Lecture 18 Review CH431 10/27/16

$[V(CN)_6]^{3-}$ $[Fe(CN)_6]^{3-}$

V^{3+} Fe^{3+}

↓ ↓

d^2 d^5

e_g — — — — e_g

t_{2g} 1 1 — $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ 1 t_{2g}

$S = 1$ $S = \frac{1}{2}$

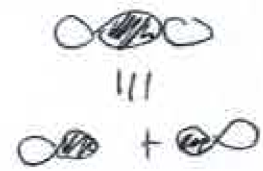
$\mu_s = 2\sqrt{1(1+1)}$ > $\mu_s = 2\sqrt{\frac{1}{2}(\frac{1}{2}+1)}$

π acceptors / π donors

CN^- CO Br^- X^-

$C\equiv N^{\ominus}$ $C\equiv O$

sigma interaction ~~between~~ with HOMO of CO/CN^- (σ bonding orbital from p_z orbitals)



π acceptor interaction ~~between~~ LUMO a with orbital $\rightarrow$ π^*

px - π^* py π^*

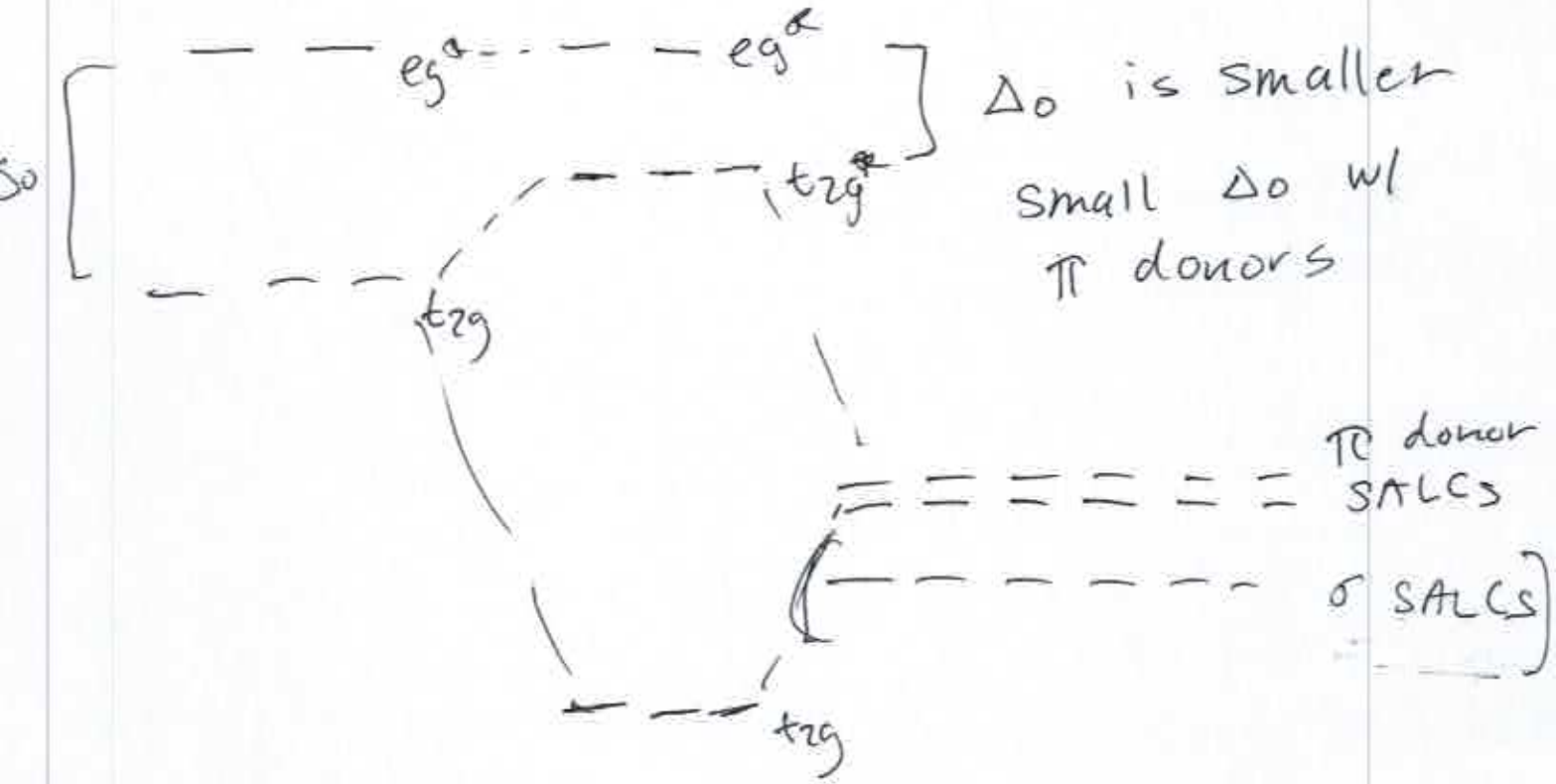
π donors

σ donor interaction

$d_{x^2-y^2}$ p_x

π donor interaction

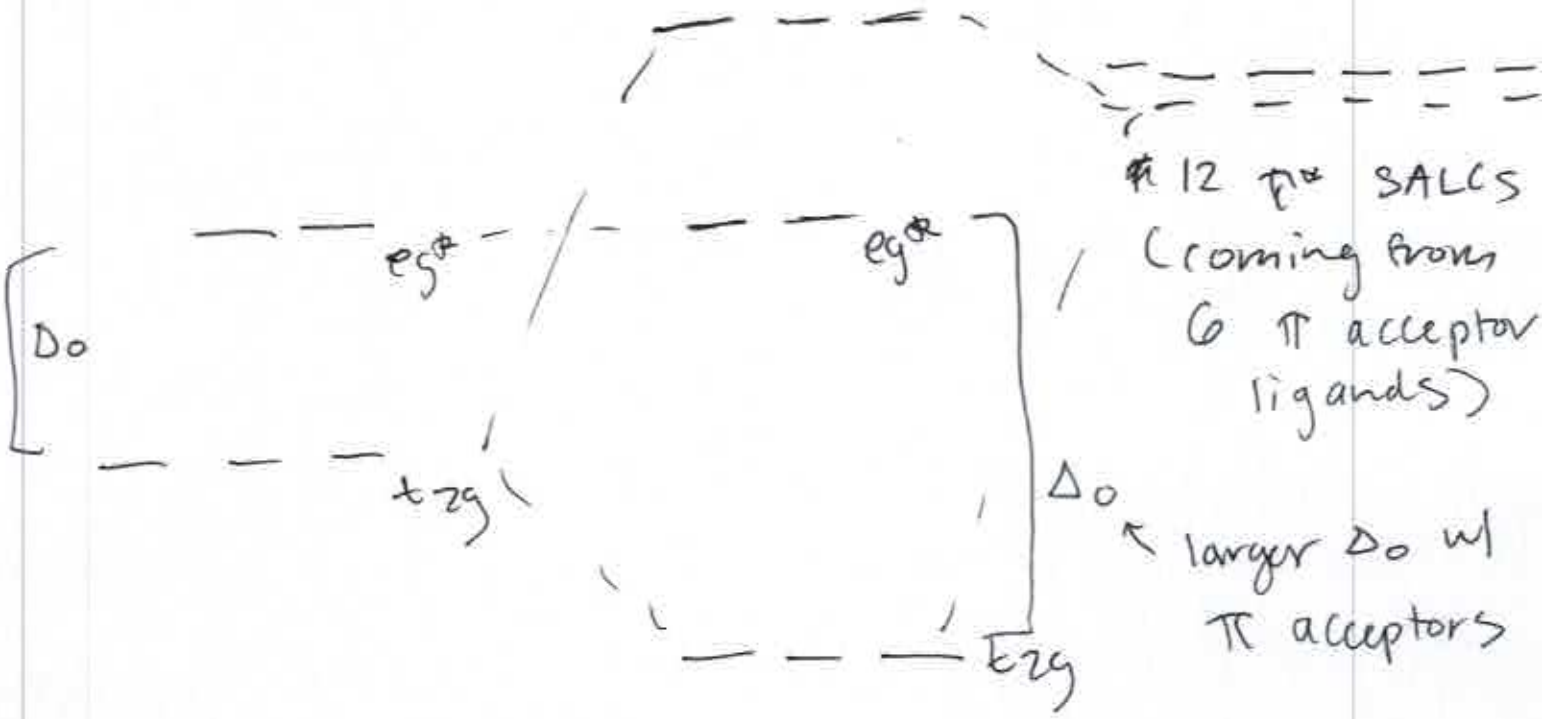
d_{xy} p_y

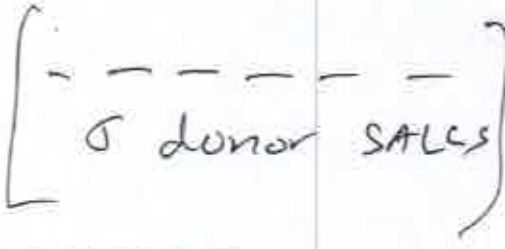


CO/CN⁻

π acceptors

sigma only





Simplified Spectrochemical Series

strong field
large Δo

weak field
small Δo

CO, CN^- > $:NH_3$ > $H_2\ddot{O}:$ > halides

π acceptors
π*

& σ only

π donors
extra lone pairs

Δ_o 1) affected by ligands

π acceptor → large Δ_o

π donor → small Δ_o

σ only donor → somewhere in between

[$M(NH_3)_6$ vs $M(Br)_6$

σ donor

π donor
smaller Δ_o
more likely to be high spin]

2) Affected by the metal center

* more positive metal center → larger Δ_o

⇒ * Δ_o 3d < 4d < 5d

(bigger orbitals as you go down periodic table → more orbital overlap → stronger bonds → larger Δ_o)

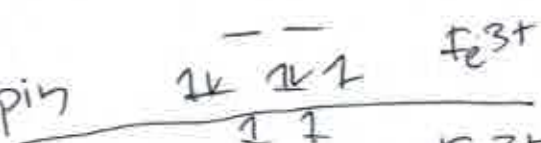
4d, 5d always low spin, very large Δ_o

Δ_o

magnetic properties

large Δ_o = low spin — Fe^{3+} low spin

small Δ_o = high spin — Fe^{3+} high spin



$\rightarrow S = ? \rightarrow \mu_s = g\sqrt{S(S+1)}$

$g \uparrow 2$

UV-vis properties

large Δ_o = large energy gap = small λ_{max} in absorption spectrum

small Δ_o = small energy gap = large λ_{max} in absorption spectrum

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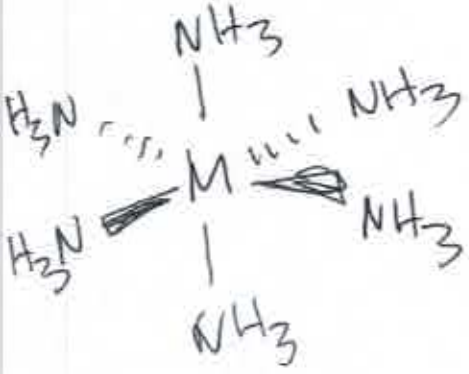
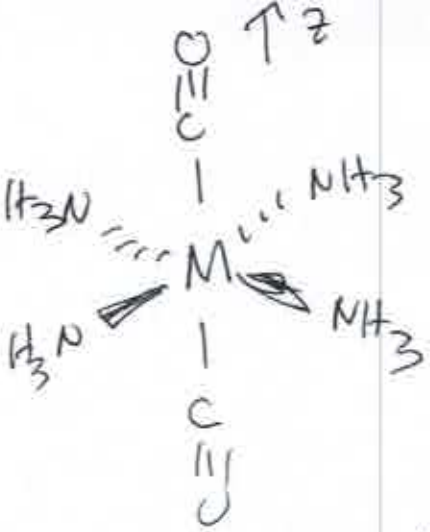
$\Rightarrow \Delta_t << \Delta_o$

3d tetrahedral complexes: always high spin

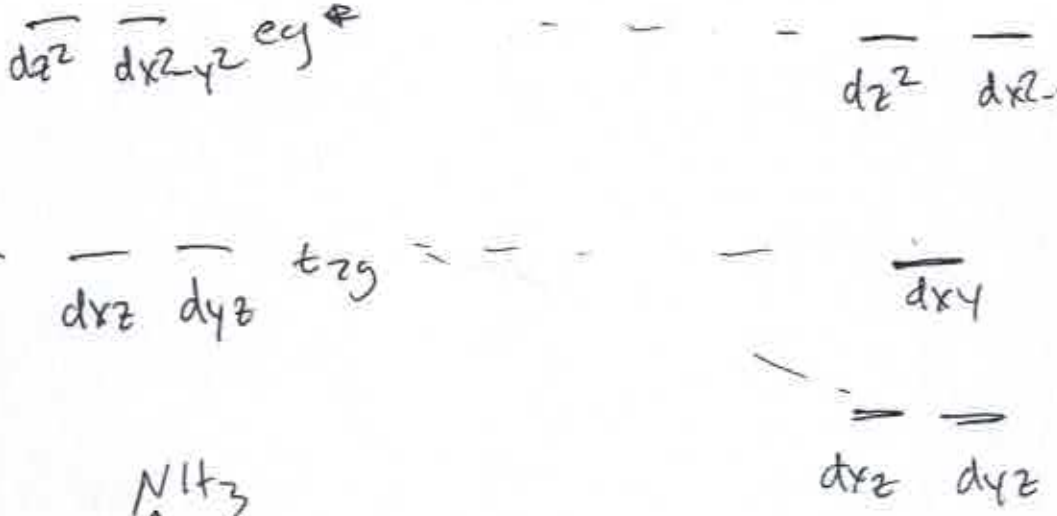
small Δ_t = small energy gap = large λ_{max} in absorption spectrum

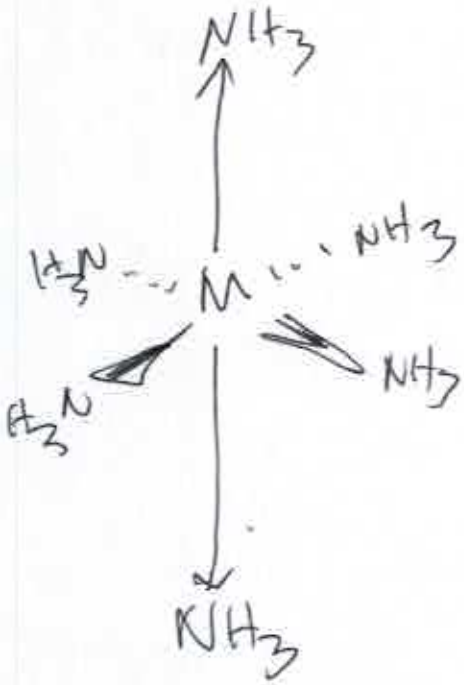


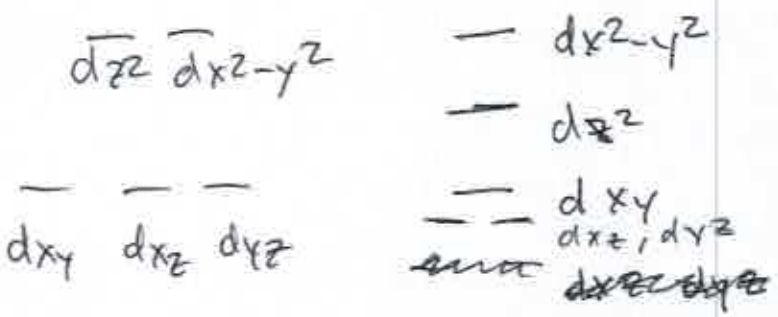
vs

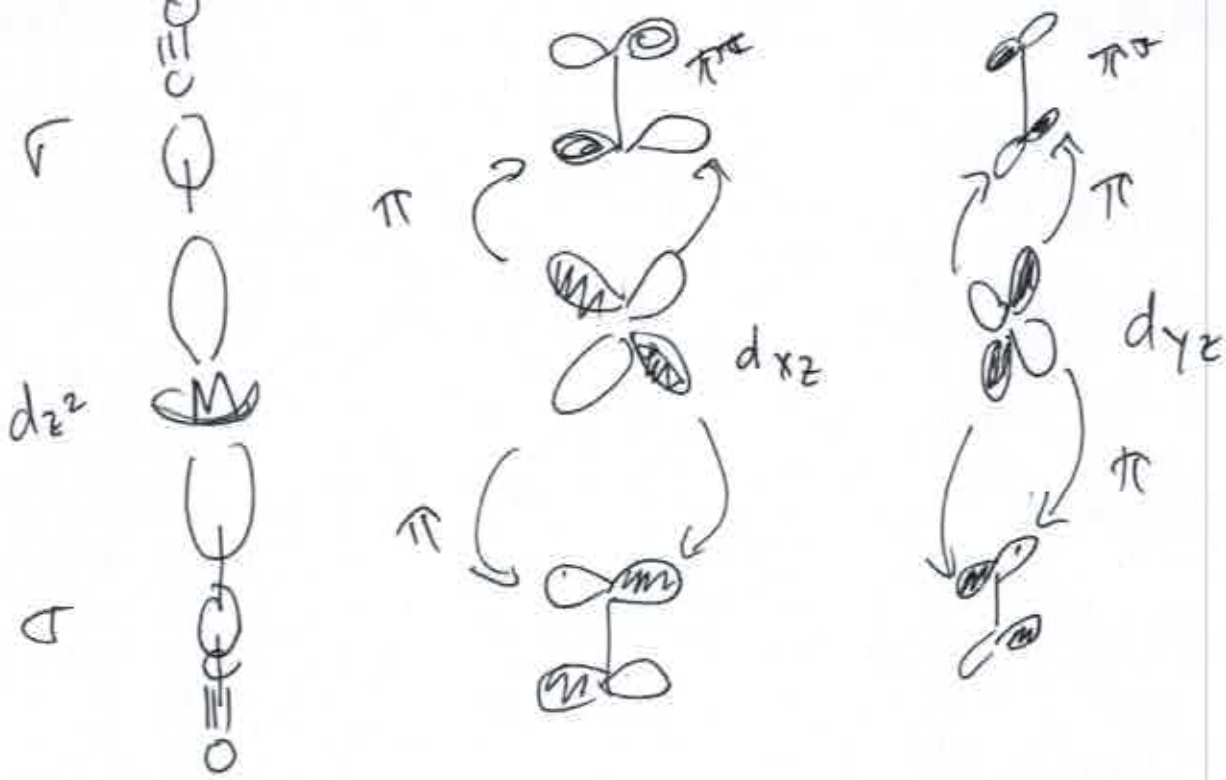


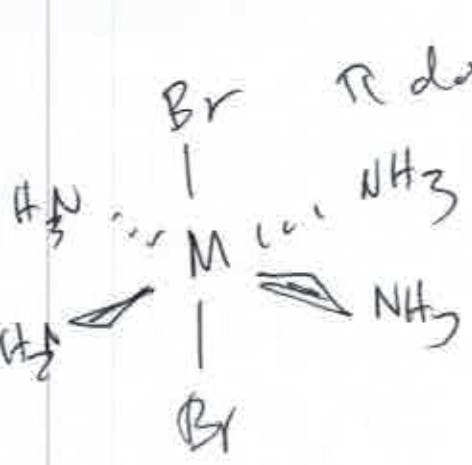
π acceptor interaction lowers energy



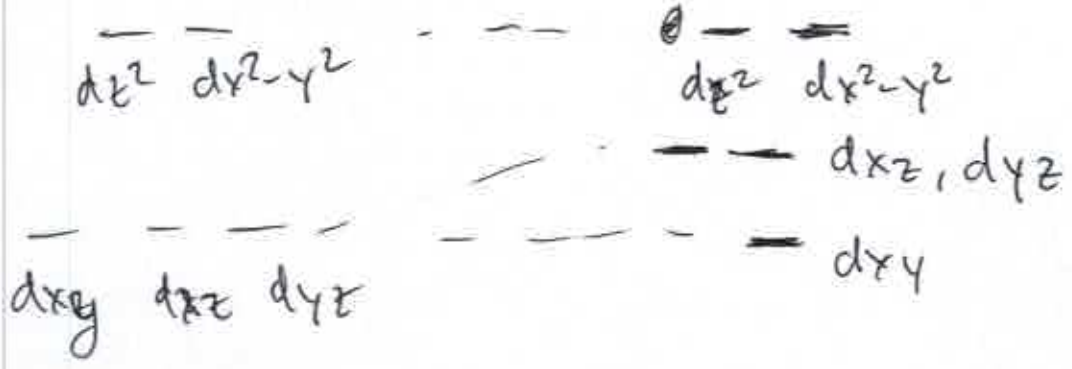


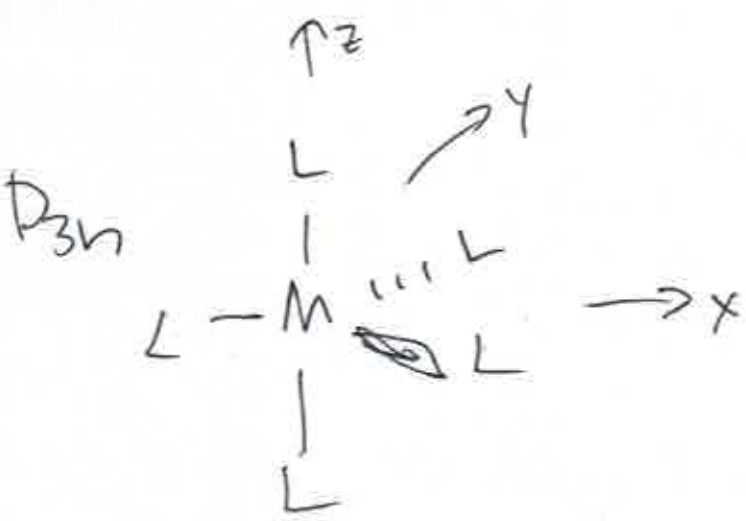



σ
d_{z^2}
σ
π
d_{xz}
π
π
d_{yz}
π

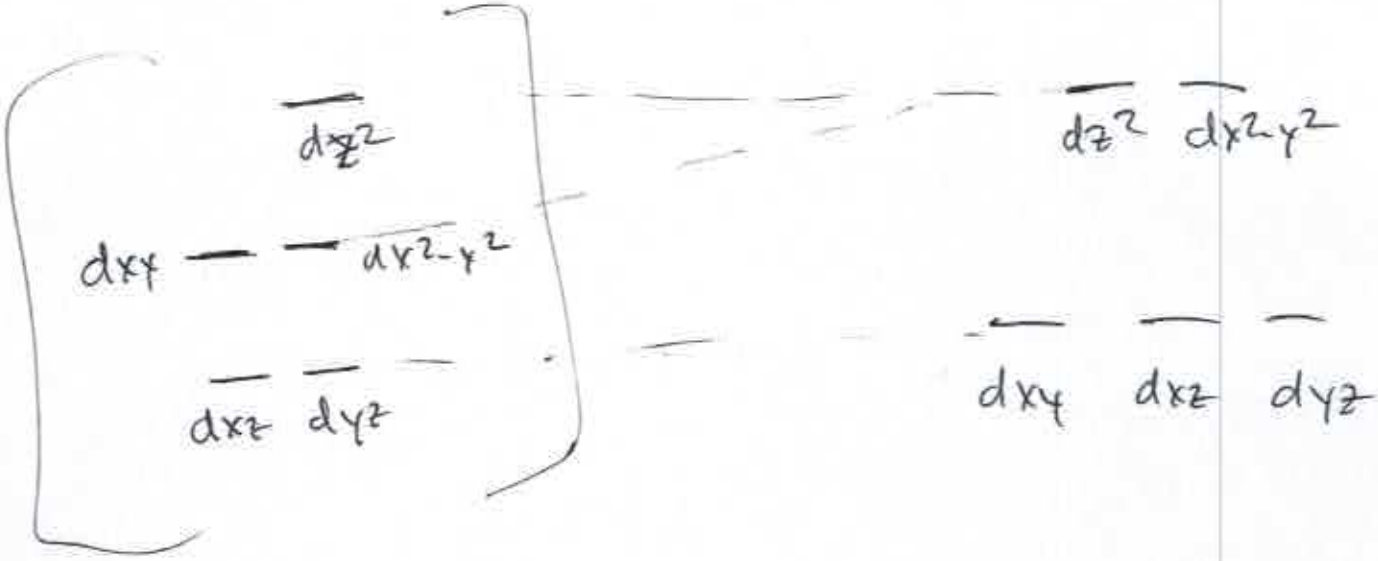


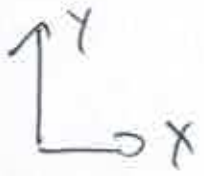
π donor interaction raises d orbital energy

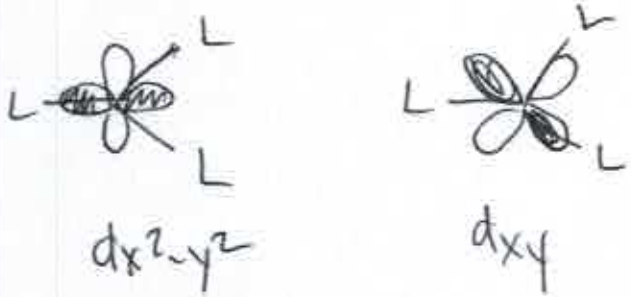


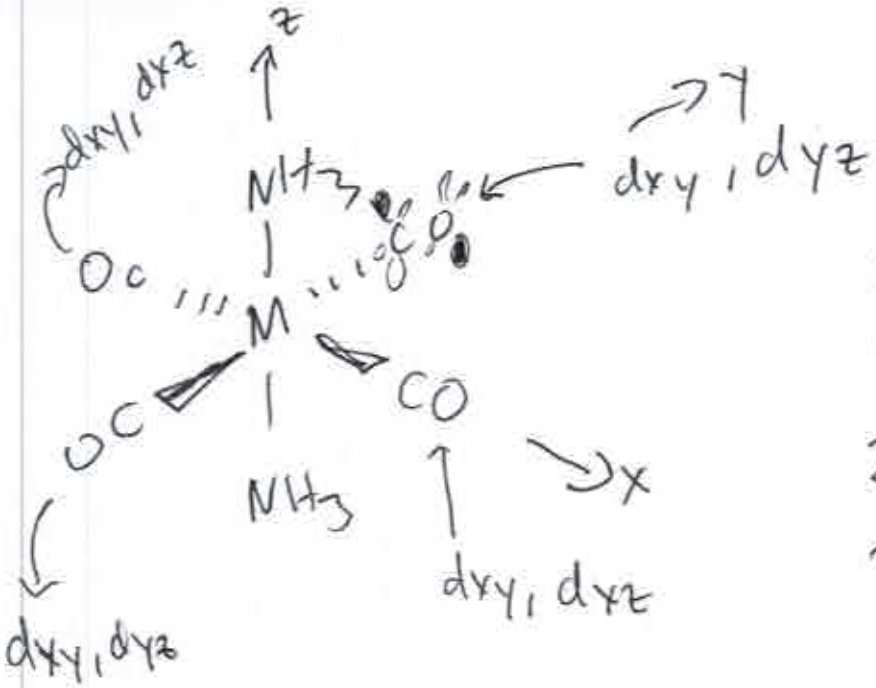

z
y
x
L
M


L
M
L


dxz²
dxy
dx²-y²
dxz
dyz
dz²
dx²-y²
dxy
dxz
dyz


y
x


L
L
L
L
L
L
dx²-y²
dxy



4 COs can backbond w/ (dxy)

2 COs w/ dyz

2 COs w/ dxz

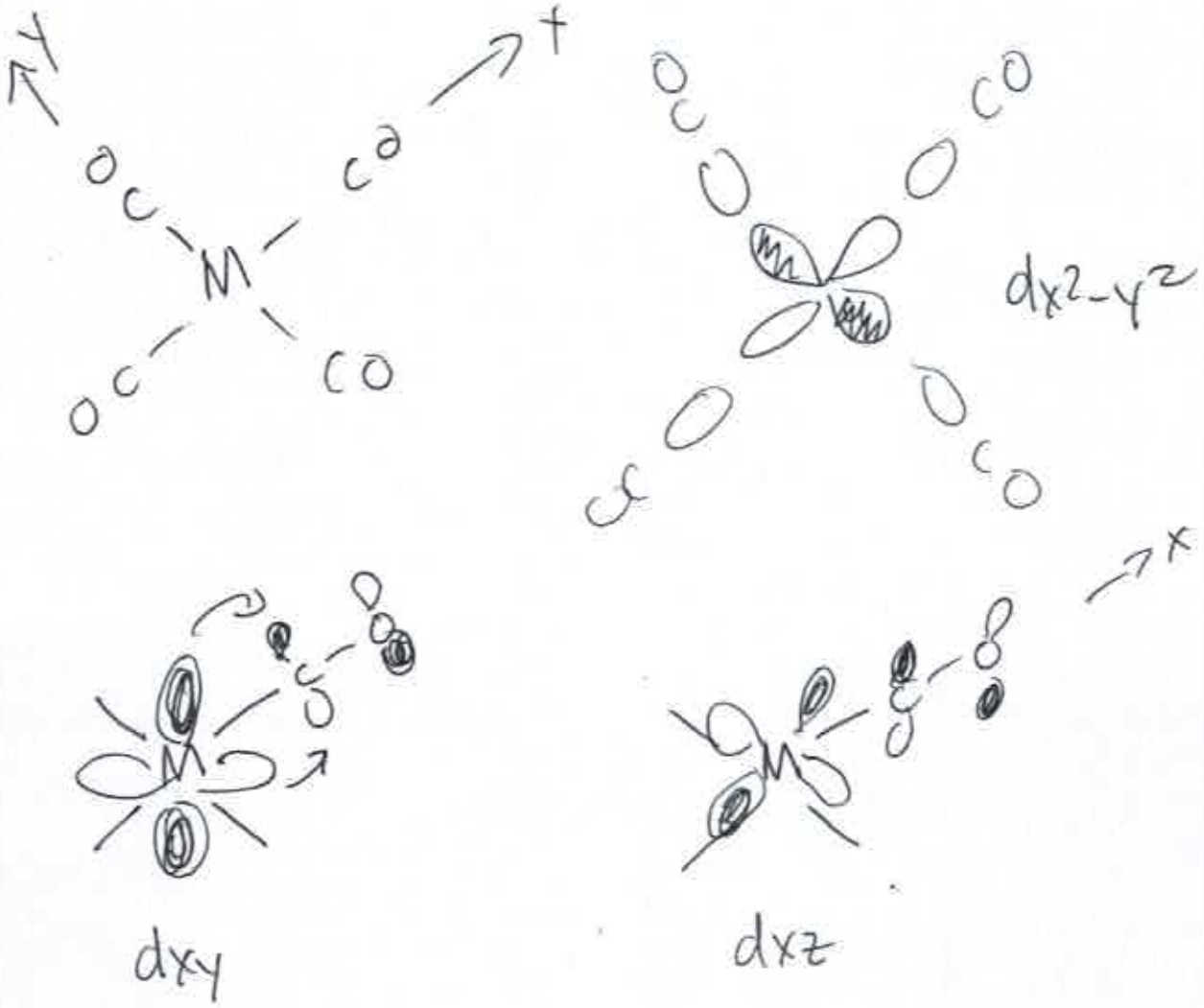
dz², dx²-y²

dz² dx²-y²

dxy dxz dyz

dxz, dyz

dxy


Y
Z
M
CO
dx²-y²
X
dxy
dxz