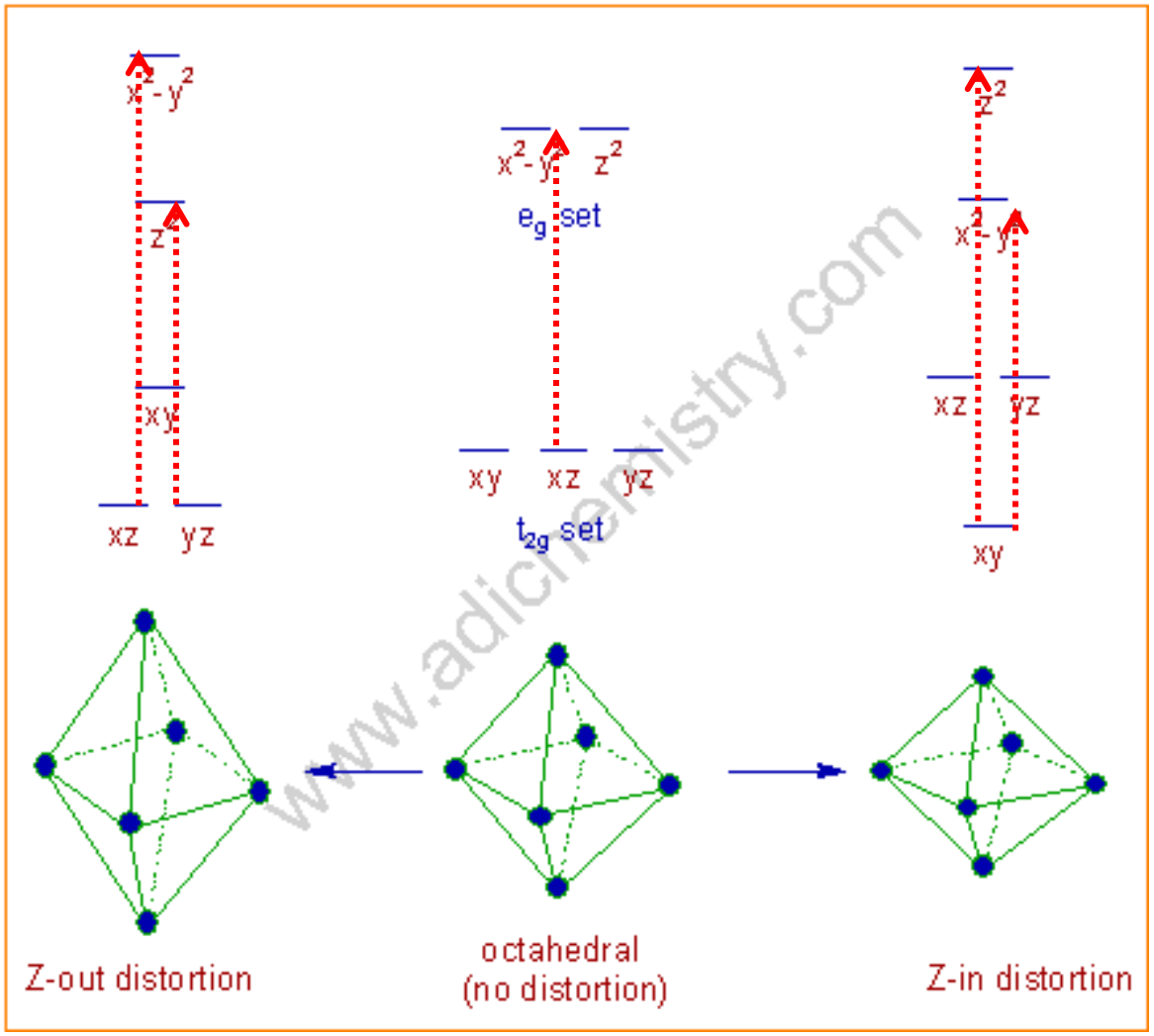


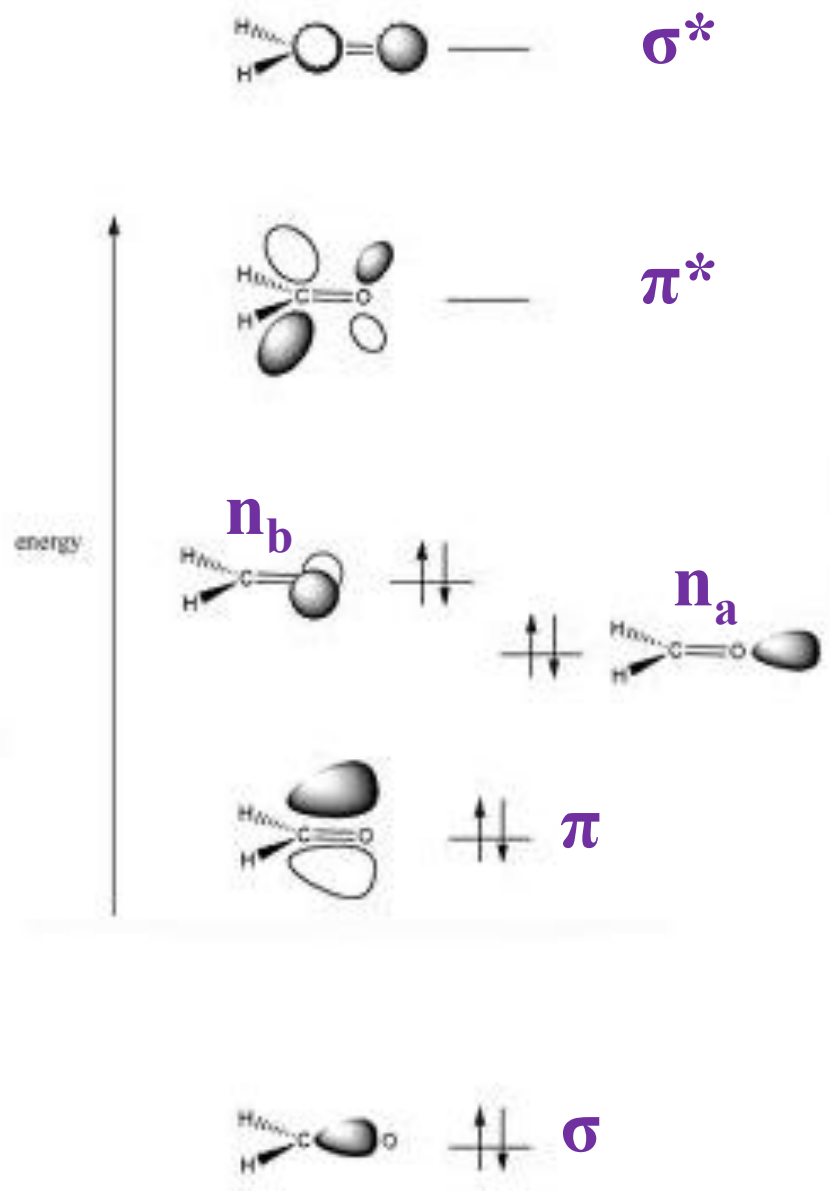


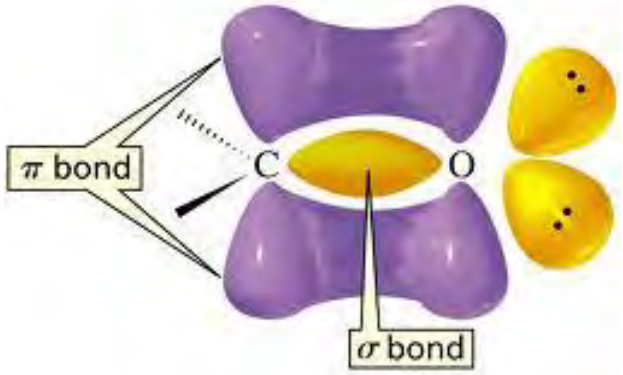
Nomenclature




π*
n_b
A
B
2S+1=1
Singlet
2S+1=1
Singlet
2S+1=3
Triplet



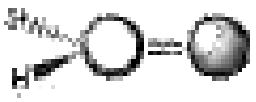

σ*
π*
energy
n_b
n_a
π
σ


π bond
C
O
σ bond

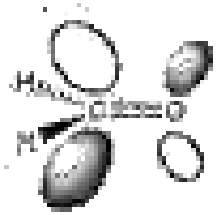
Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	Linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

π	1	-1	1	-1	B_1



σ*	1	1	1	1	a_1



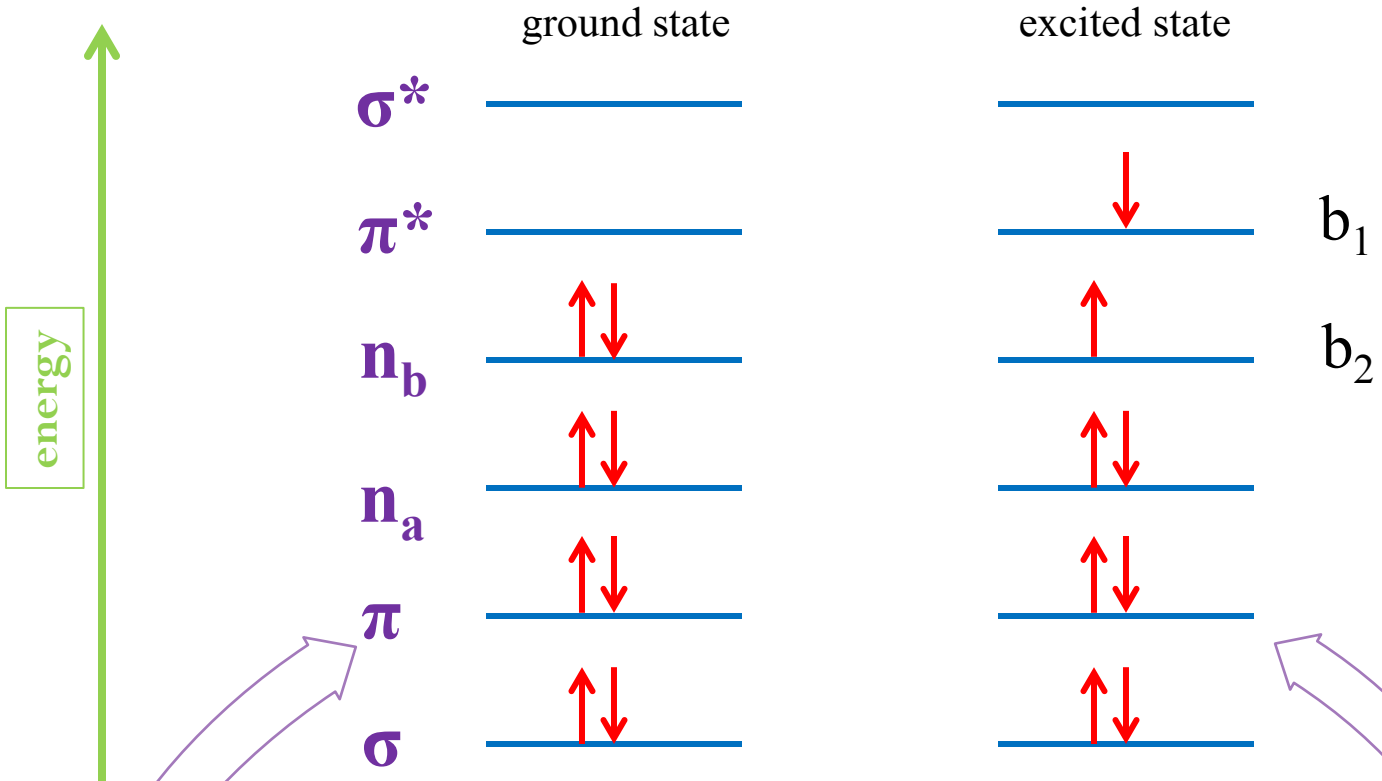
π*	1	-1	1	-1	b_1

n_b	1	-1	-1	1	b_2

n_a	1	1	1	1	a_1

π	1	-1	1	-1	b_1

σ	1	1	1	1	a_1



	E	C_2 (z)	σ_v(xz)	σ_v(yz)
$b_2 \times b_1$	1×1	-1×-1	-1×1	1×-1
A_2	1	1	-1	-1

$^1A_1 \rightarrow {}^1A_2$

$^1A_1$ (n,π*) → $^1A_2$

General symbol $\Gamma_1 \rightarrow \Gamma_2$

A. Organics: Involving π, σ, n electrons

Saturated compounds

σ→σ* (<150 nm), n →σ* (<250 nm): deep UV

Double bonds/unsaturated systems

less energy to π*

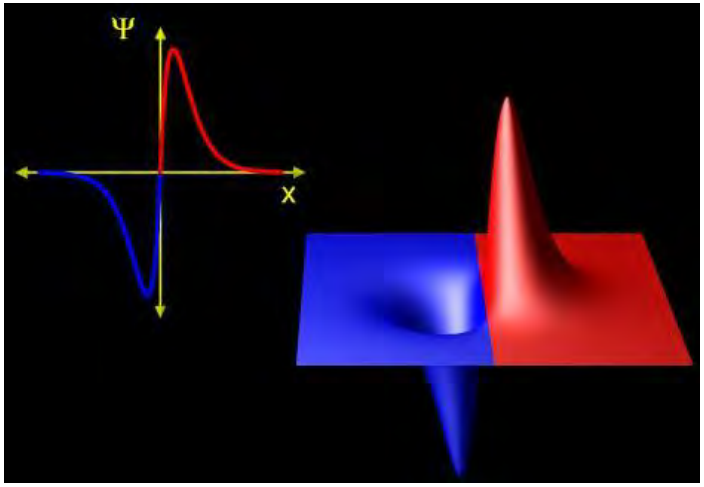
π→π*, n →π* transitions: (200-700 nm)

B. Metal-ligand complexes: charge transfer transition

Electron moves between ligand and metal. One must act as donor and other as acceptor.

C. Inorganics: d-d transition

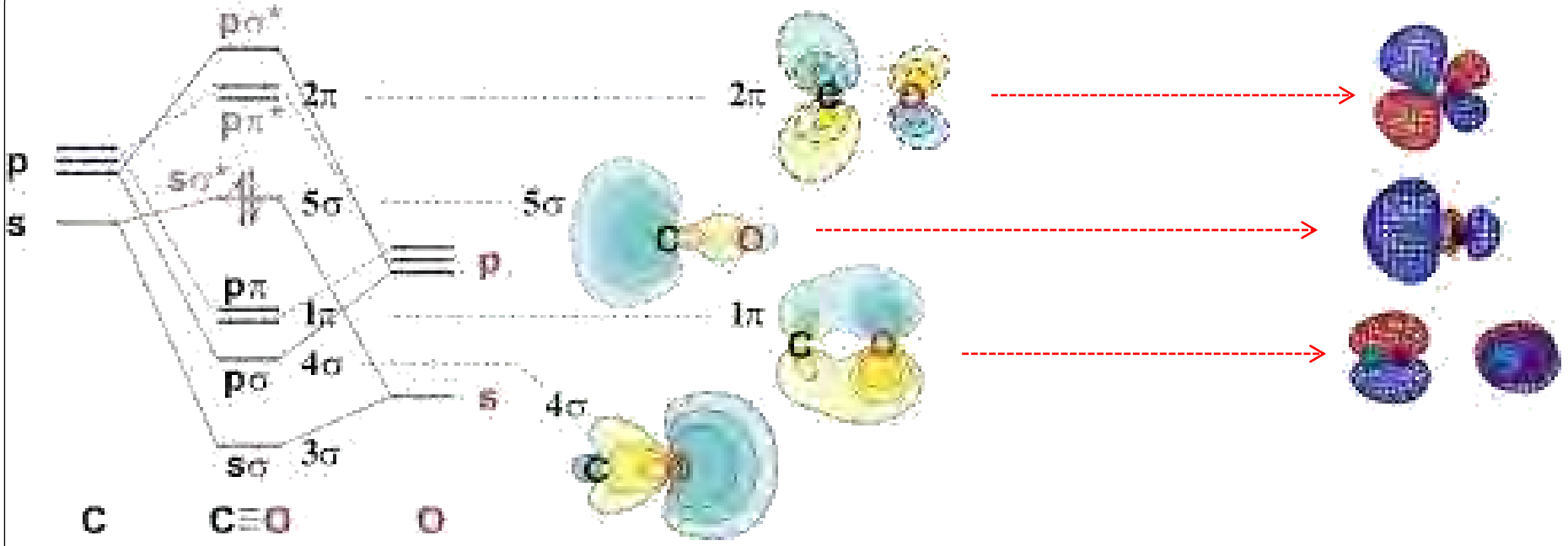
Additionally, transitions between d orbitals split by presence of ligand field. Usually in visible.

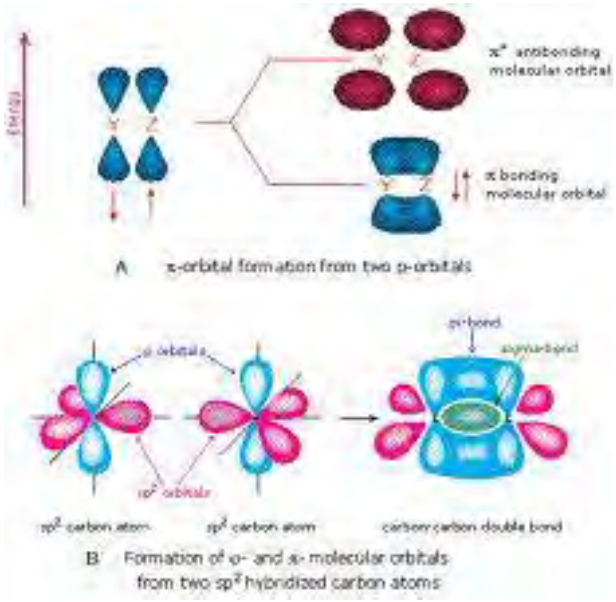


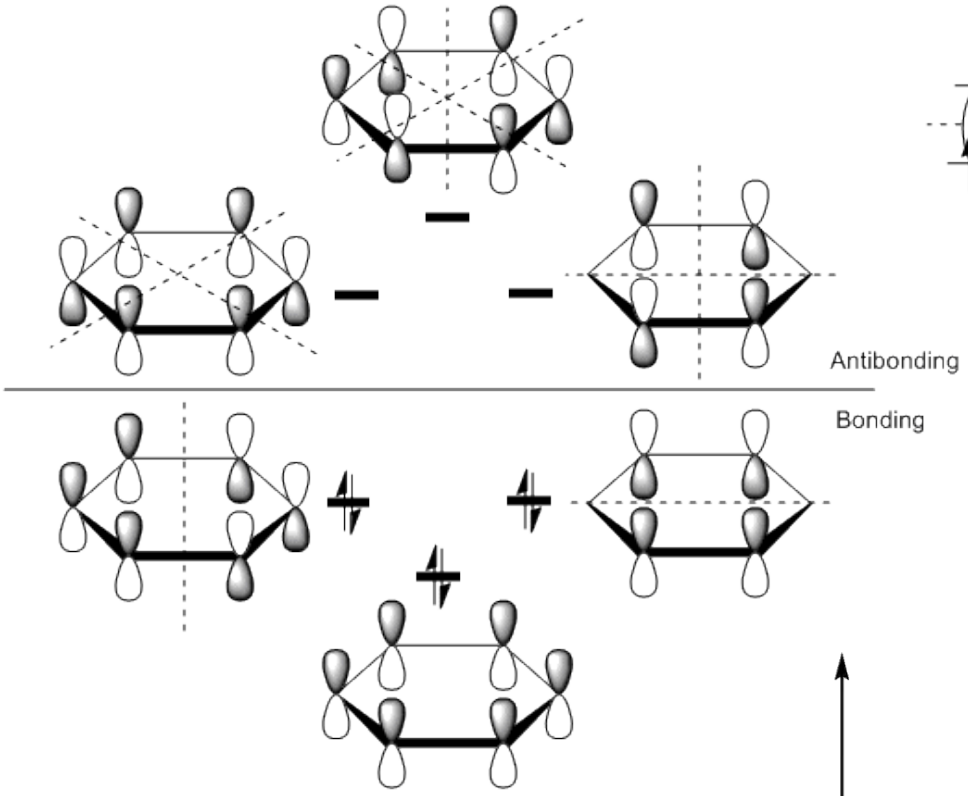
$2p_x$ wave function ψ_{2px}.

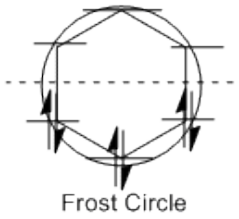
$$\psi_{\pi} = a\varphi_{p^o} + b\varphi_{p^c}$$

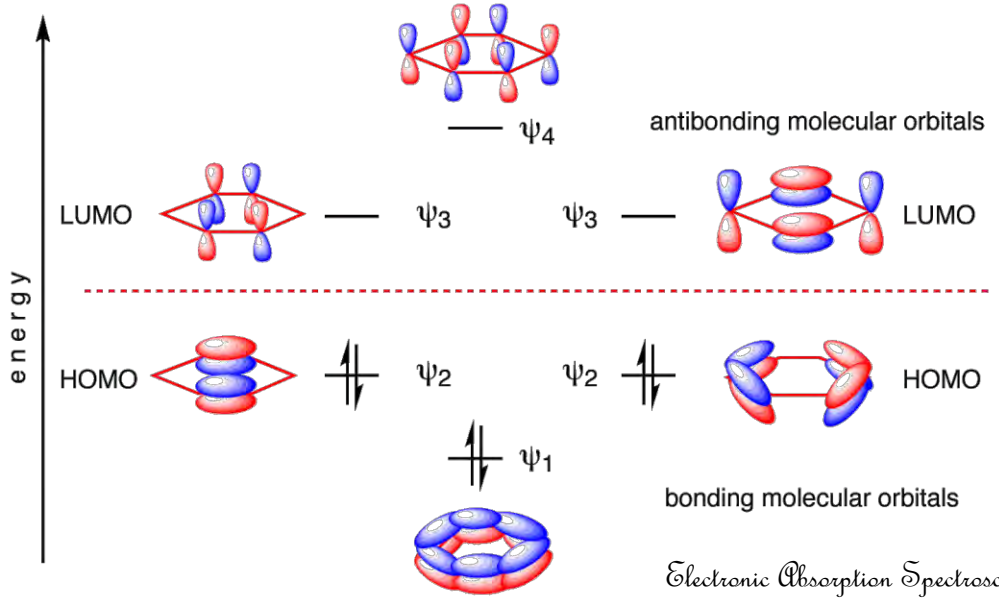
$$\psi_{\pi^*} = b'\varphi_{p^o} - a'\varphi_{p^c}$$

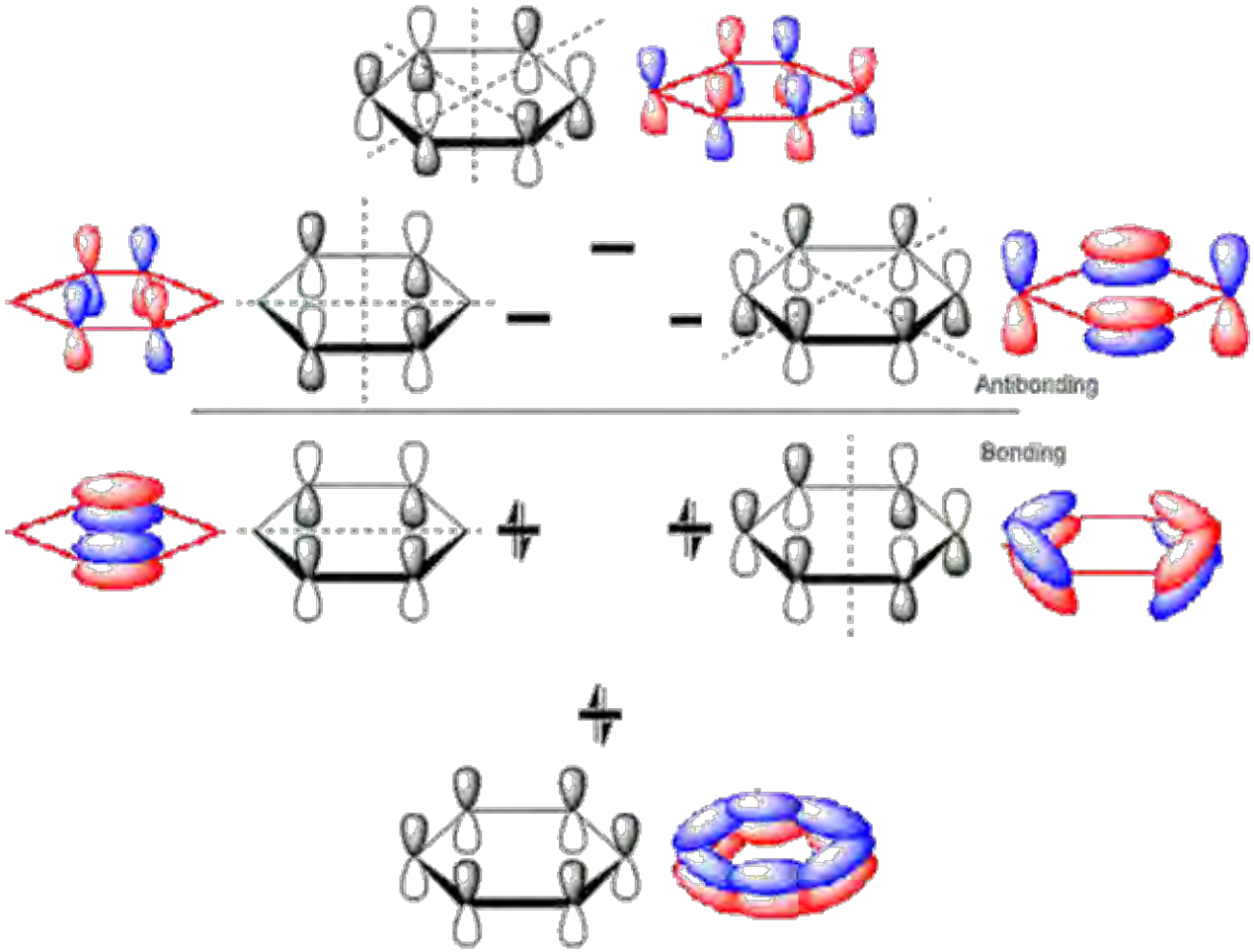

pσ*
pπ*
sσ*
2π
5σ
pπ
1π
pσ
4σ
sσ
3σ
p
s
C
C≡O
O

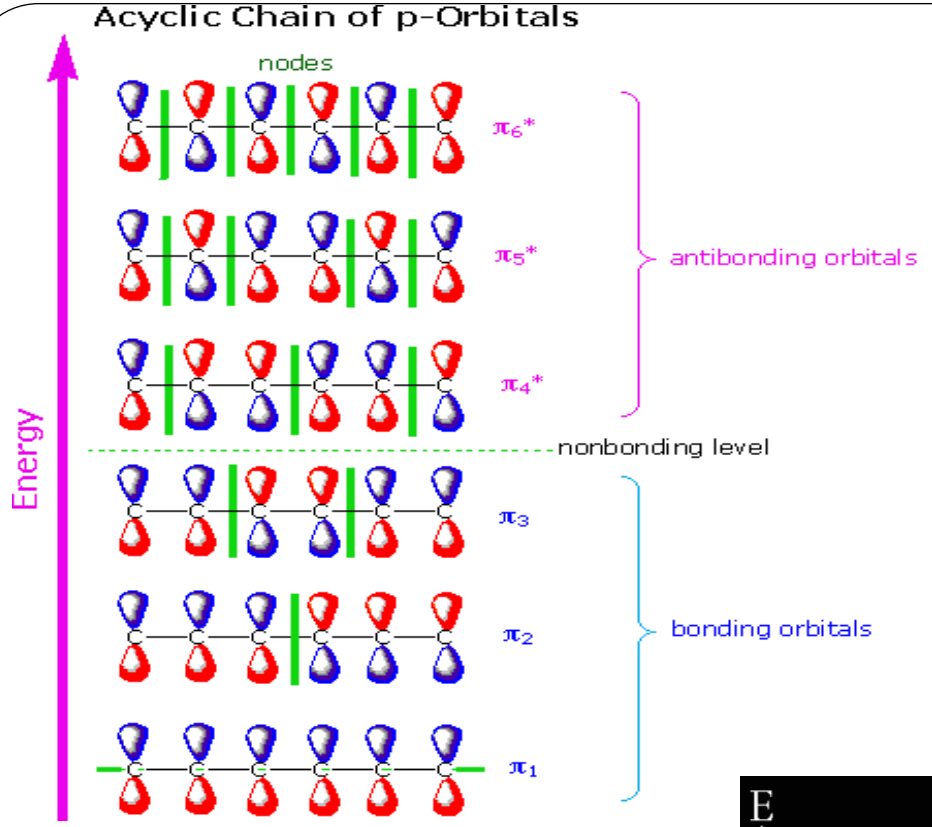

π* antibonding molecular orbital
π bonding molecular orbital
A π-orbital formation from two p-orbitals
π-bond
σ-bond
sp² carbon atom
sp² carbon atom
carbon-carbon double bond
B Formation of π- and σ- molecular orbitals from two sp² hybridized carbon atoms

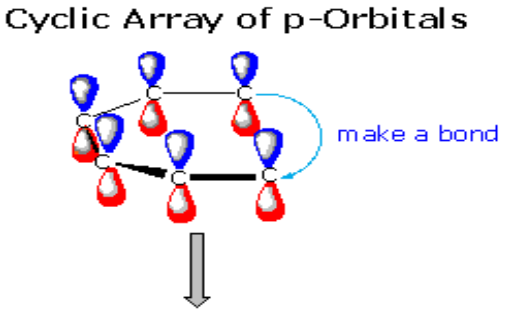

Antibonding
Bonding

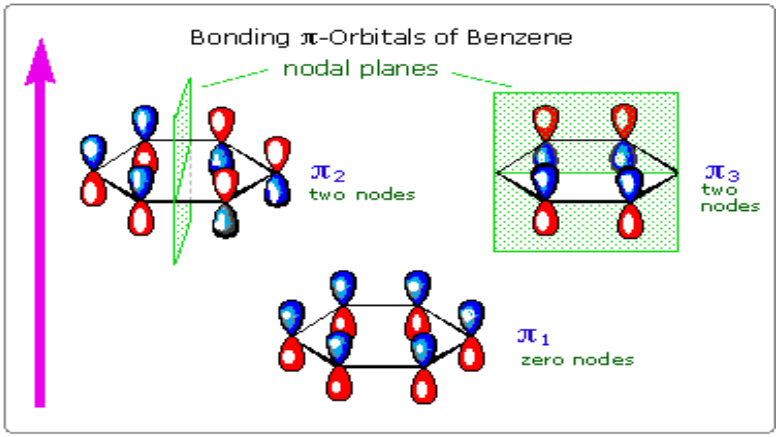

Frost Circle

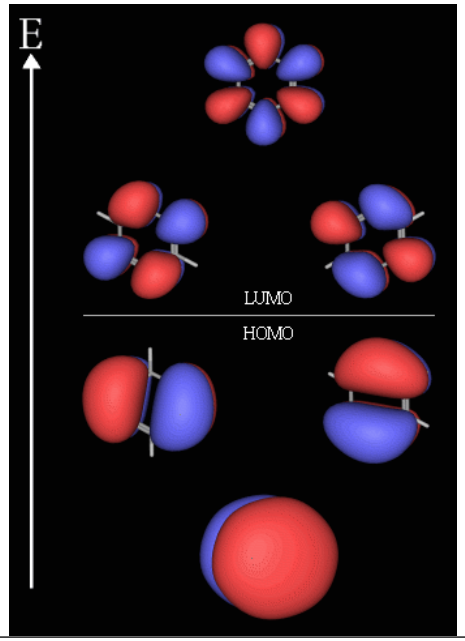

energy
ψ4
antibonding molecular orbitals
LUMO
ψ3
ψ3
LUMO
HOMO
ψ2
ψ2
HOMO
ψ1
bonding molecular orbitals


3 node
2 node
Antibonding
Bonding
1 node
0 node


Acyclic Chain of p-Orbitals
nodes
Energy
π6*
π5*
π4*
antibonding orbitals
nonbonding level
π3
π2
π1
bonding orbitals

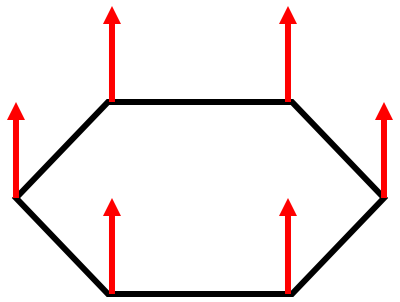

Cyclic Array of p-Orbitals
make a bond


Bonding π-Orbitals of Benzene
nodal planes
π2
two nodes
π3
two nodes
π1
zero nodes


E
LUMO
HOMO

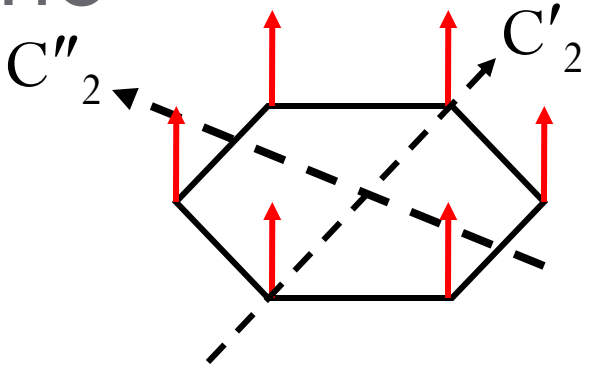
π Bonding of Benzene

Benzene belongs to point group D_{6h}. In determining the orbital combinations for π bonding, we need to obtain Γ_π by looking only at the p_z orbitals on each carbon atom.



We need only consider those orbitals on carbon atoms that remain in place for a given symmetry operation.

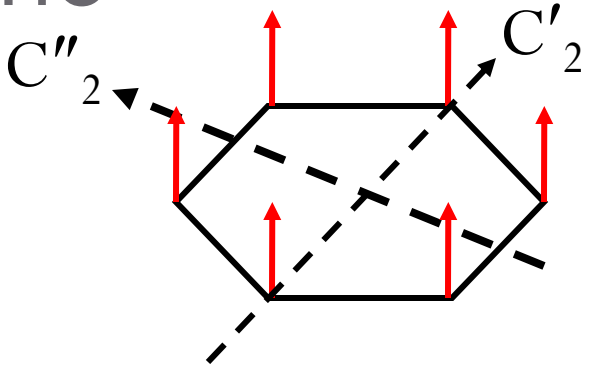
π Bonding of Benzene



z axis

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π												

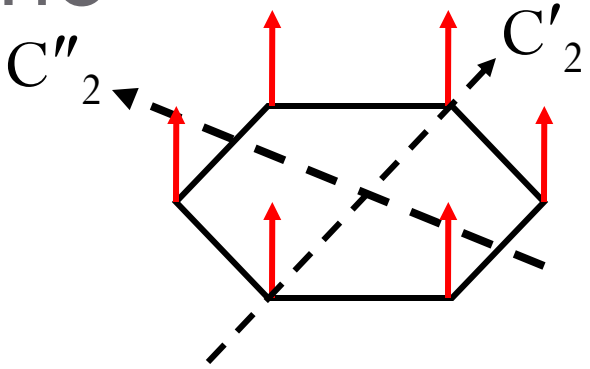
π Bonding of Benzene



z axis

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

π Bonding of Benzene



z axis

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

This reduces to: $B_{2g} + E_{1g} + A_{2u} + E_{2u}$

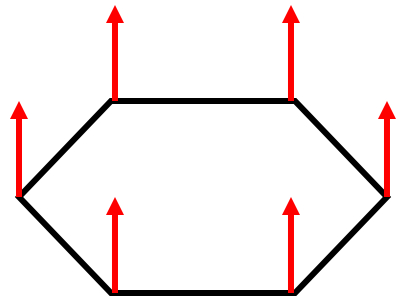
π Bonding of Benzene

$$\Gamma\pi: \; B_{2g} + E_{1g} + A_{2u} + E_{2u}$$

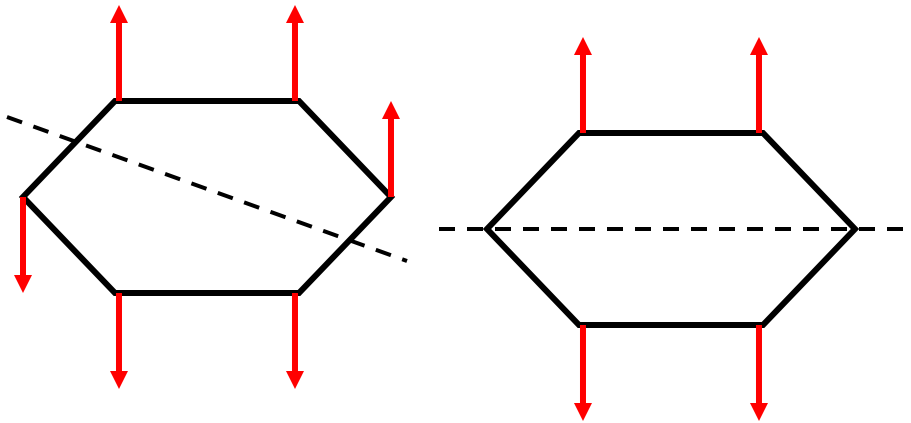
Group theory can be used to draw each of the π molecular orbitals. Molecular orbitals with fewer nodes are lower in energy (more bonding), and those with more nodes are higher in energy (more antibonding).

π Bonding of Benzene

$\Gamma\pi$: $B_{2g} + E_{1g} + A_{2u} + E_{2u}$



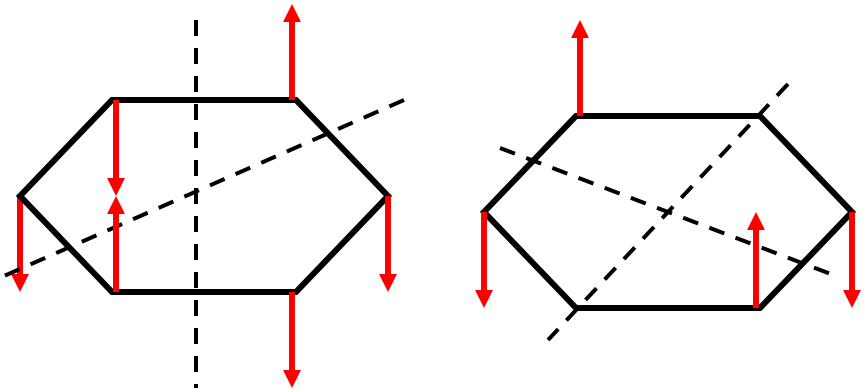
A_{2u} fully bonding and lowest in energy



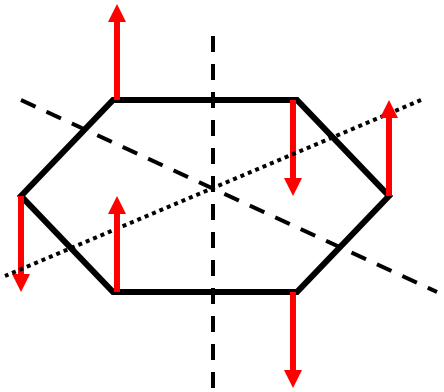
E_{1g} degenerate bonding orbitals with one node

π Bonding of Benzene

$\Gamma\pi$: $B_{2g} + E_{1g} + A_{2u} + E_{2u}$



E_{2u} degenerate largely anti-bonding orbitals with two nodes



B_{2g} fully anti-bonding orbital with three nodes