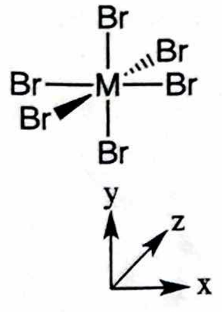
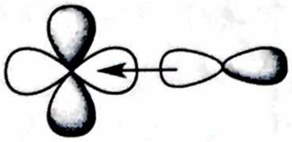
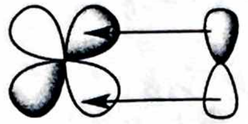
CH431: π interactions in metal complexes

π donor and π acceptor ligands interact with metal centers in both a σ and π type fashion.

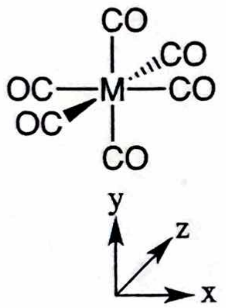


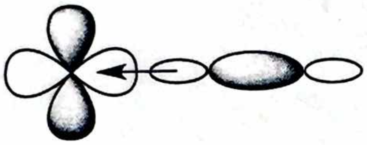


σ donor interaction between metal d_{x2-y2} and Br p_x

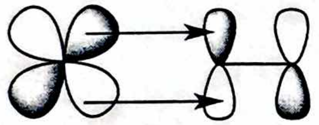


π donor interaction between metal d_{xy} and Br p_y
(also occurs between d_{xz} and p_z)





σ donor interaction between metal d_{x2-y2} and CO HOMO (σ bonding orbital between two p orbitals)



π acceptor interaction between metal d_{xy} and CO LUMO (π* orbital)
(also occurs between d_{xz} and other π*)

In all, 12 different orbitals from the 6 ligands can interact with the metal in a pi-type fashion (2 orbitals per ligand).

Γ_π can be calculated for these interactions:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_π	12	0	0	0	−4	0	0	0	0	0

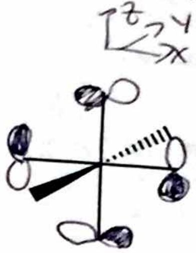
Using the reduction formula, $\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$

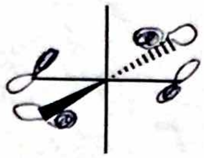
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(xy, xz, yz)
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

End result: as we determined by our drawings, we see that the π interactions will occur with the metal d_{xy}, d_{xz}, and d_{yz} orbitals (t_{2g} orbitals)

What do the different T_{2g} SALCs look like for Br^- and CO?

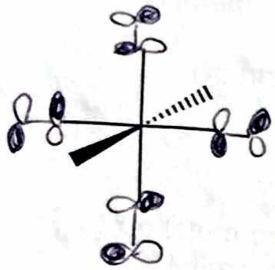
Br^-

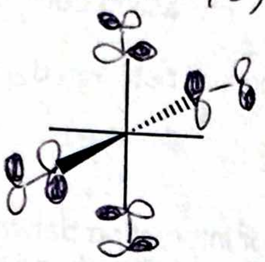


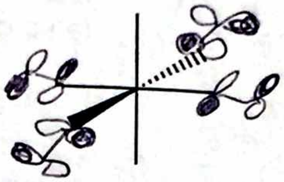


(like d_{xz}) (like d_{yz}) (like d_{xy})

CO

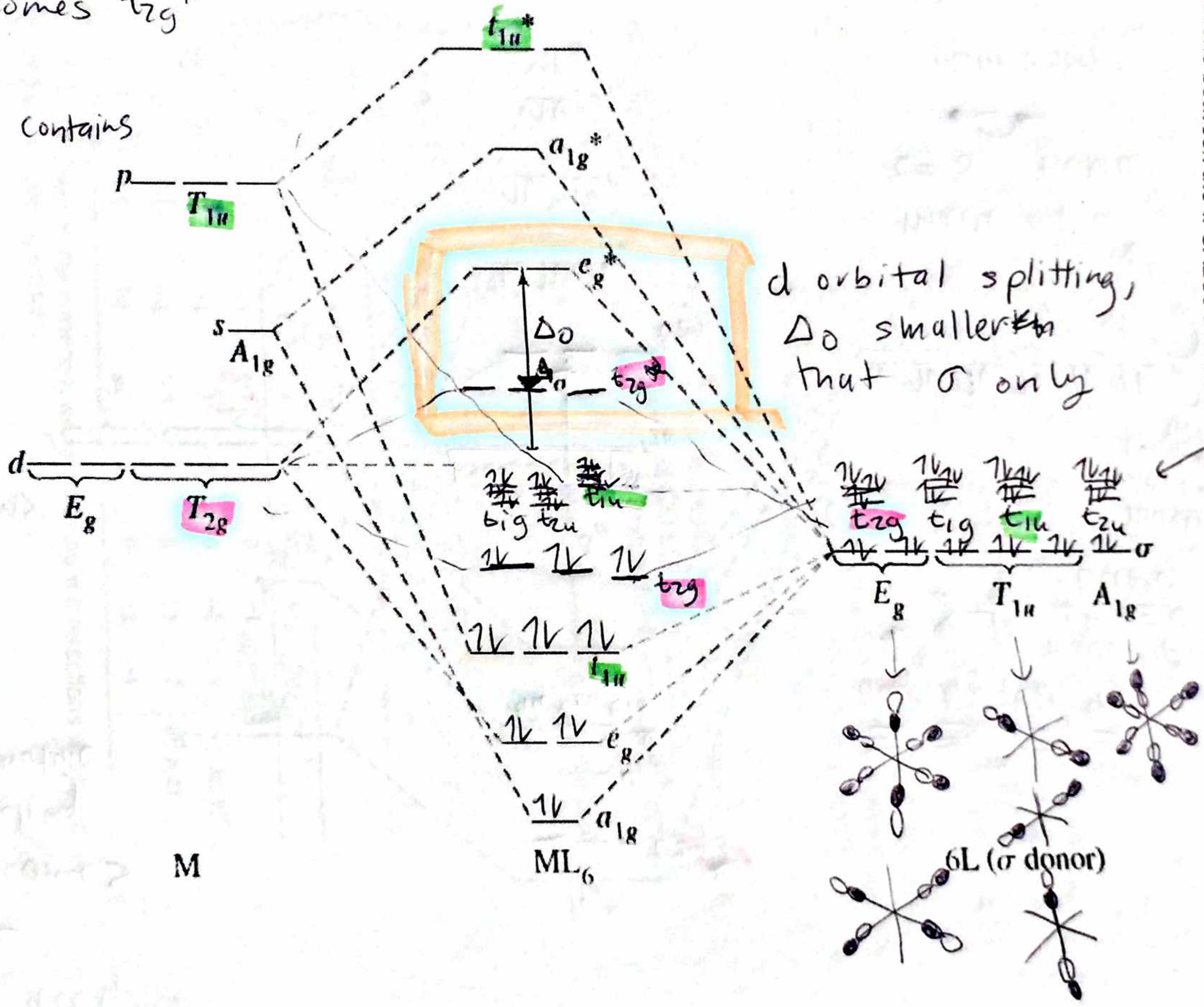






Consider Br⁻. Below is the MO diagram showing only the sigma interactions between one set of the Br p orbitals (the σ SALCs) and the metal center. 1) Where do the π SALCs show up on the right hand side of the diagram? (how do they compare in energy to the σ SALCs) 2) Draw in the interactions between the π SALCs and the metal d orbitals.

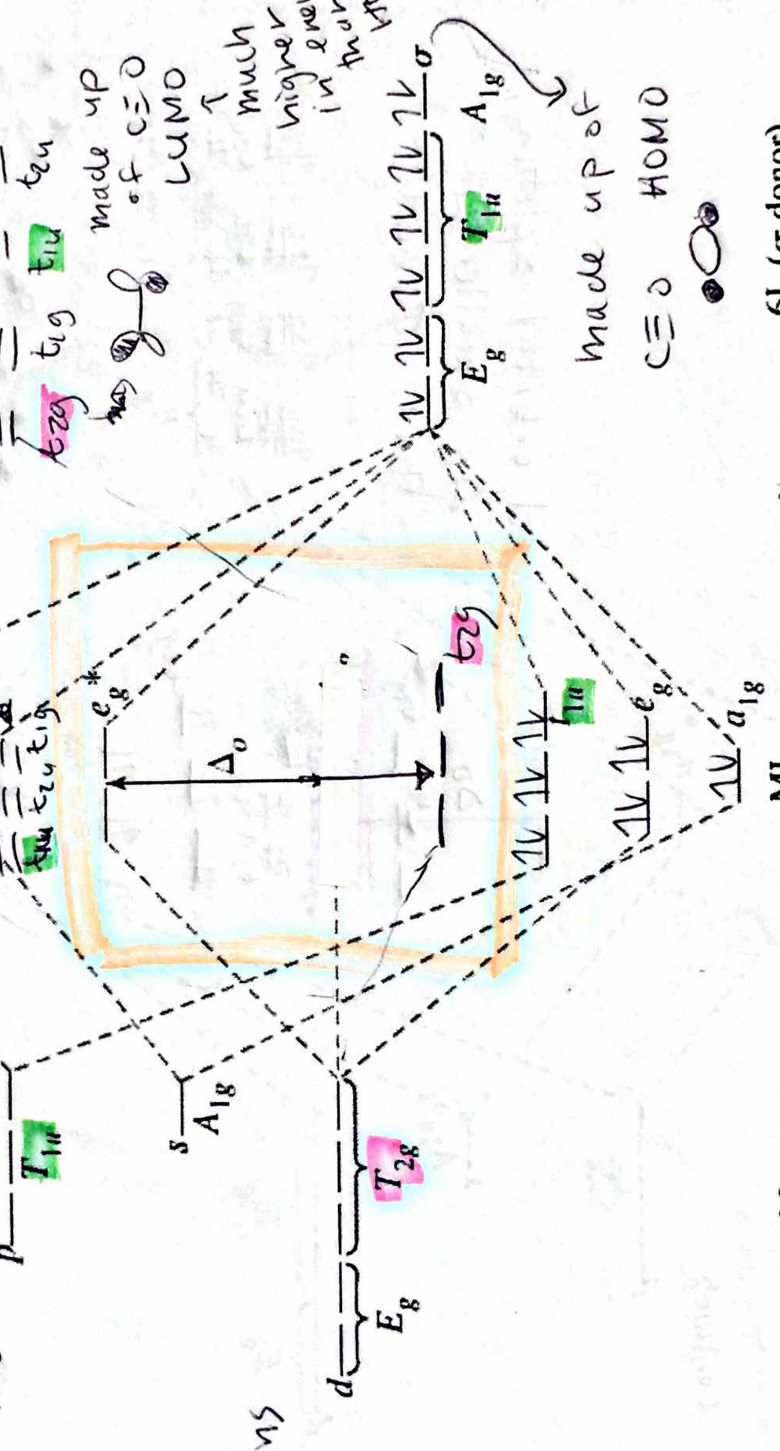
Δ_o decreases w/ π donor because t_{2g} becomes t_{2g}^*
↑
t_{2g} that contains metal d electrons



d orbital splitting, Δ_o smaller ~~than~~ that σ only

π SALCs are close in energy to σ SALCs, but the are made of Br⊖ p orbitals

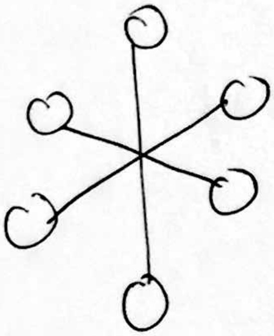
Consider CO. Below is the MO diagram showing only the sigma interactions between the σ SALCs for the CO HOMOs and the metal center. 1) Where do the π SALCs show up on the right hand side of the diagram? (how does the energy of the CO π* LUMO compare to the HOMO?) 2) Draw in the interactions between the π SALCs and the metal d orbitals.



Δ_o increases w/ π acceptor because t_{2g} becomes ↑ bonding in nature

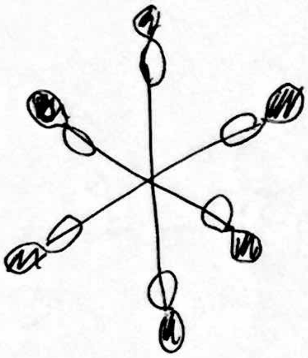
t_{2g} that contains metal d electrons

σ SALCs in octahedral



(w/ s orbitals)

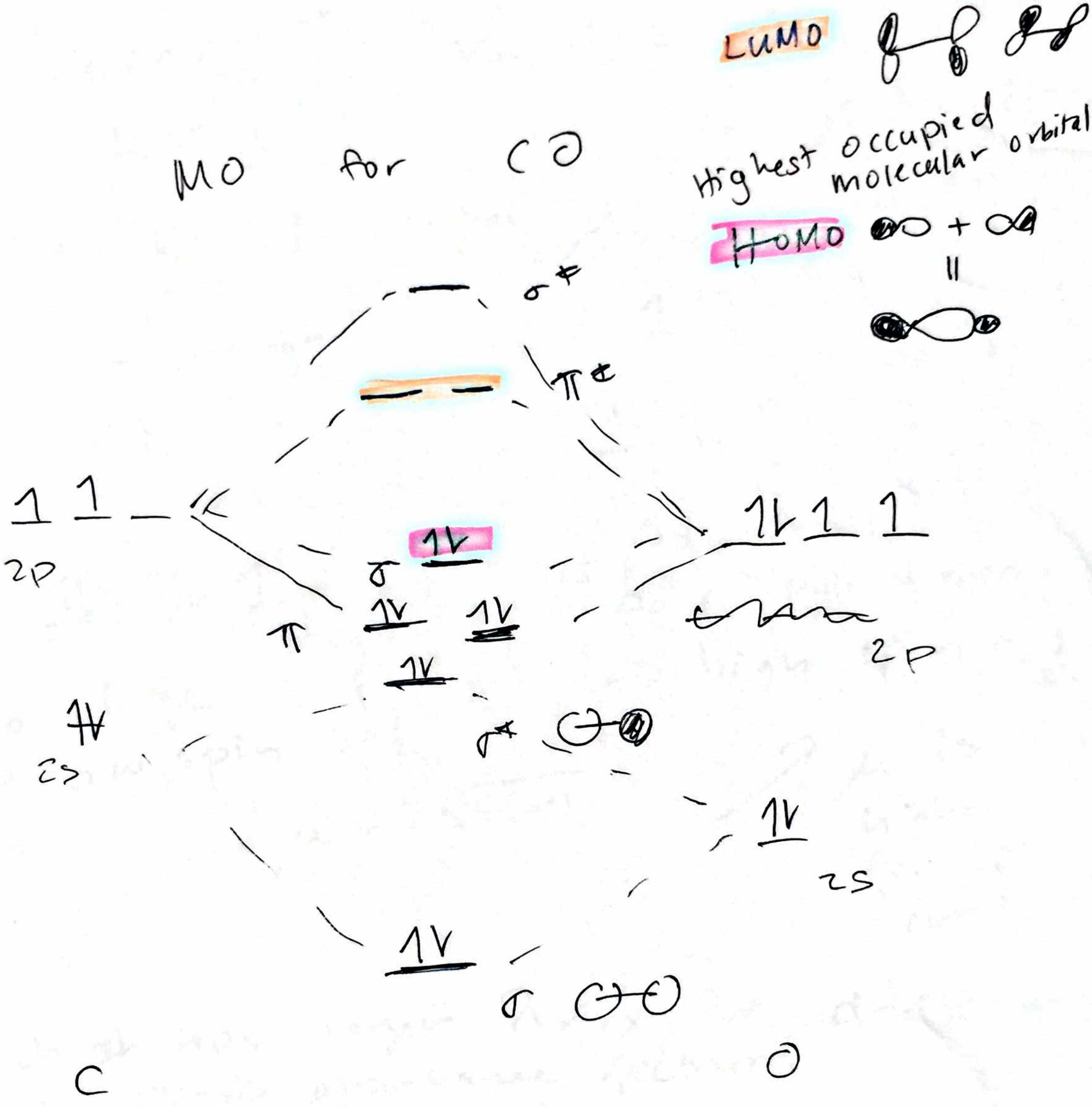
both are a_{1g} symmetry, both can interact with metal S orbital



(w/ p orbitals)

Lowest unoccupied molecular orbital

MO for CO



$[Fe(CO)_6]^{3+}$ vs. $[Fe\,Cl_6]^{3-}$

Fe^{3+} d^5 Fe^{3+} d^5

which has the higher μ_s?

$\_\ \_$ e_g^*

$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow$ t_{2g}

Δ_o large

→ low spin $S = \frac{1}{2}$

$\mu = 2\sqrt{S(S+1)}$

$\uparrow\ \uparrow$ e_g^*

$\uparrow\ \uparrow\ \uparrow$ t_{2g}^*

Δ_o small

$\Delta_o <$ pairing energy

→ high spin $S = \frac{5}{2}$

↗ μ is higher for Cl^- complex

Whish has larger λ_{max} for d-d transiti
in UV-vis absorbance spectrum

$$E = h\nu = \frac{hc}{\lambda}$$

Larger energy = smaller λ

Smaller Δo = larger λ for d-d transition

$FeCl_6]^{3-}$ has Δo , so the absorbance for d-d in UV-vis will occur at a longer wavelength than for $Fe(CO)_6]^{3+}$

→ however the colors we see with our eyes are complementary to what we see in UV-vis absorption spectrum

→ so if $FeCl_6]^{3-}$ absorbs at 700 nm (red), it will appear green (~500 nm)

→ $Fe(CO)_6]^{3+}$ will absorb at lower wavelength (lets say 500 nm)(green) → it will appear red (~700 nm)

which complex has more negative LFSE?

→ $Fe(CO)_6]^{3+}$, it has more electrons in the t_{2g} orbitals