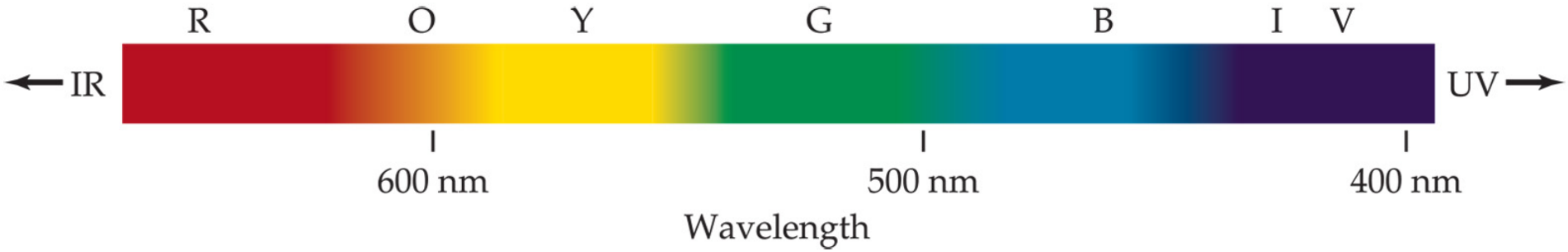
Metal complexes and color

The ligands of a metal complex effect its color

Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

Why does anything have color?



Light of different frequencies give different colors

We learned that elements can *emit* light of different frequency or color.

But these coordination complexes are not emitting light

They absorb light.

How does that give color?

Light can bounce off an object or get absorbed by object

No light absorbed, all reflected get **white** color
All light absorbed, none reflected get Black color
What if only one color is absorbed?

Complimentary color wheel

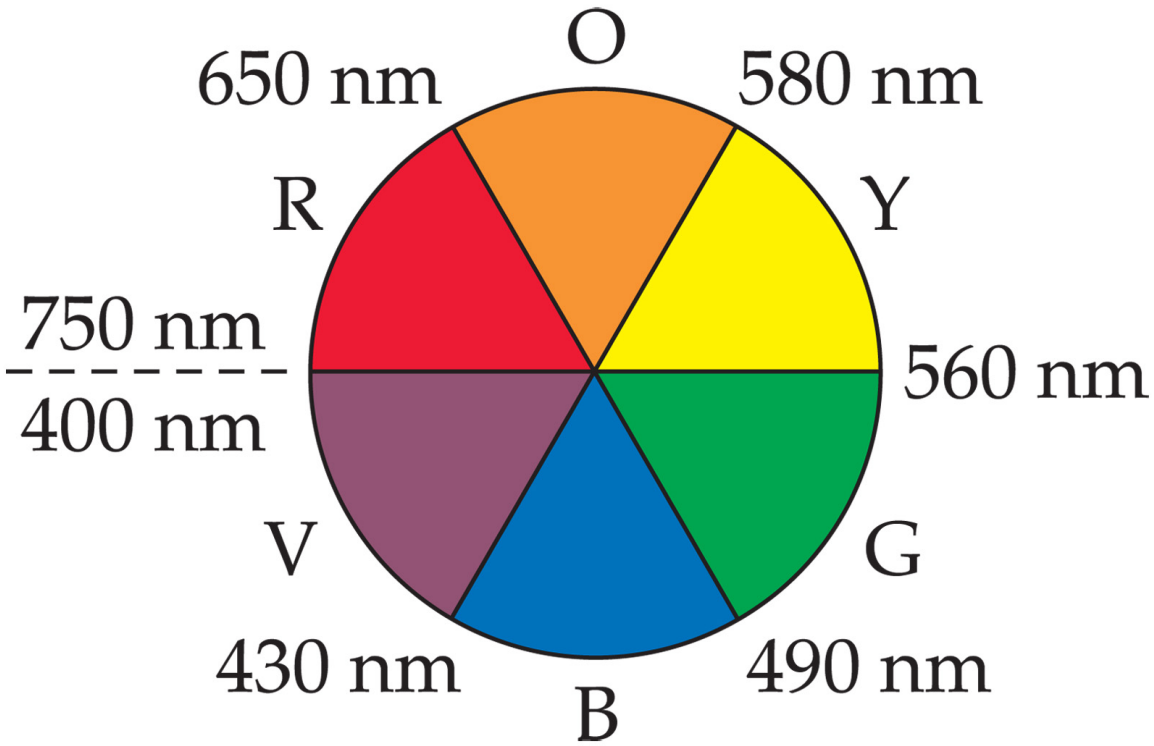
If one color absorbed, the color opposite is perceived.

Absorb **Orange**

See **Blue**

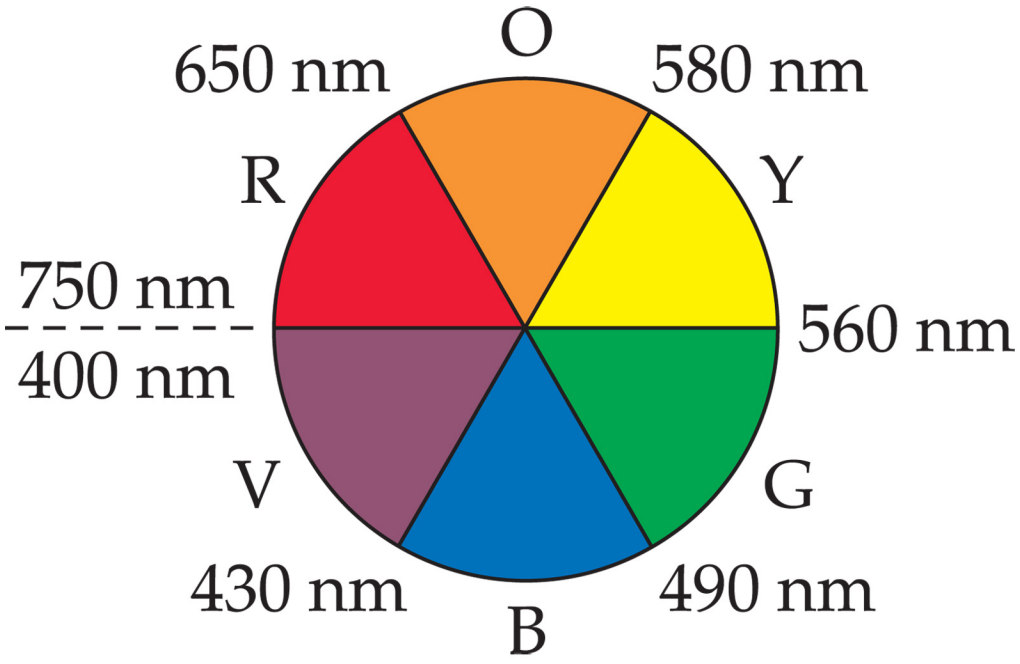
Absorb **Red**

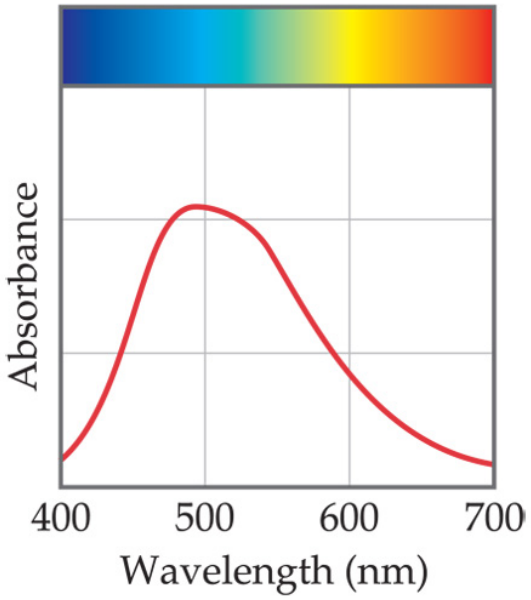
See **Green**



$[Ti(H_2O)_6]^{3+}$
Absorbs in green yellow.
Looks purple.

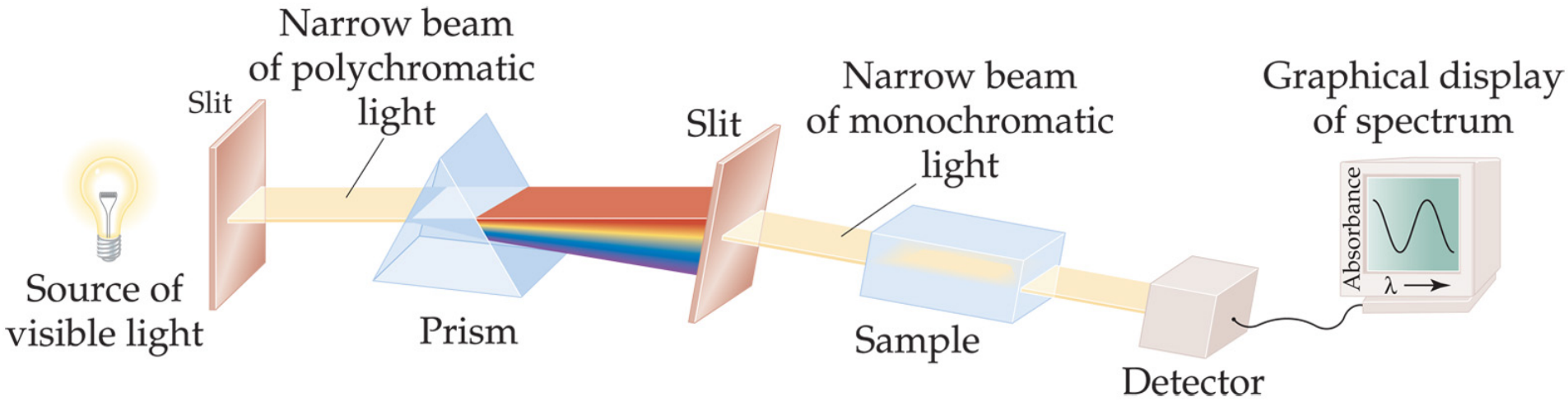
(a)





(b)

How is an absorption spectrum of a Compound measured?
A spectrophotometer.



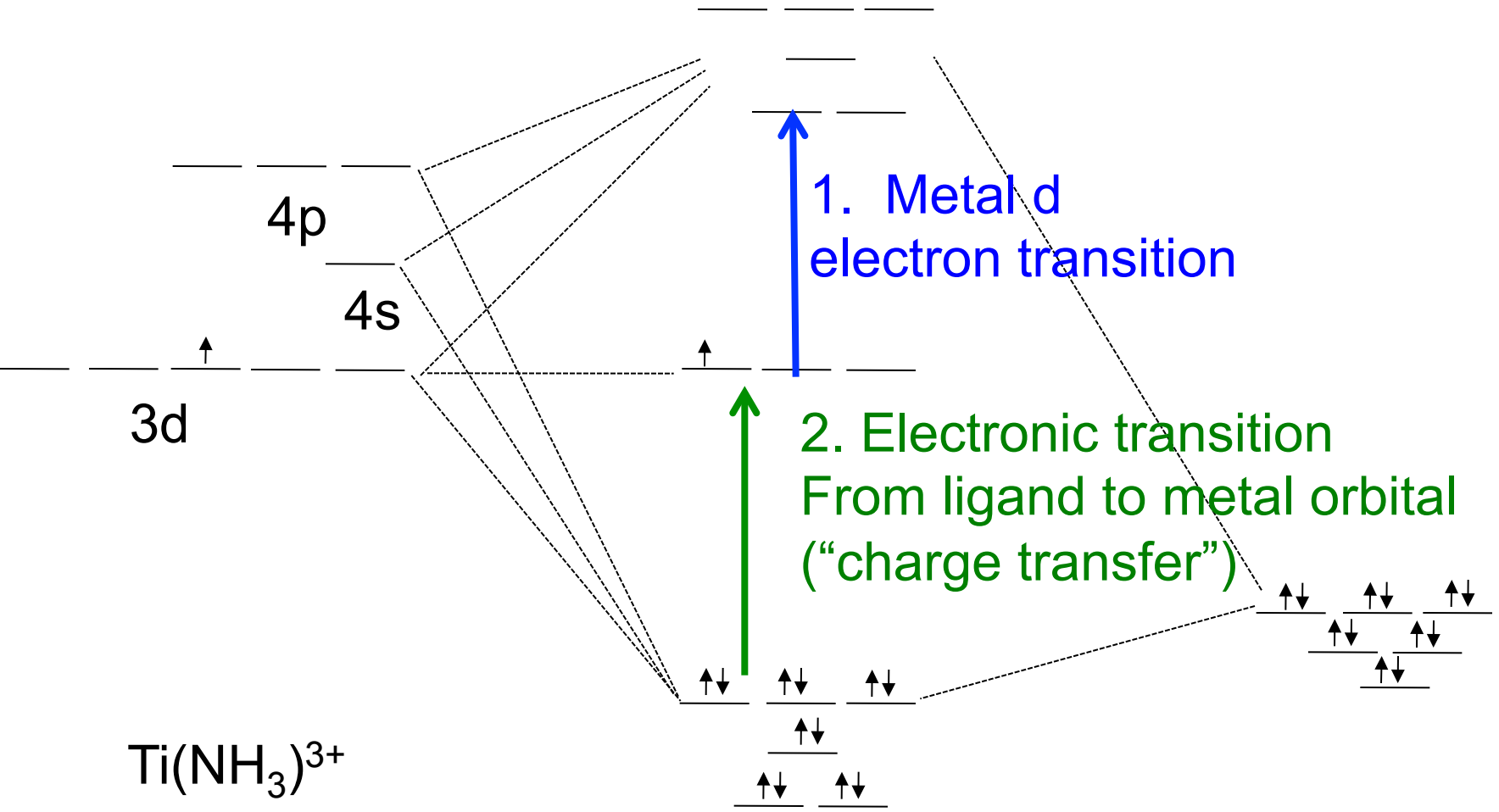
So color comes from:

Absorption (metal complexes)

Emission (element line spectra)

How is light absorbed in a metal complex?

Ligand Field theory: 2 possibilities



Metal complexes and color

But why do different ligands on same metal give Different colors?

Why do different ligands change absorption?

Metal complexes and color

But why do different ligands on same metal give Different colors?

Why do different ligands change absorption?

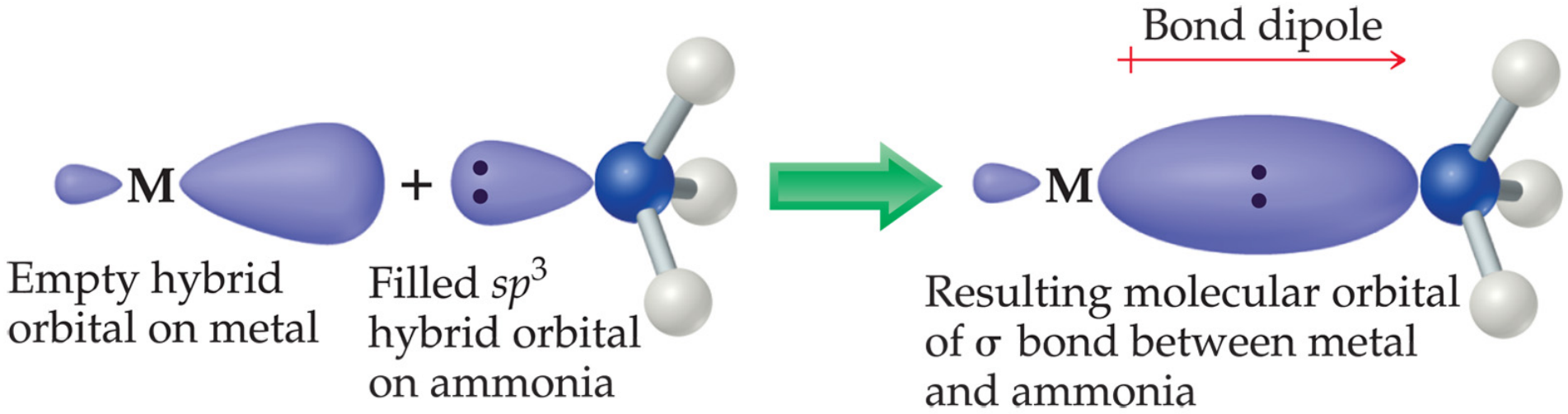
Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

Model of ligand/metal bonding.

Electron pair comes from ligand

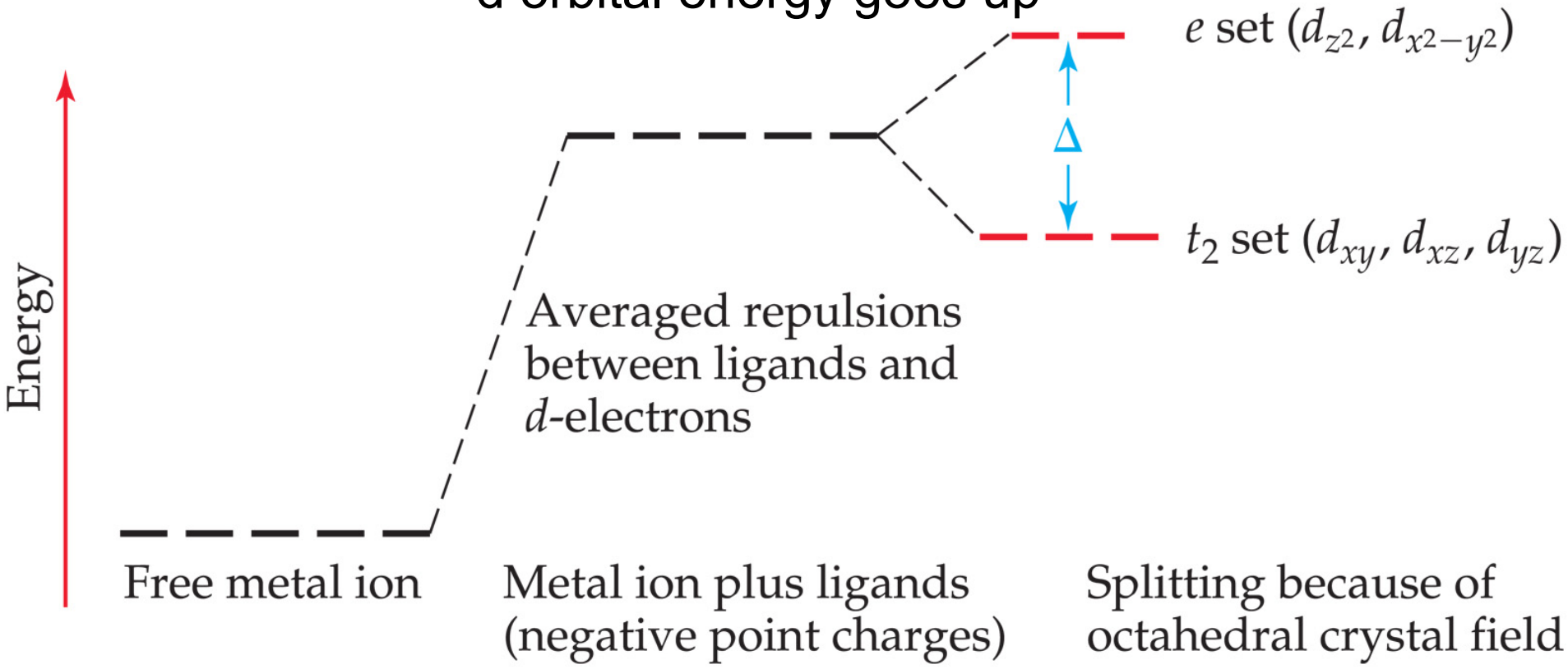
Bond very polarized.

Assumption: interaction pure electrostatic.



Now, think of point charges being attracted to metal nucleus
Positive charge. What about electrons in d orbitals?

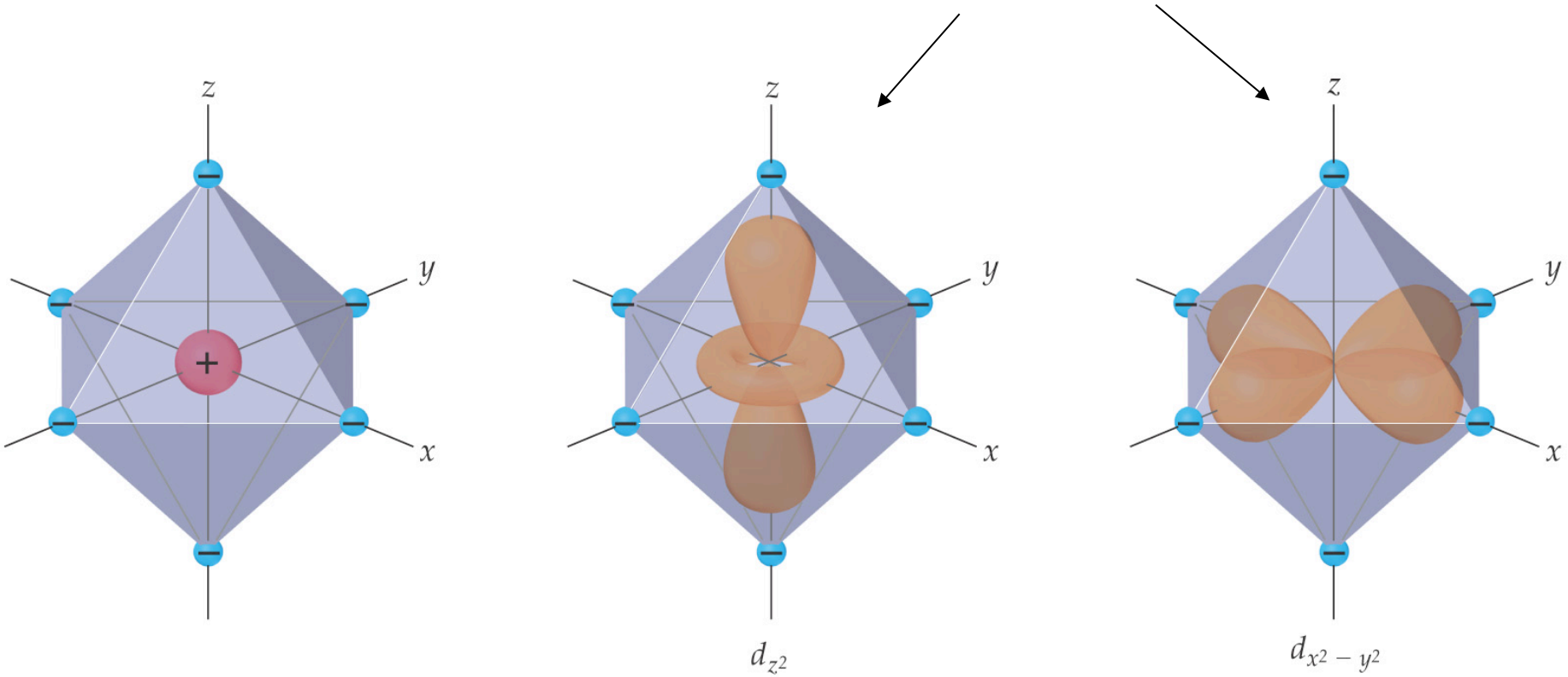
Ligand negative charge
Is repelled by d electrons,
d orbital energy goes up



Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand

Ligands point right at lobes

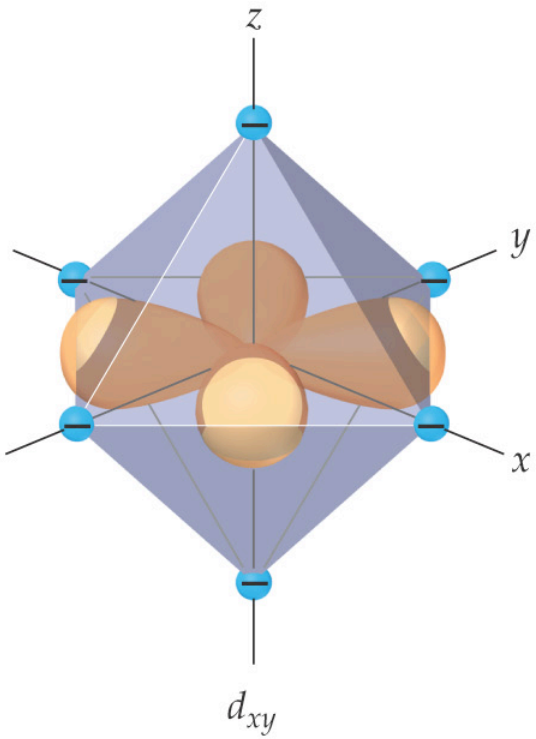


d_{z^2} $d_{x^2-y^2}$

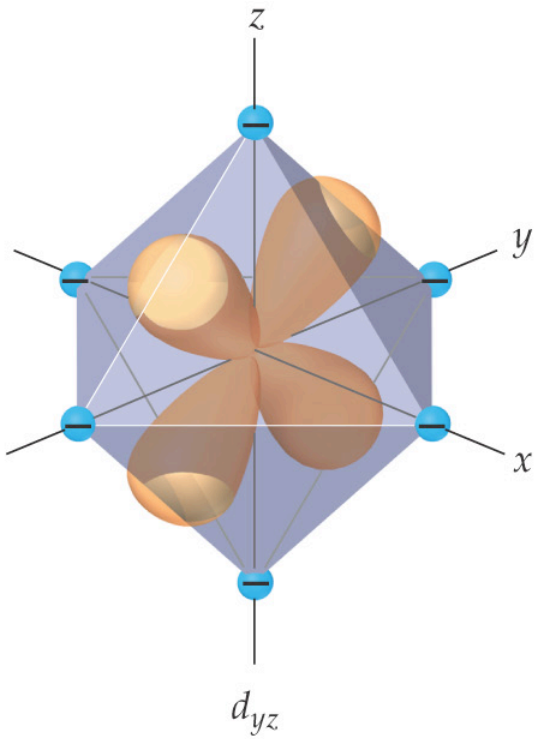
(a) (b) (c)

In these orbitals, the ligands are between the lobes

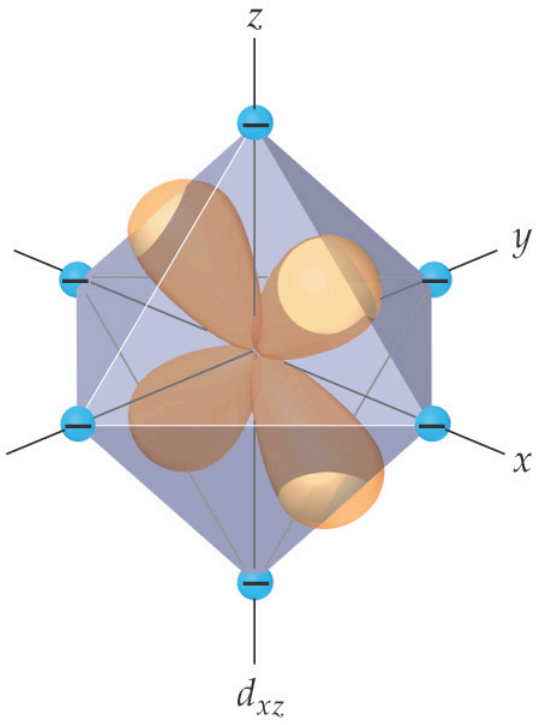
Interact less strongly



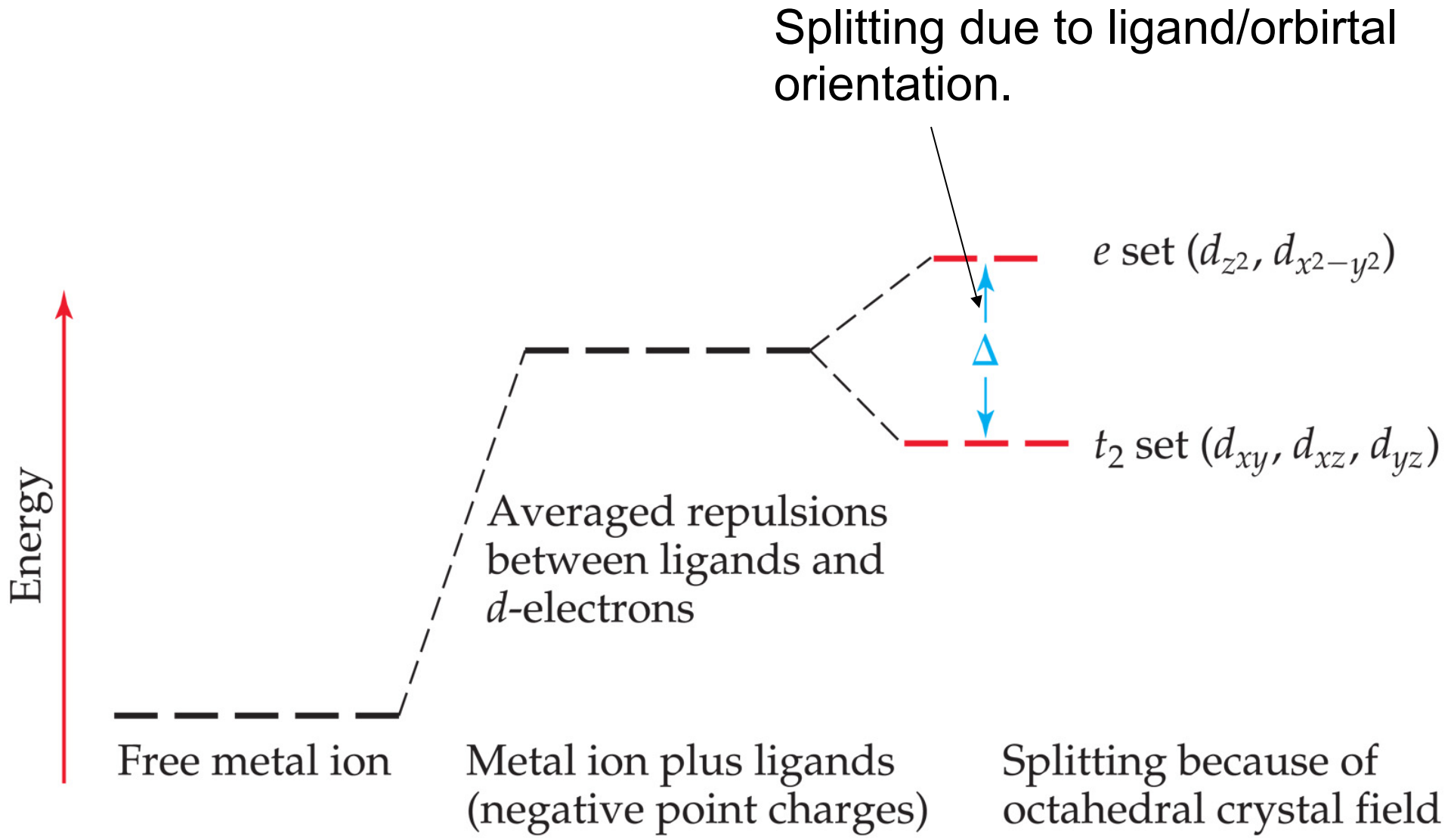
(d)



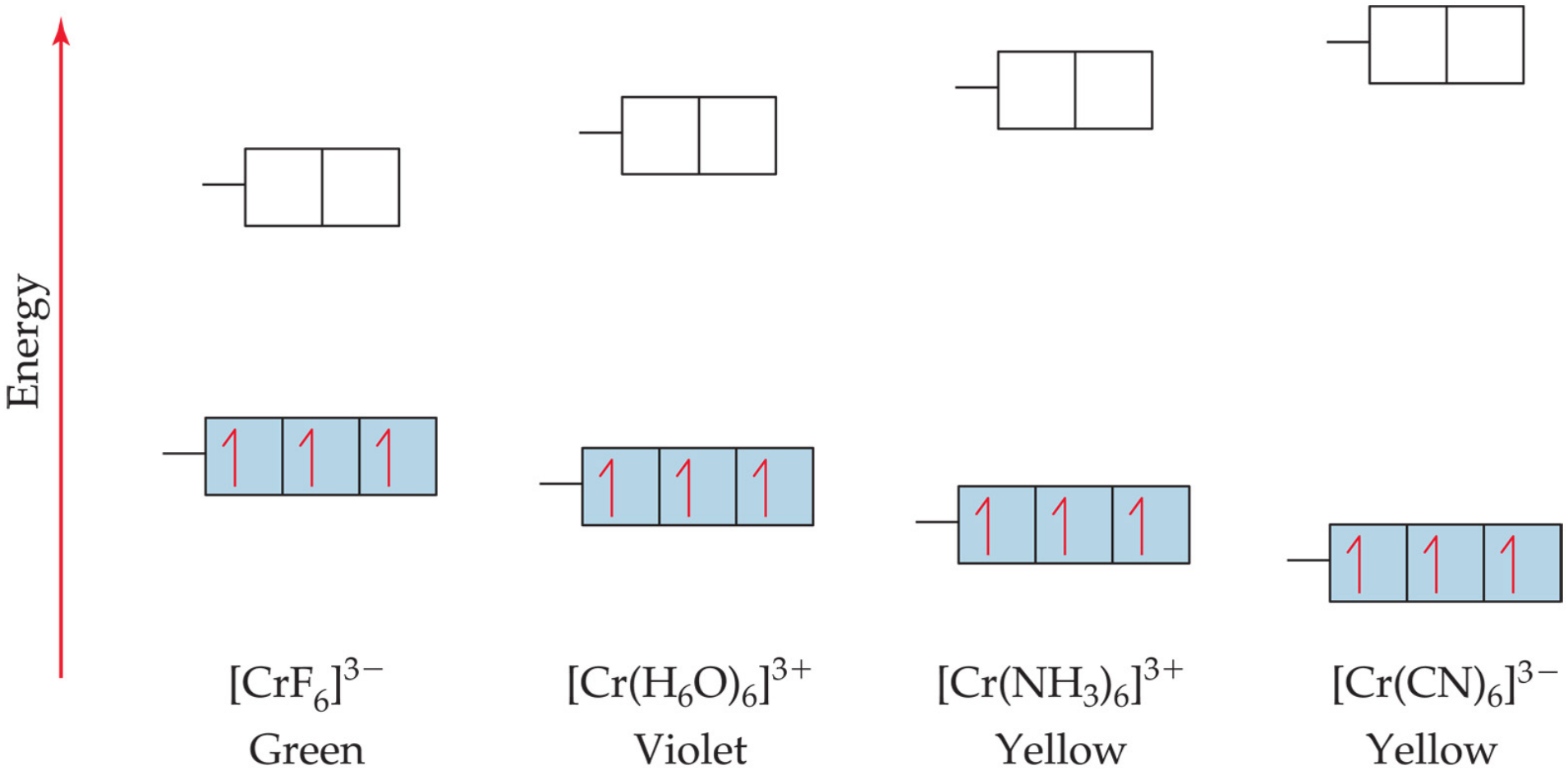
(e)



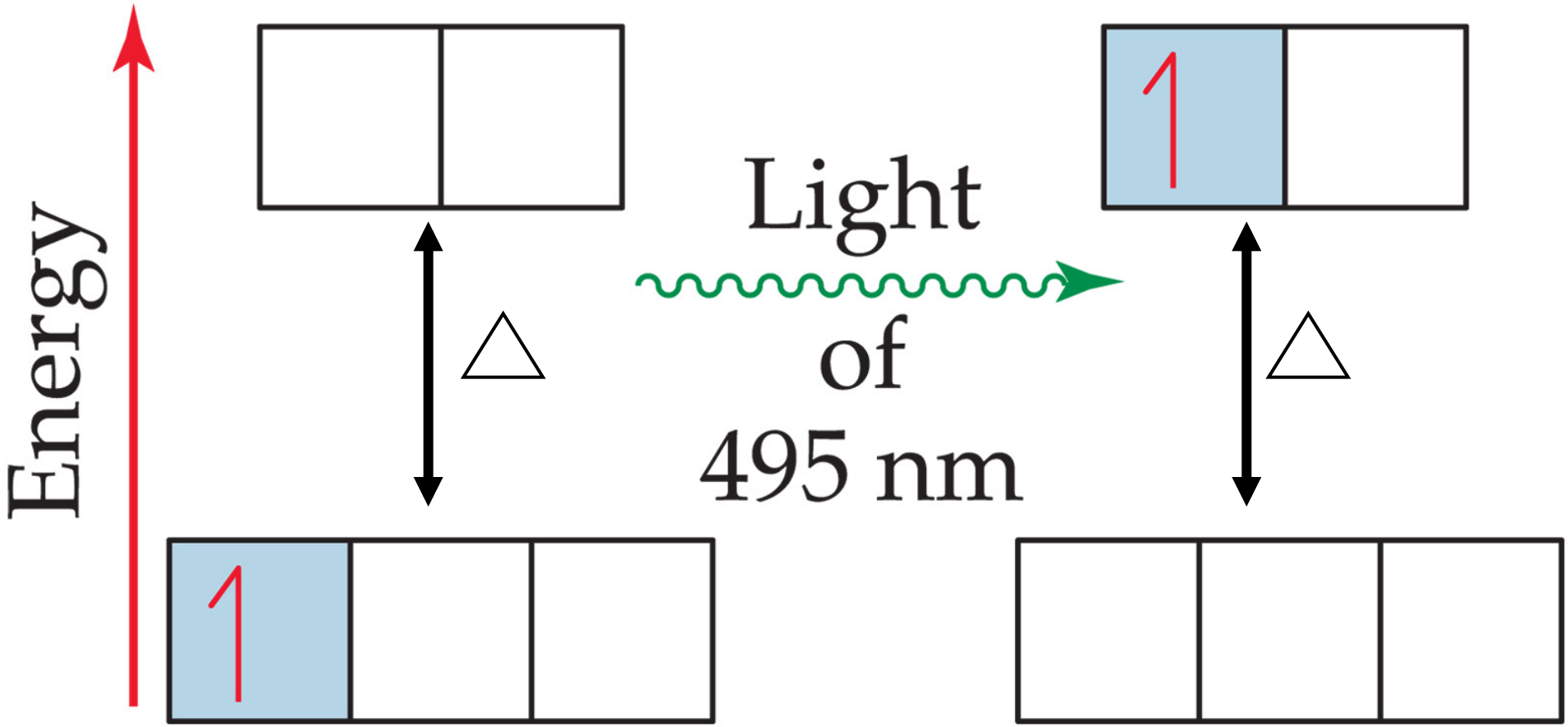
(f)



Different ligands interact more or less, change E spacing
Of D orbitals.



Absorption of light promotes an electron to a higher in E d orbital. Δ is E of the photon that can be absorbed.

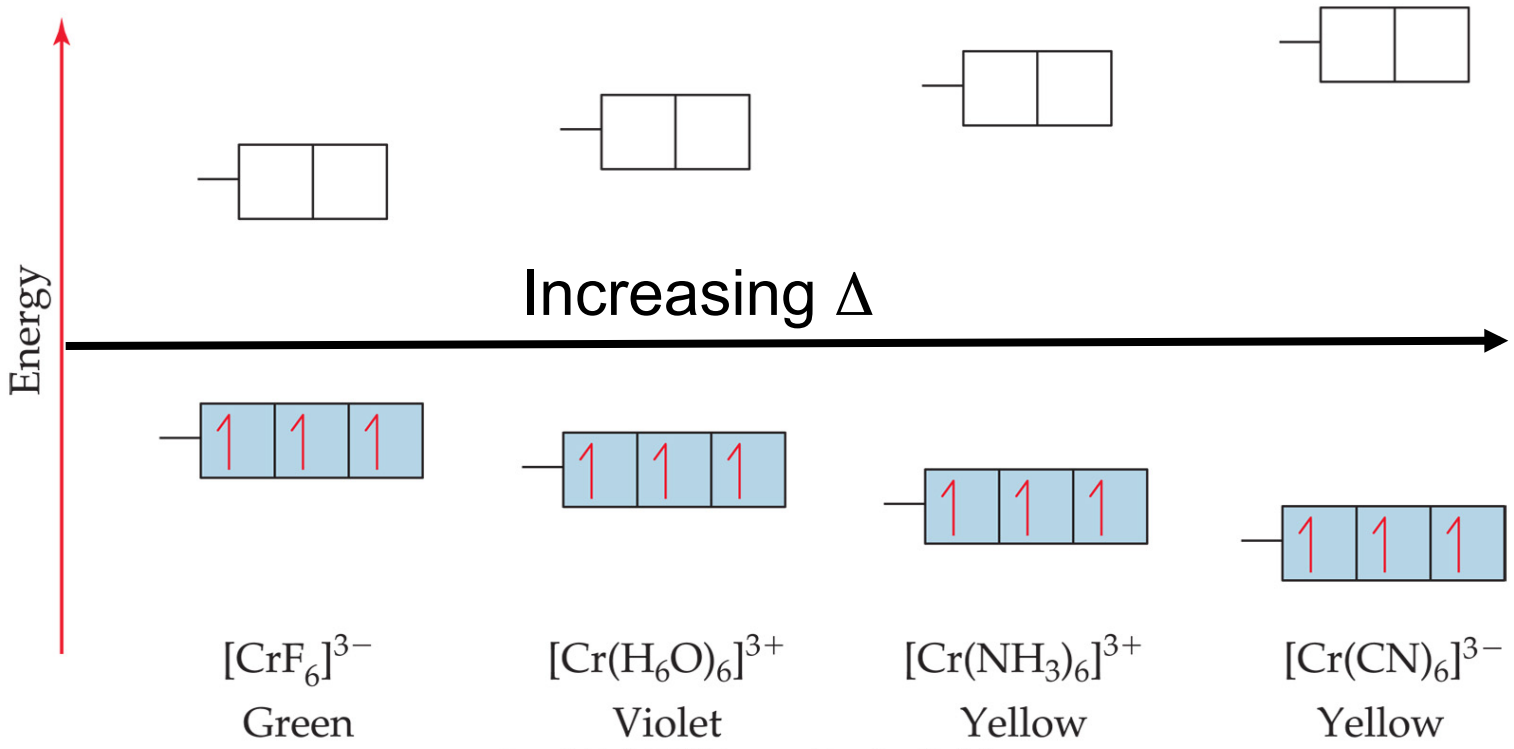


△ = 495 nm

Spectrochemical series (strength of ligand interaction)

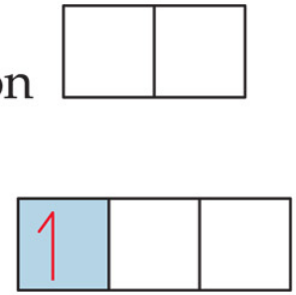
Low field — Increasing Δ — High field

$Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$

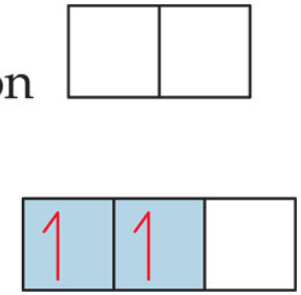


Electron configurations of some octahedral complexes

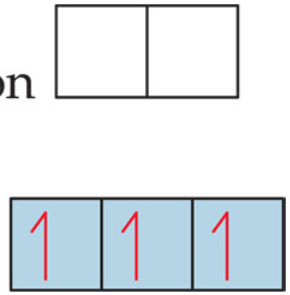
Ti^{3+}, a d^1 ion



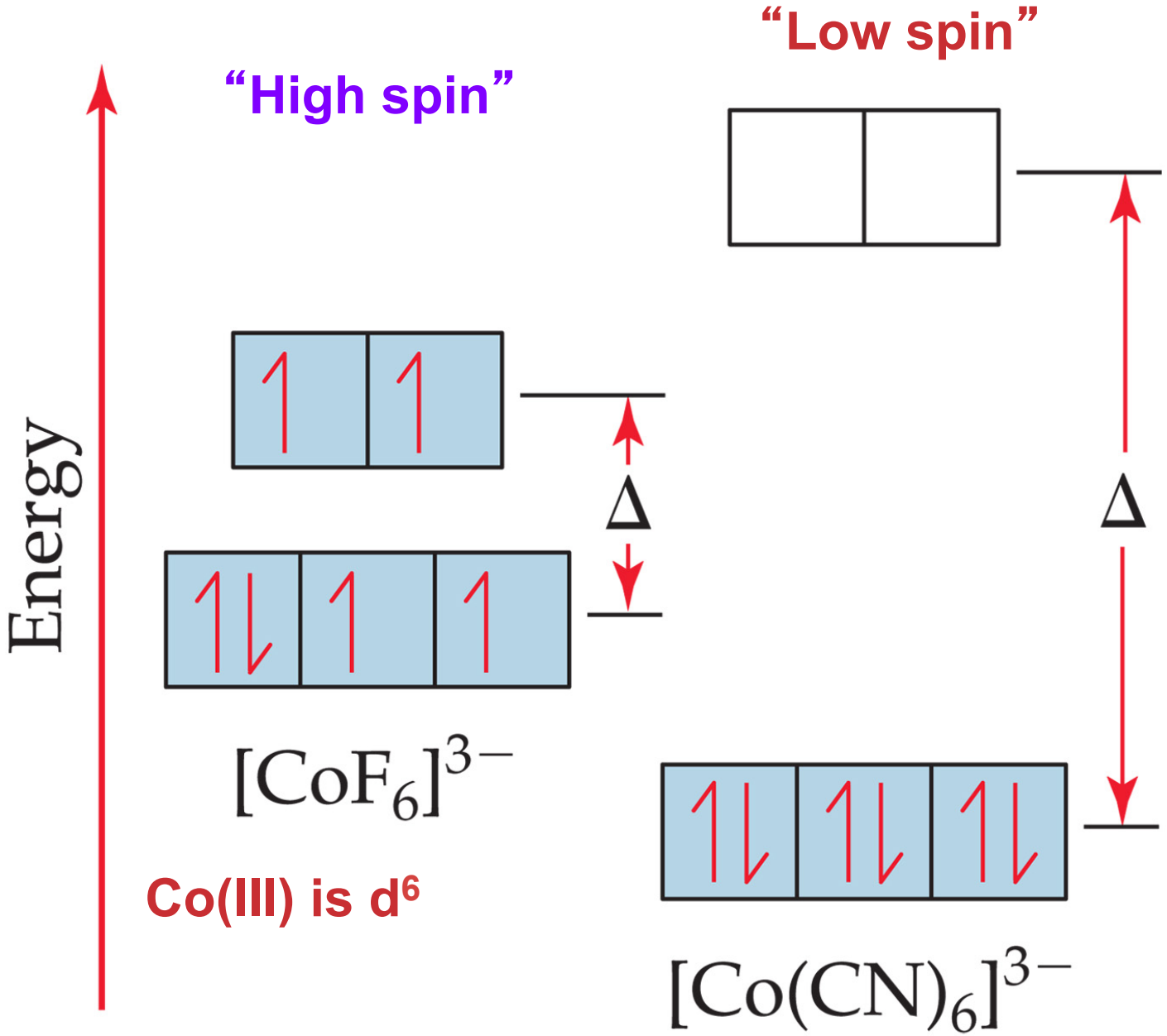
V^{3+}, a d^2 ion



Cr^{3+}, a d^3 ion

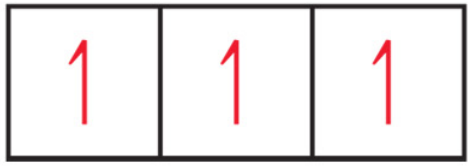


As Energy difference increases, electron configuration Changes. Huhn's rule breaks down because d orbitals are not degenerate

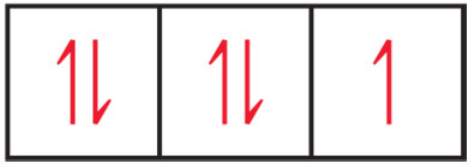


The 2 choices for a d^5 metal, high spin (more unpaired electrons) or low spint (more paired electrons)

High spin

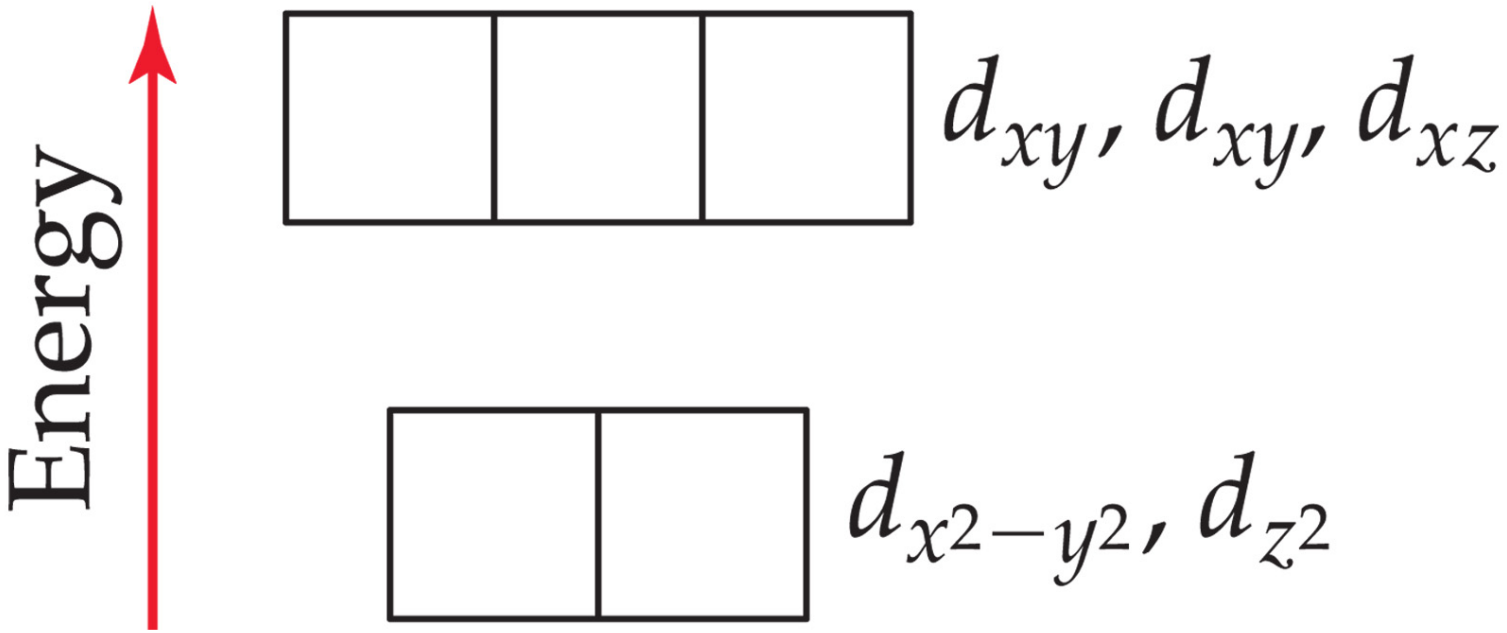


Low spin

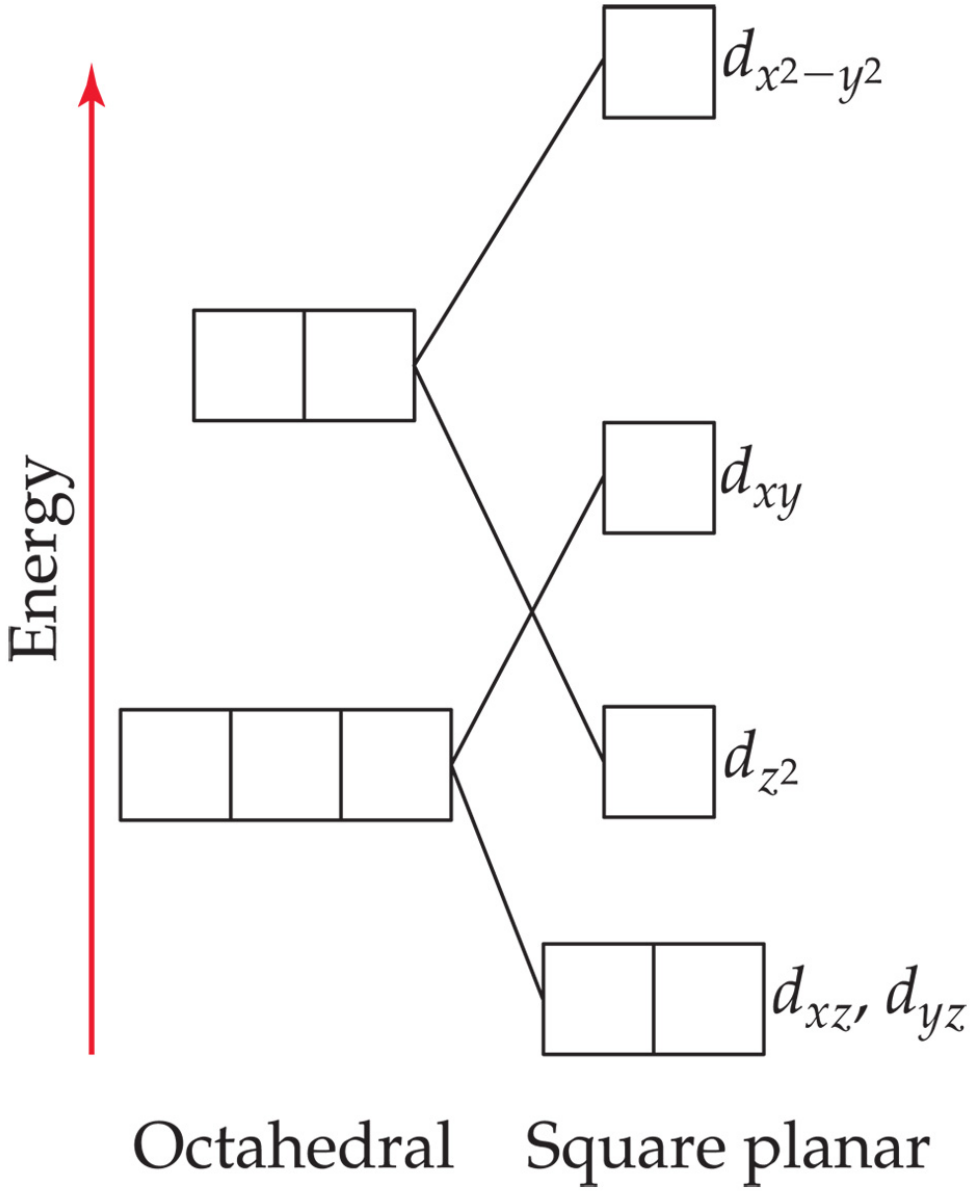


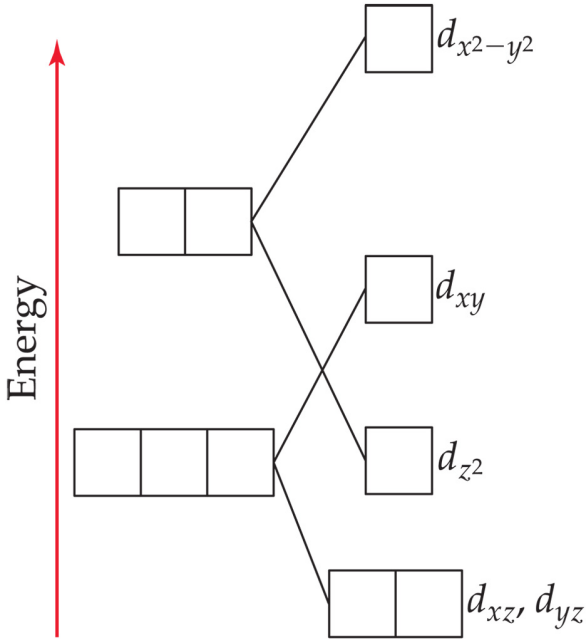
Tetrahedral Complexes

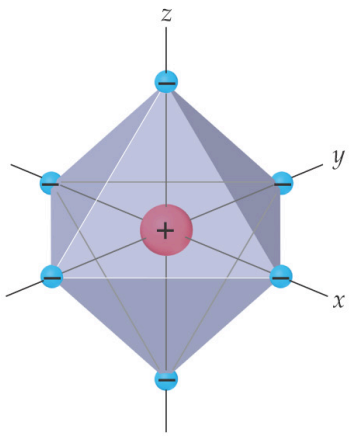
In tetrahedral complexes, orbitals are inverted.
Again because of orientation of orbitals and ligands.
Δ is always small, always high spin (less ligands)



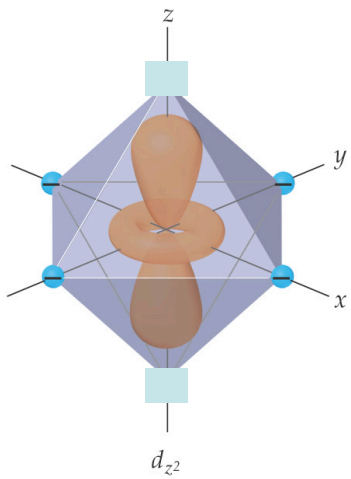
Square planar complexes are different still



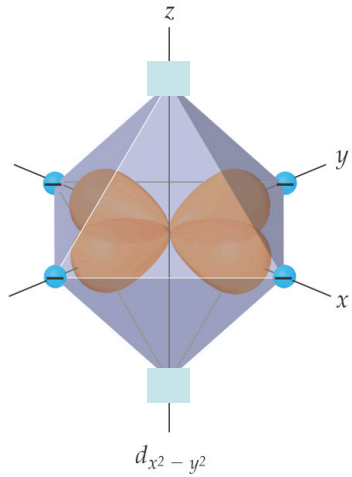




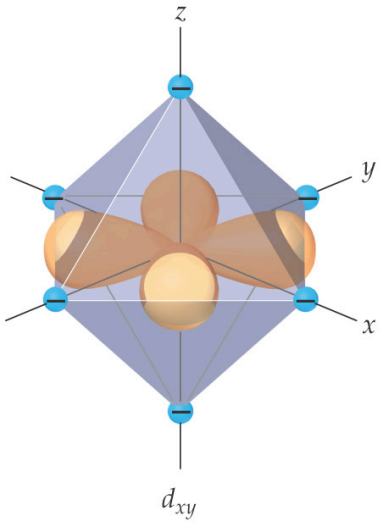
(a)



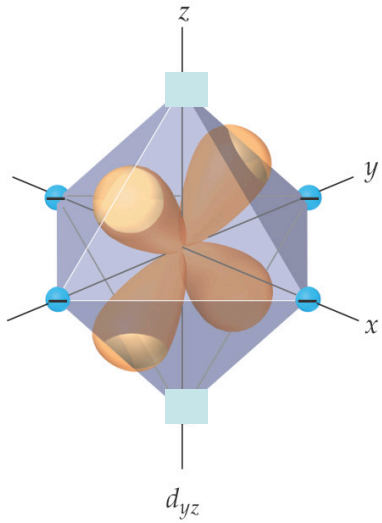
(b)



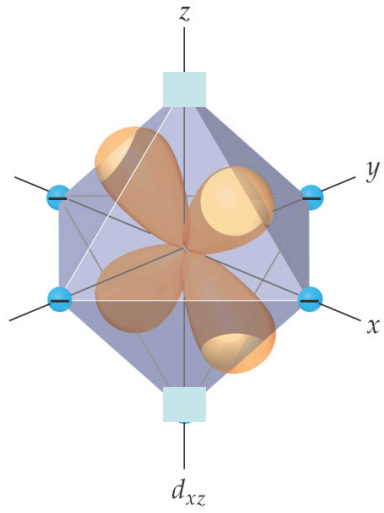
(c)



(d)

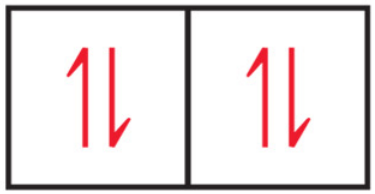


(e)



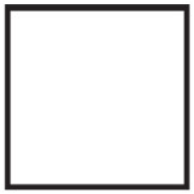
(f)

d_{xy}, d_{yz}, d_{xz}



$d_{x^2-y^2}, d_{z^2}$

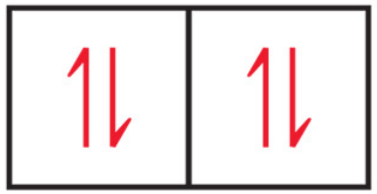
Tetrahedral



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

d_{xy}

d_{z^2}



d_{xz}, d_{yz}

Square planar

Intense color can come from “charge transfer”
Ligand electrons jump to empty metal orbitals

$KMnO_4$ K_2CrO4 $KClO_4$

No d orbitals in
Cl, orbitals higher
In energy