

# *A brief review of inorganic chemistry - a spectroscopic perspective*

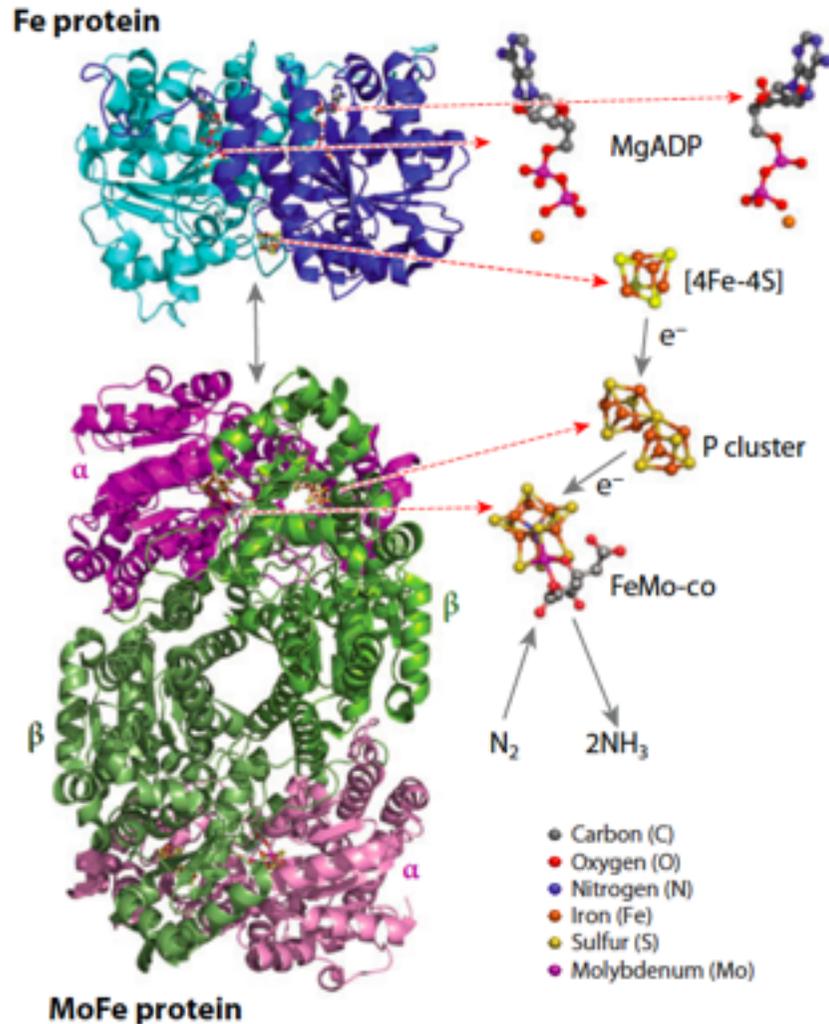
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*Serena DeBeer*  
*Max Planck Institute for Chemical Energy Conversion*

*Penn State Bioinorganic Workshop*  
*June 2016*

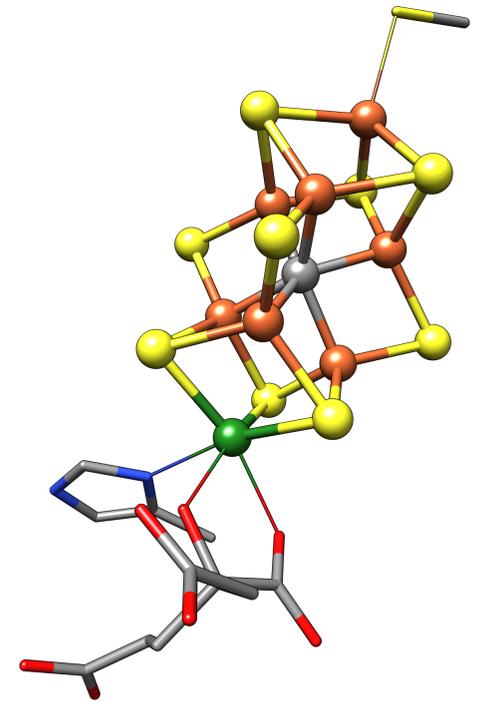
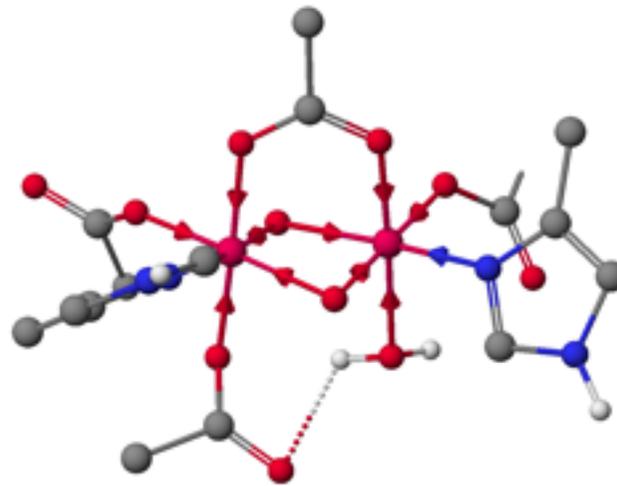
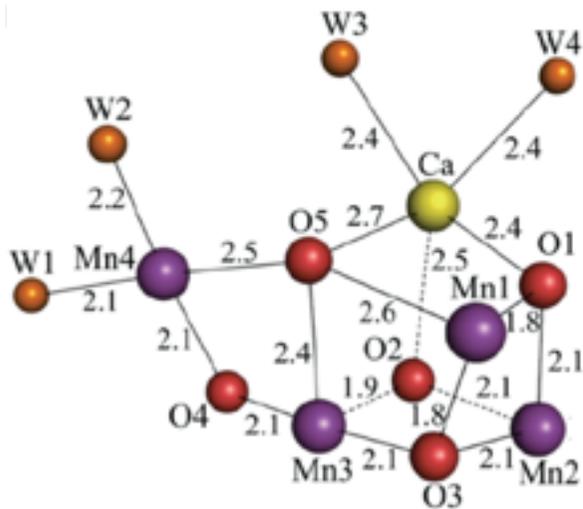
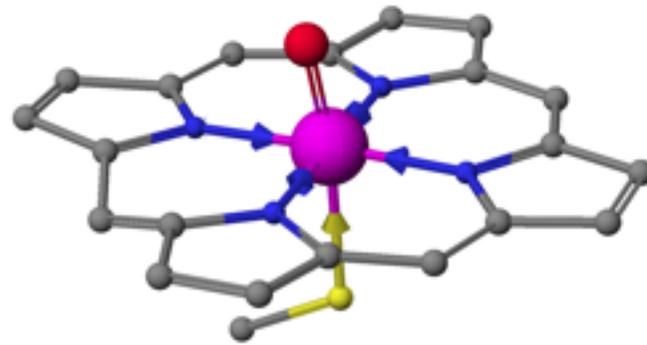
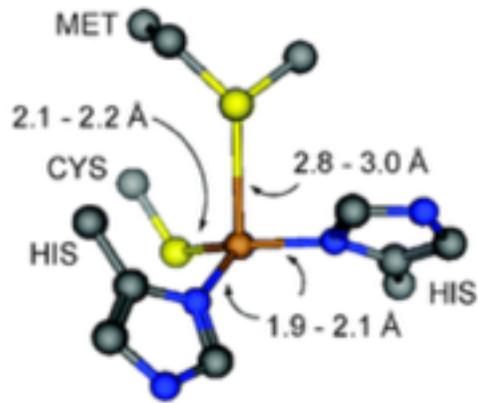


# The role of spectroscopy in bioinorganic chemistry



- \* ~1/3 of all metalloproteins contain metal cofactors
- \* these cofactors are the site of redox processes, substrate binding, reactivity
- \* a crystal structure does not tell the whole story...
- \* spectroscopy provides a route to understanding changes that occur at the active sites during electron transfer and catalytic processes

# Active Sites in Biology



*how do these unique coordination environments enable different functions?*

# What is spectroscopy?

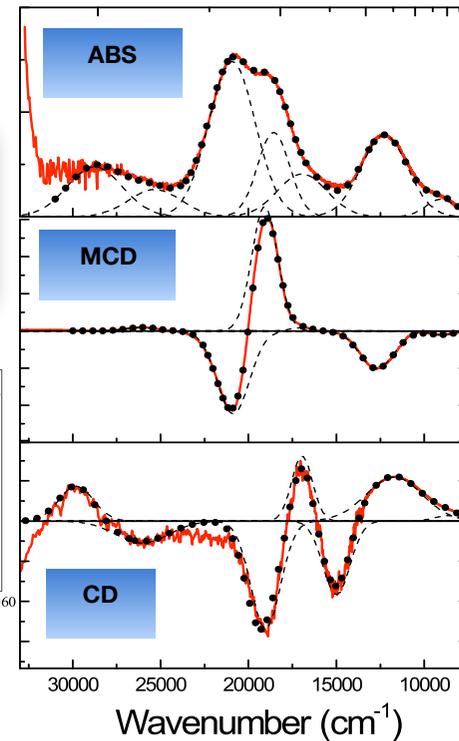
*the interaction between radiated energy and matter...*

	Gamma	X-Ray	UV/vis	Infrared	Microwave	Radiowave
eV	14000	8000	2000	4 - 1	0.1-0.01	10 <sup>-4</sup> -10 <sup>-5</sup>

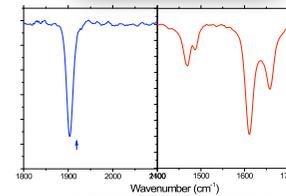


**Mössbauer**

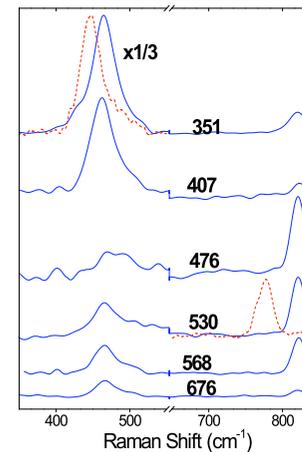
**XAS/ EXAFS  
XES**



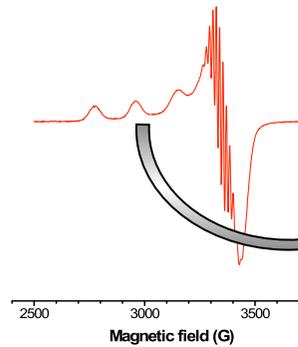
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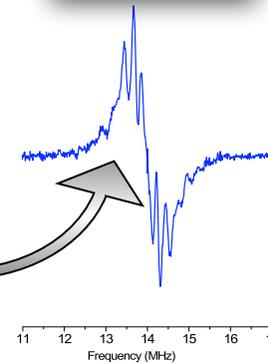
**Raman**



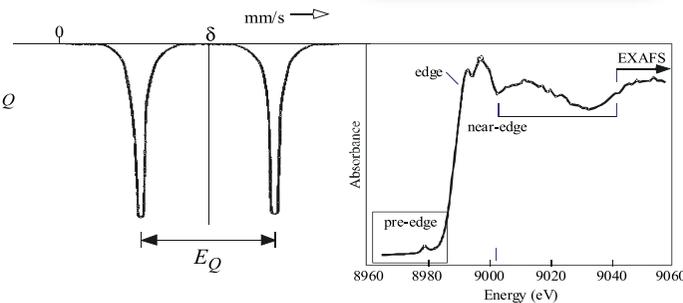
**EPR**



**ENDOR**



**NMR**



# A brief review of important topics in inorganic chemistry

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- \*Coordination Chemistry
- \*Crystal Field Theory (CFT)
- \*Ligand Field Theory (CFT + MO Theory)
- \*Spectroscopy
  - From Orbitals to States
  - Selection Rules (Ground State and Excited State Spectroscopy)
  - Determination of Allowed Transitions

# Coordination Compounds

General Formula  $[L_nM]^z$  or  $[X_nM]^z$

M= transition metal

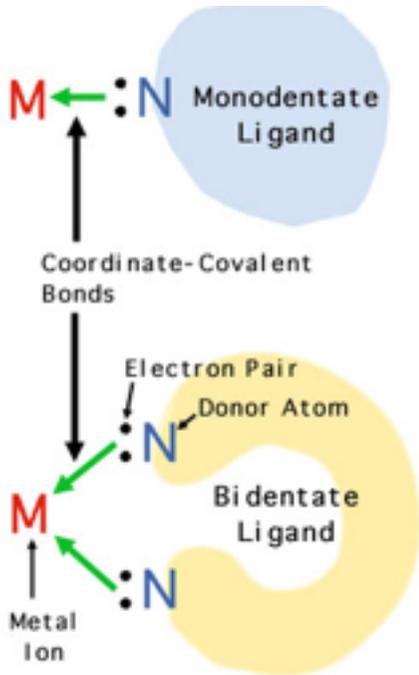
L= ligand, neutral

X = ligand, anion

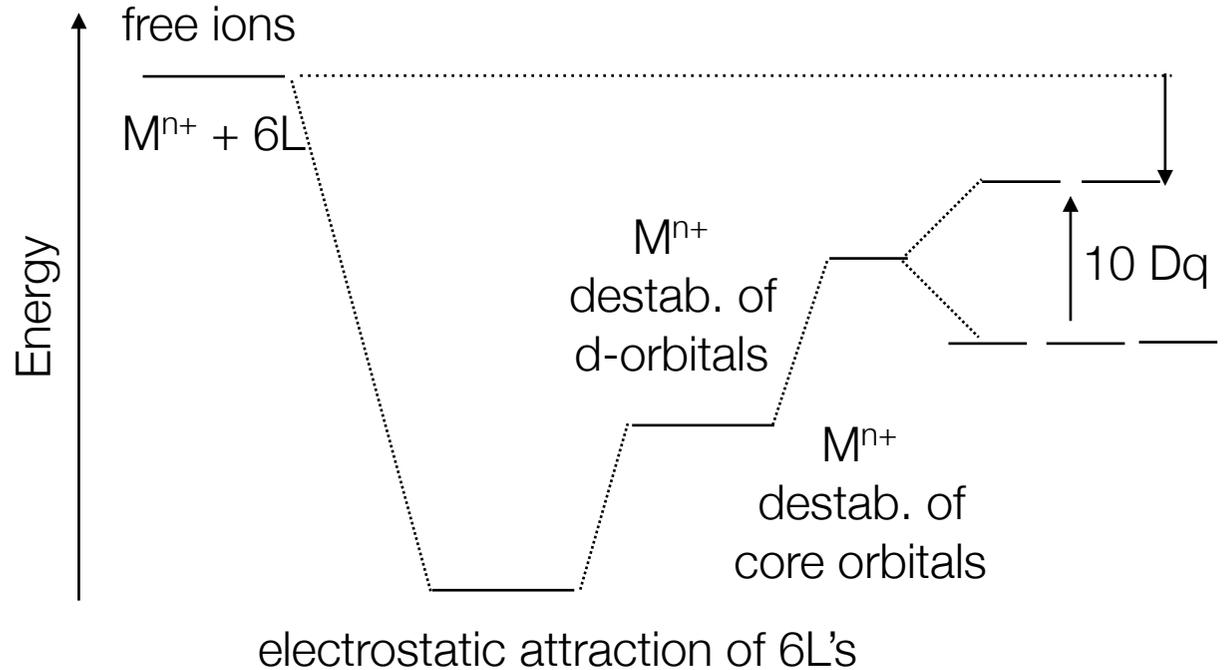
n= number of ligands

z= overall charge

$M^+$  (Lewis Acid); L,  $X^-$  Lewis Base



\*Why do coordination complexes form?



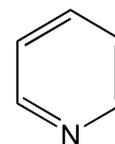
Formation is due to stabilization of ligand orbitals!  
Metal Orbitals actually increase in energy!

# Some Typical Ligands

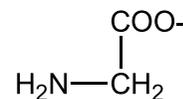
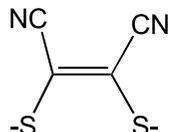
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The number of bonding contacts that a ligand makes with the metal is called the „denticity“ of the ligand

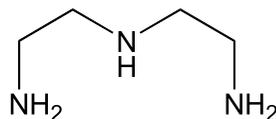
**Monodentate:**  $F^-$ ,  $Br^-$ ,  $Cl^-$ ,  $I^-$ ,  $O^{2-}$ ,  $S^{2-}$ ,  $R-O^-$ , Pyridine



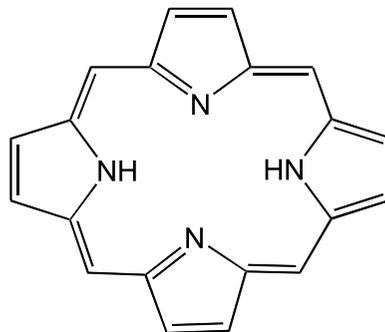
**Bidentate** : Ethylenediamine, MNT, Glycine



**Tridentate** : Triethylenetriamin (TREN)

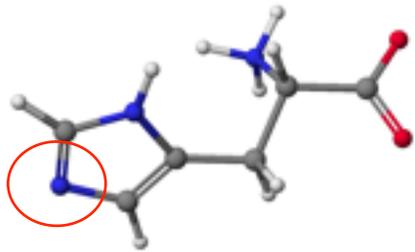


**Tetradentate** : Porphyrin



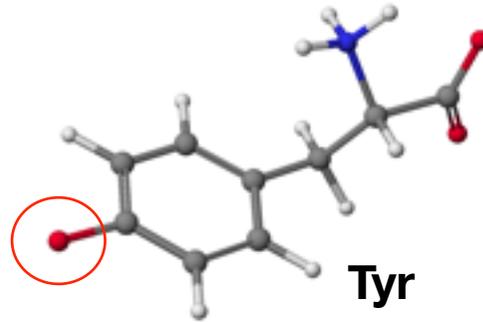
# Protein Derived Ligands

**N**

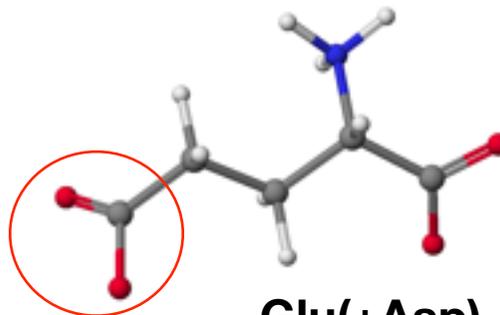


**His**

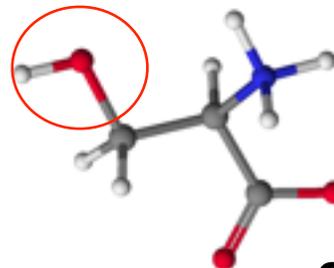
**O**



**Tyr**

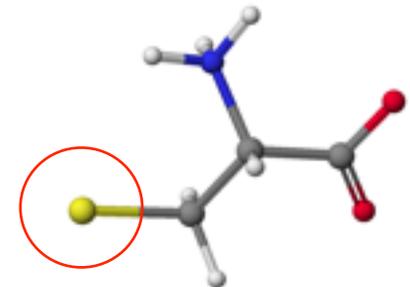


**Glu(+Asp)**

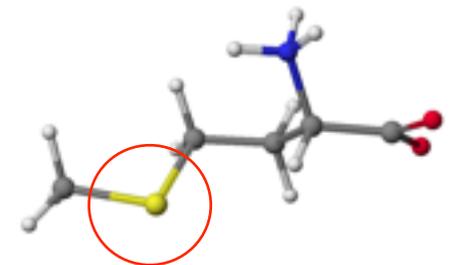


**Ser**

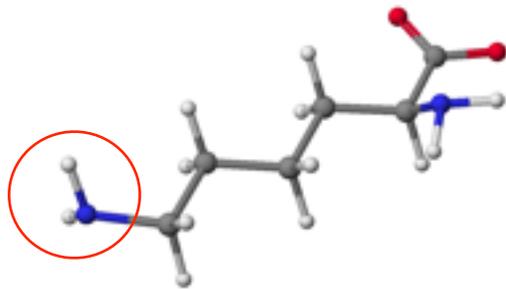
**S**



**Cys**



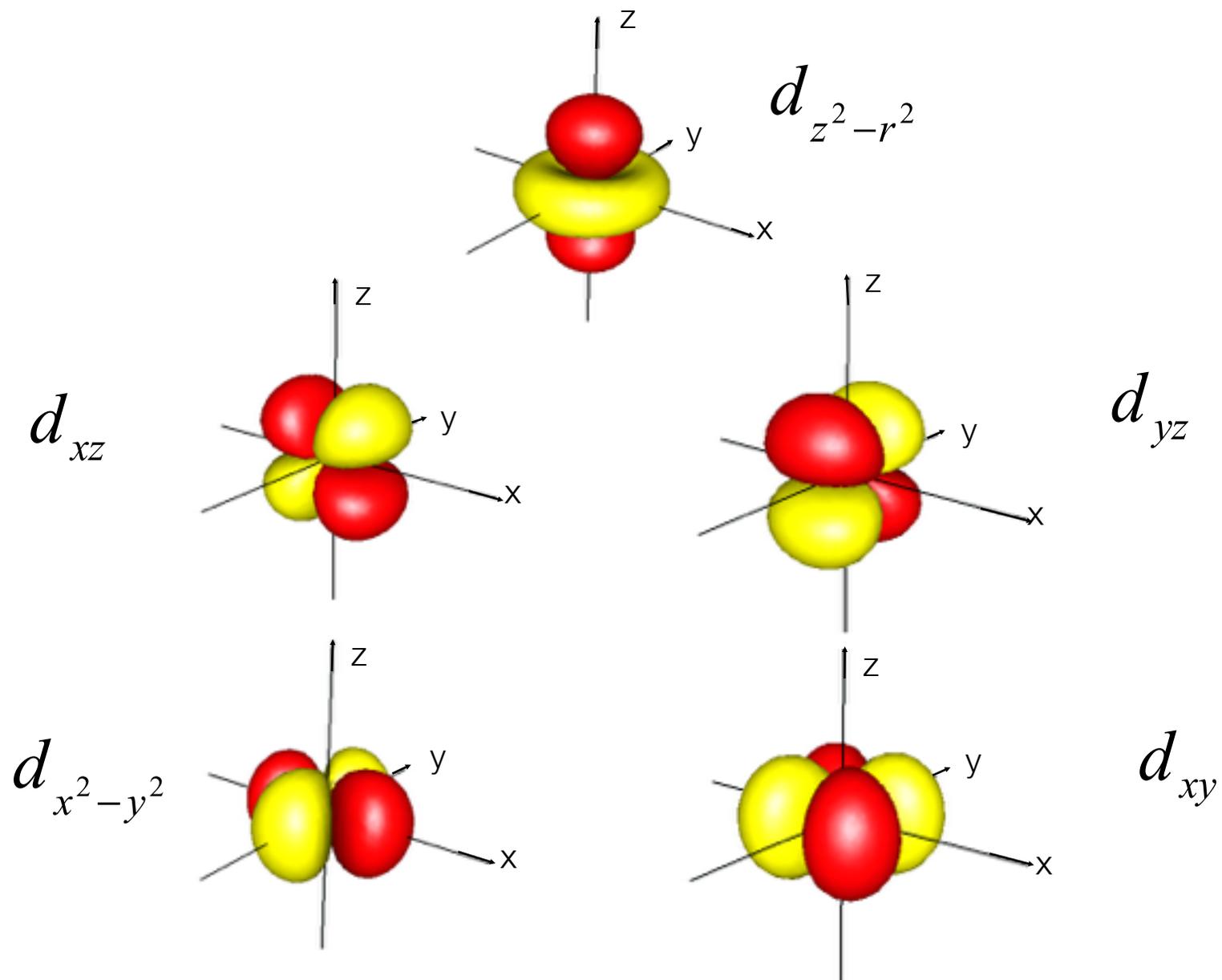
**Met**



**Lys**

# The Shape of Orbitals

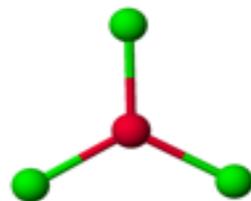
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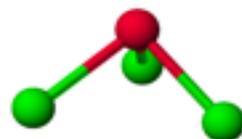
# Complex Geometries

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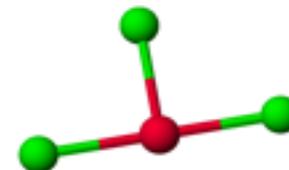
3



Trigonal

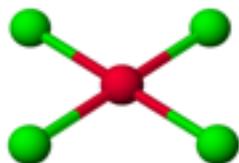


Trigonal Pyramidal

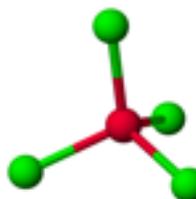


T-Shaped

4

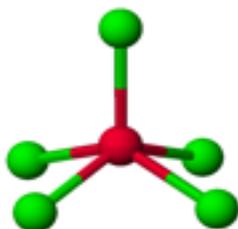


Quadratic Planar

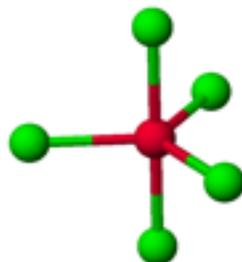


Tetrahedral

5



Quadratic Pyramidal



Trigonal Bipyramidal

6

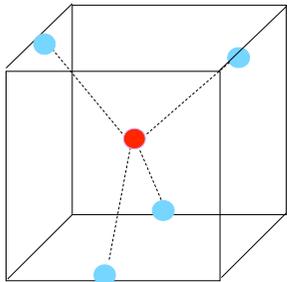


Octahedral

# Coordination Geometries

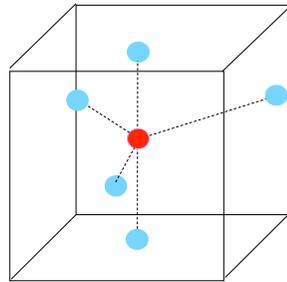
- Approximate Symmetries Observed in Enzyme Active Sites -

Tetrahedral



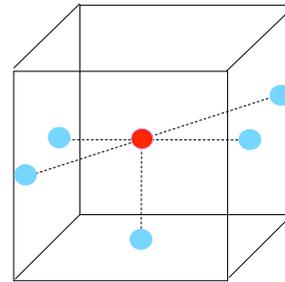
$T_d$

Trigonal Bipyramidal



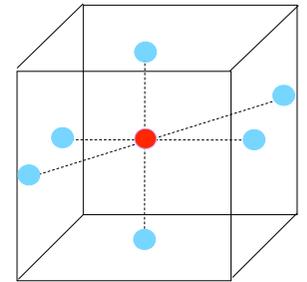
$D_{3h}$

Tetragonal Pyramidal

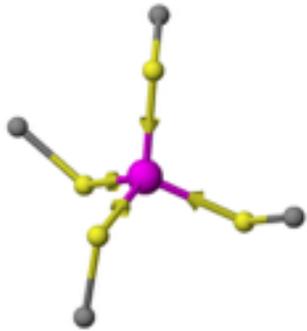


$C_{4v}$

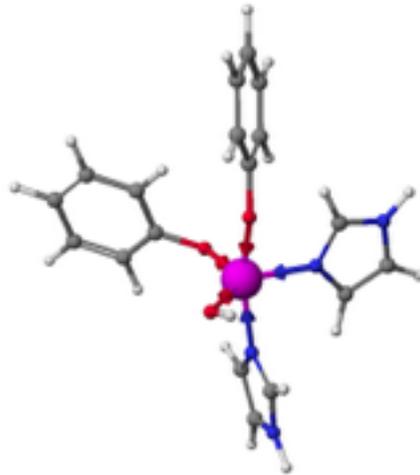
Octahedral



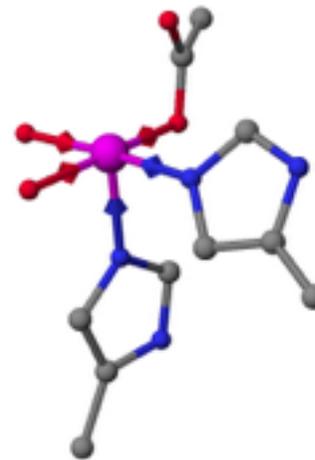
$O_h$



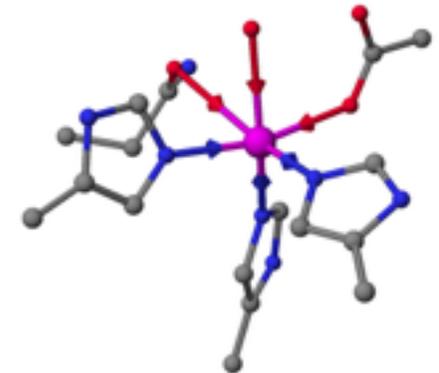
Rubredoxin



3,4-PCD



Tyrosine Hydroxylase

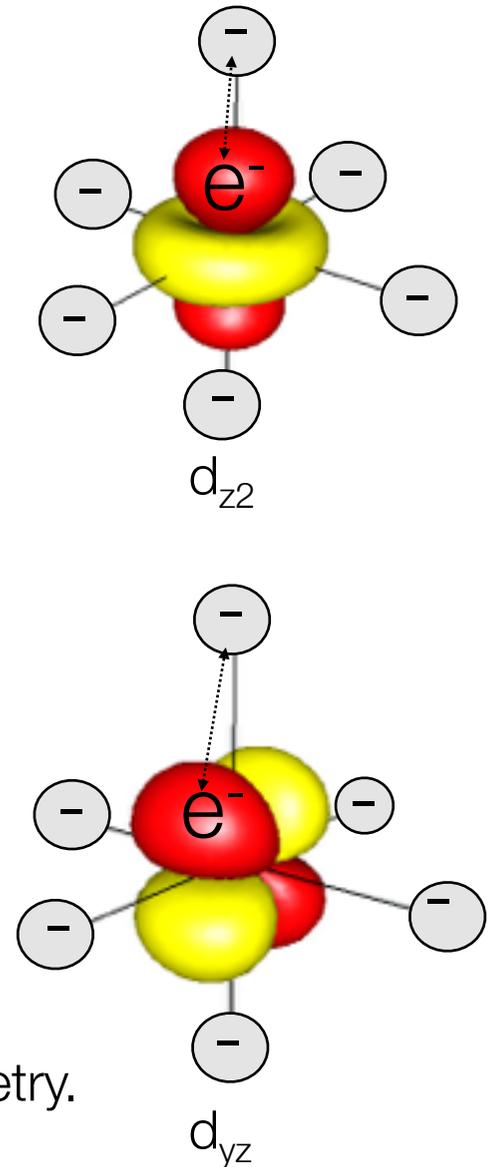
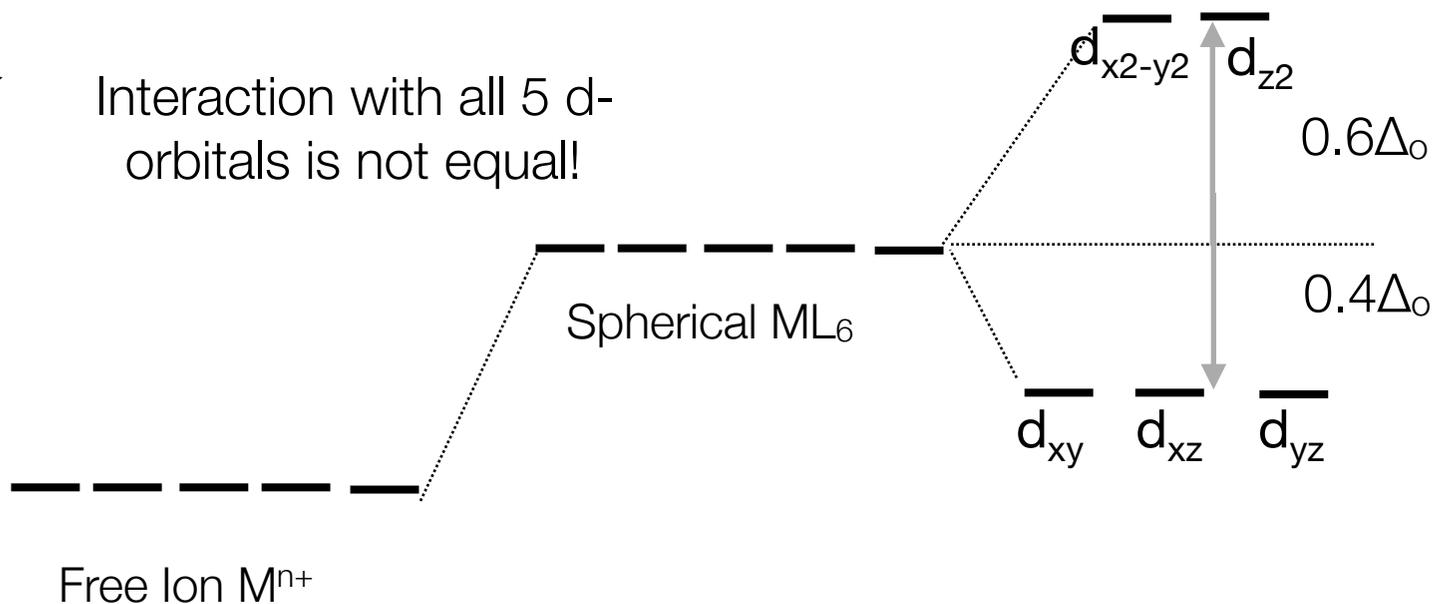


Lipoxygenase

# Crystal Field Theory (CFT)

Hans Bethe (1929)

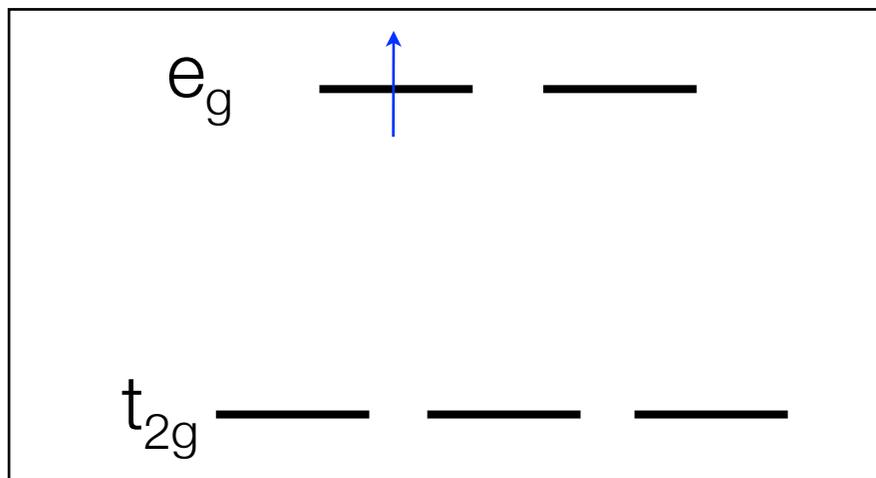
- ✓ Orbitals directed at the ligands are raised in energy.
- ✓ Interaction with all 5 d-orbitals is not equal!



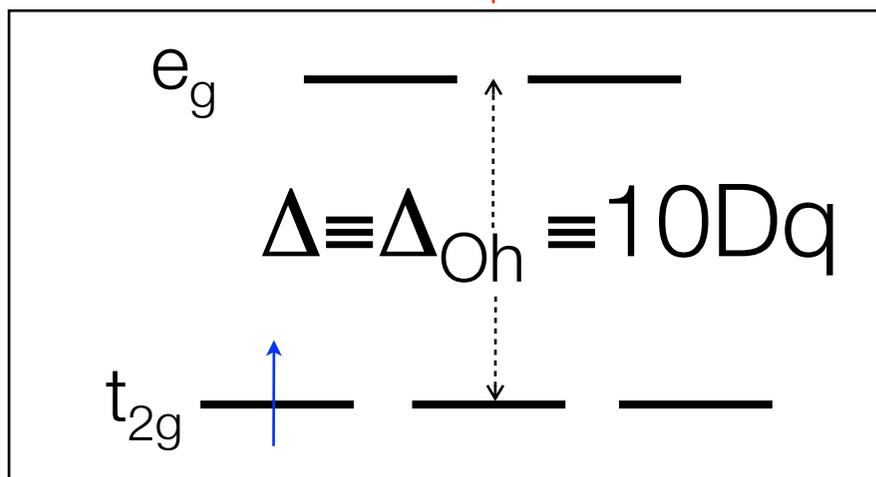
- ✓  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  45 degrees off axis in  $O_h$  symmetry.

# Prediction of Experimental Spectra by CFT

Excited State

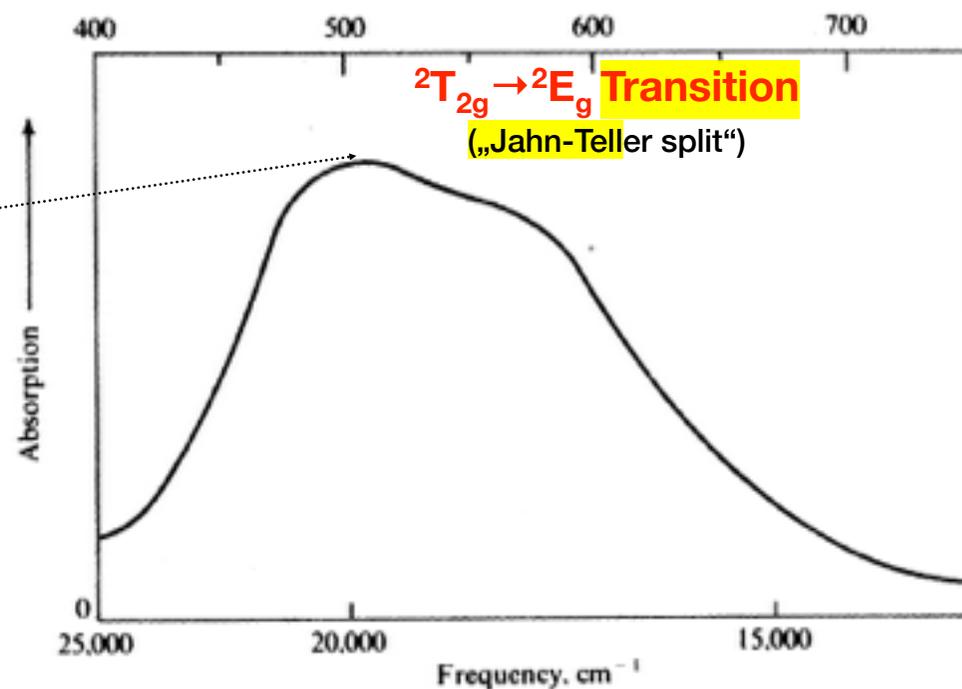
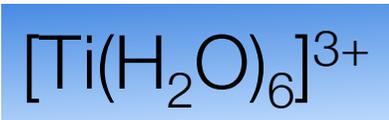


Ground State



$h\nu = \Delta_{Oh}$

Optical **Measurement** of  $\Delta$ : d-d Transitions



Limitations of CFT...

# Failures of CFT...

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10Dq parameters, however not always correctly predicted by CFT!

Example,  $[\text{Fe(III)F}_6]^{3-}$  vs  $[\text{Fe(III)(CN)}_6]^{3-}$

CFT predicts  $10Dq [\text{Fe(III)F}_6]^{3-} > 10Dq [\text{Fe(III)(CN)}_6]^{3-}$

However, from experiment....

$10Dq [\text{Fe(III)(CN)}_6]^{3-} \gg 10Dq [\text{Fe(III)F}_6]^{3-}$

$\sigma$ -DONOR

$\sigma$ -DONOR

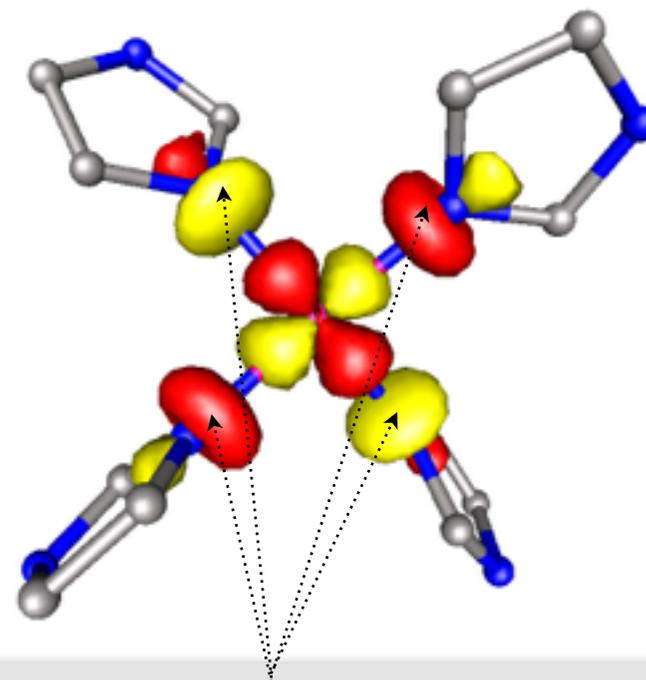
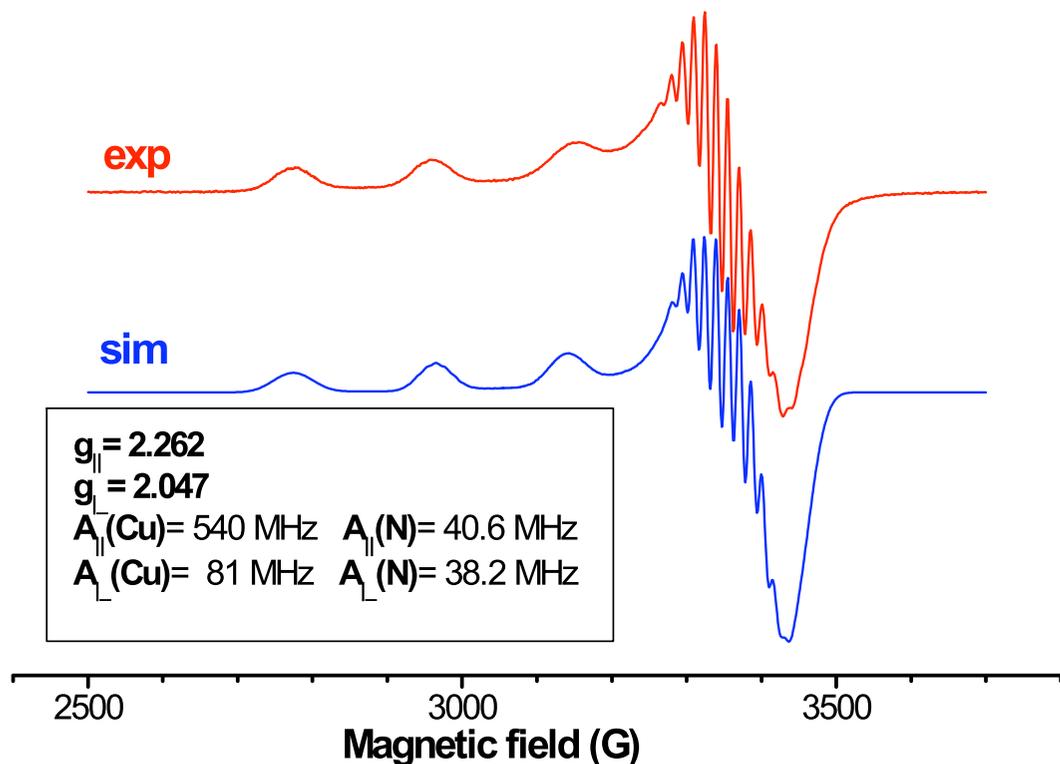
$\pi$ -ACCEPTOR

$\pi$ -DONOR

The nature of the ligand matters! Experiment can't be accounted for by electrostatics alone!

# Failures of CFT...

CFT predicts unpaired electron in  $d^9$   
Cu(II) should have free ion value, but...



The Unpaired Electron is Partly  
Delocalized Onto the Ligands

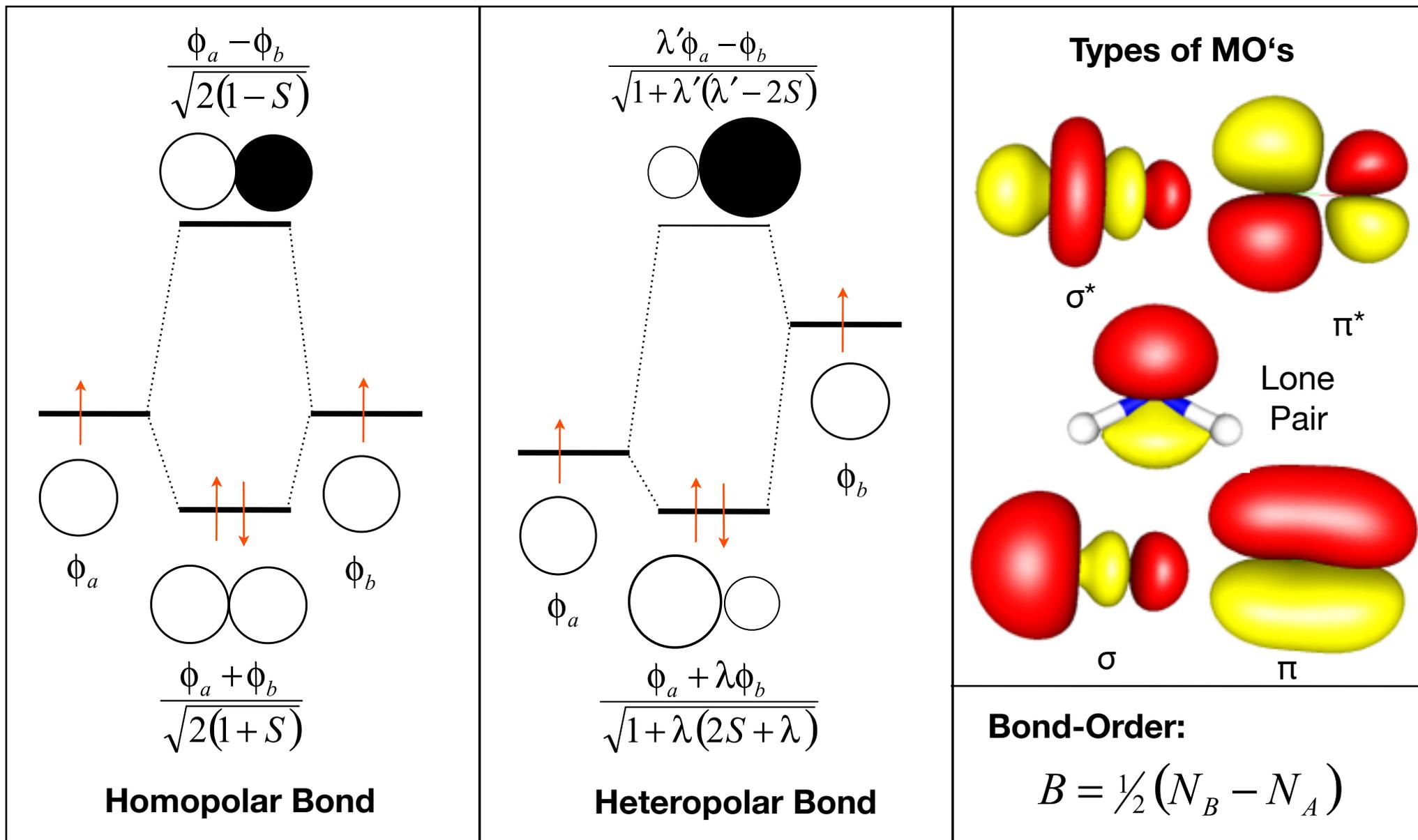
Need to go beyond CFT...

# Ligand Field Theory (LFT)

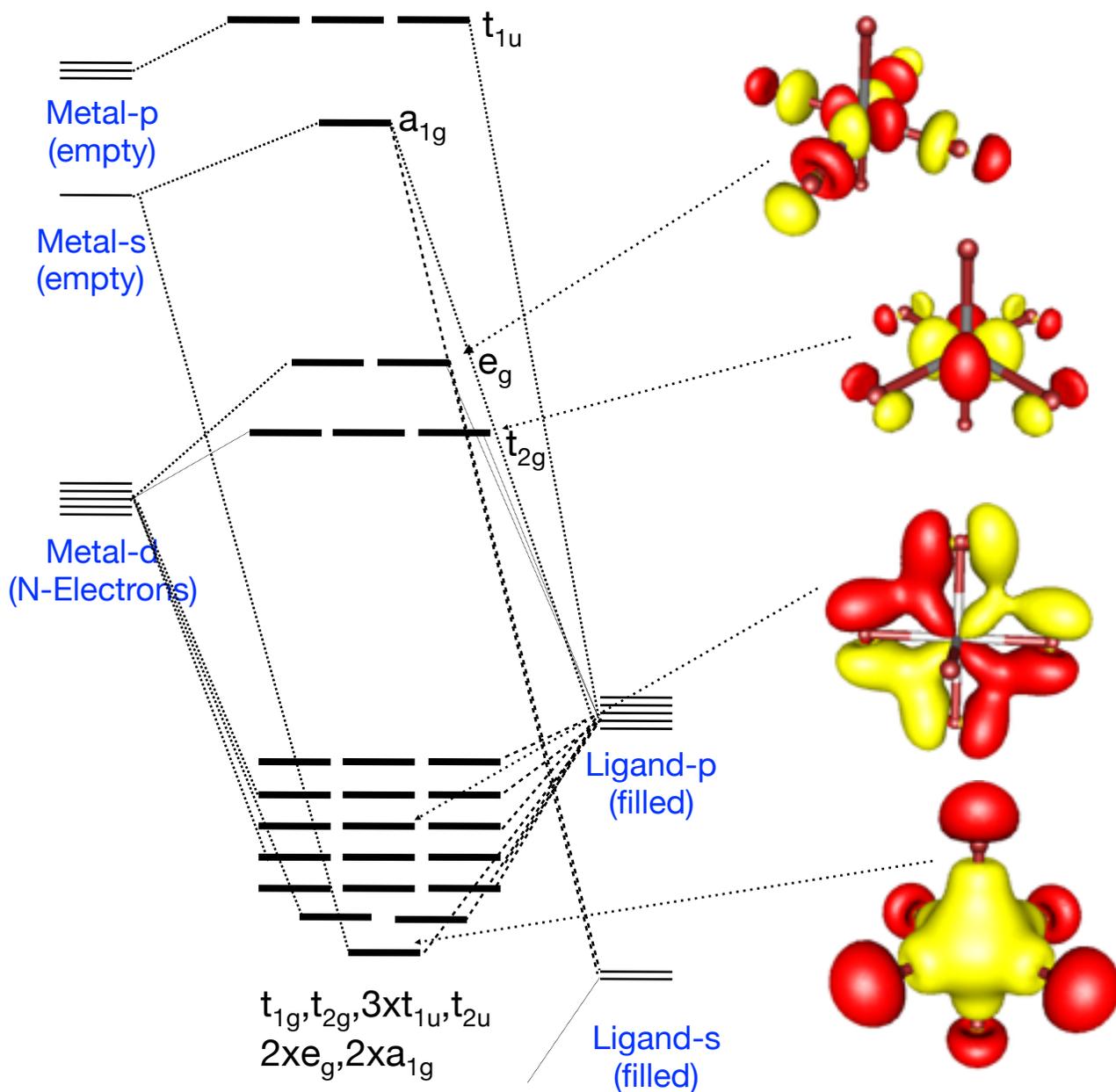
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- \*LFT combines principles laid out in CFT with molecular orbital theory
- \* Accounts for the nature of the ligand donor properties
- \*Relies on symmetry and covalency to form sigma, pi and delta bonds

# Description of Bonds in MO Theory



# MO Theory of $ML_6$ Complexes



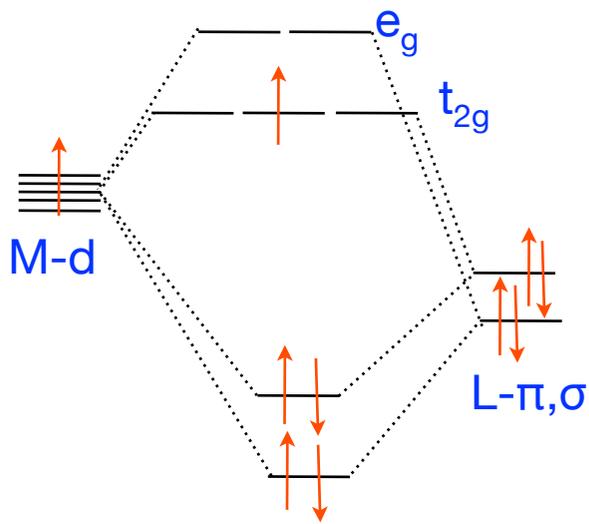
- ▶ Filled ligand orbitals are **lower in energy** than metal d-orbitals
- ▶ **The orbitals that are treated in CFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- ▶ Through bonding some **electron density** is transferred from the ligand to the metal
- ▶ The extent to which this takes place defines the **covalency** of the M-L bond

***How does this MO diagram explain the EPR?***

# Ligand Donor Types

## $\pi$ -DONOR

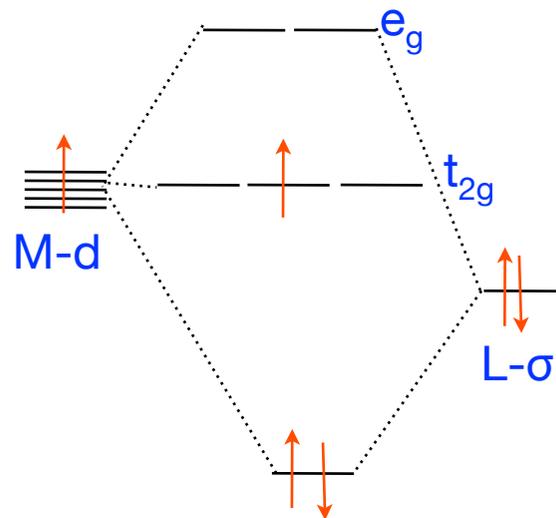
ex.  $\text{Cl}^-$ ,  $\text{F}^-$



$\Delta$  SMALL

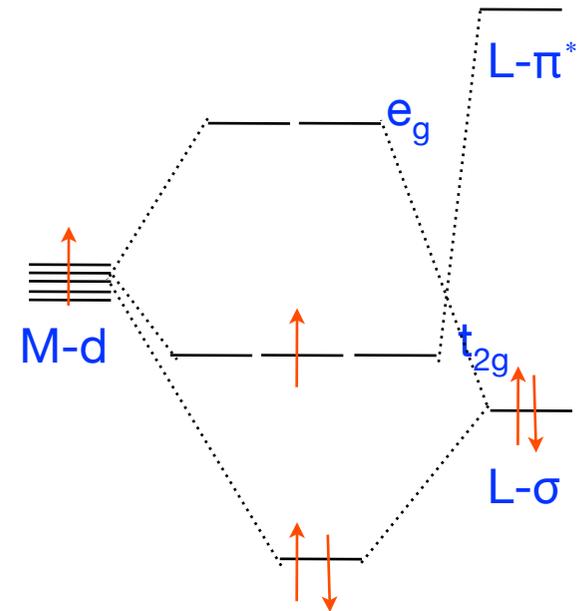
## $\sigma$ -DONOR

ex.  $\text{NH}_3$



## $\pi$ -ACCEPTOR

ex.  $\text{CN}^-$ ,  $\text{CO}$



$\Delta$  LARGE

# The Spectrochemical Series

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A „Chemical“ Spectrochemical Series



$\Delta$  SMALL

$\Delta$  LARGE

A „Biochemical“ Spectrochemical Series (A. Thomson)

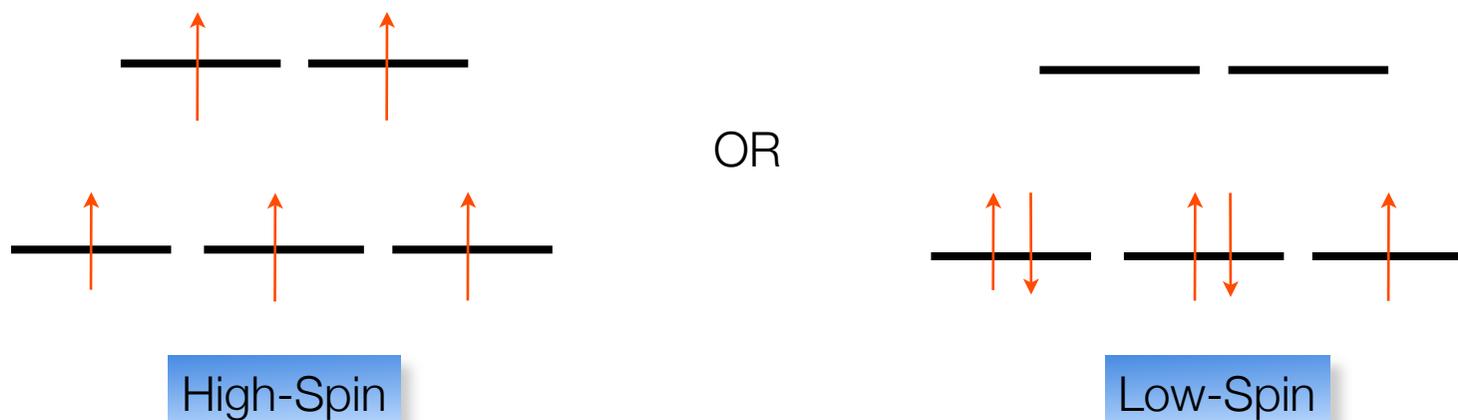


$\Delta$  SMALL

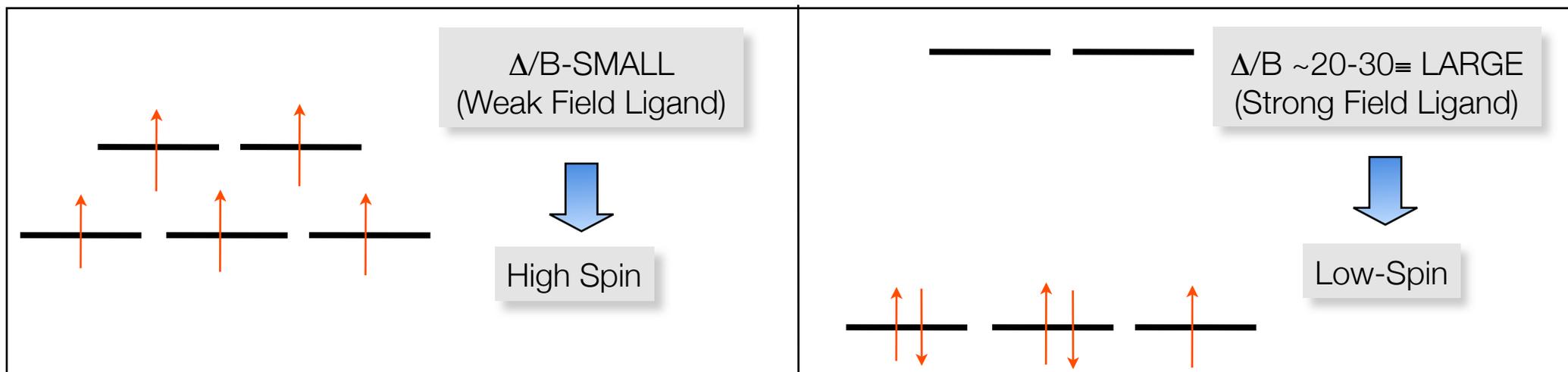
$\Delta$  LARGE

# High-Spin and Low-Spin Complexes

QUESTION: What Determines The Electron Configuration?

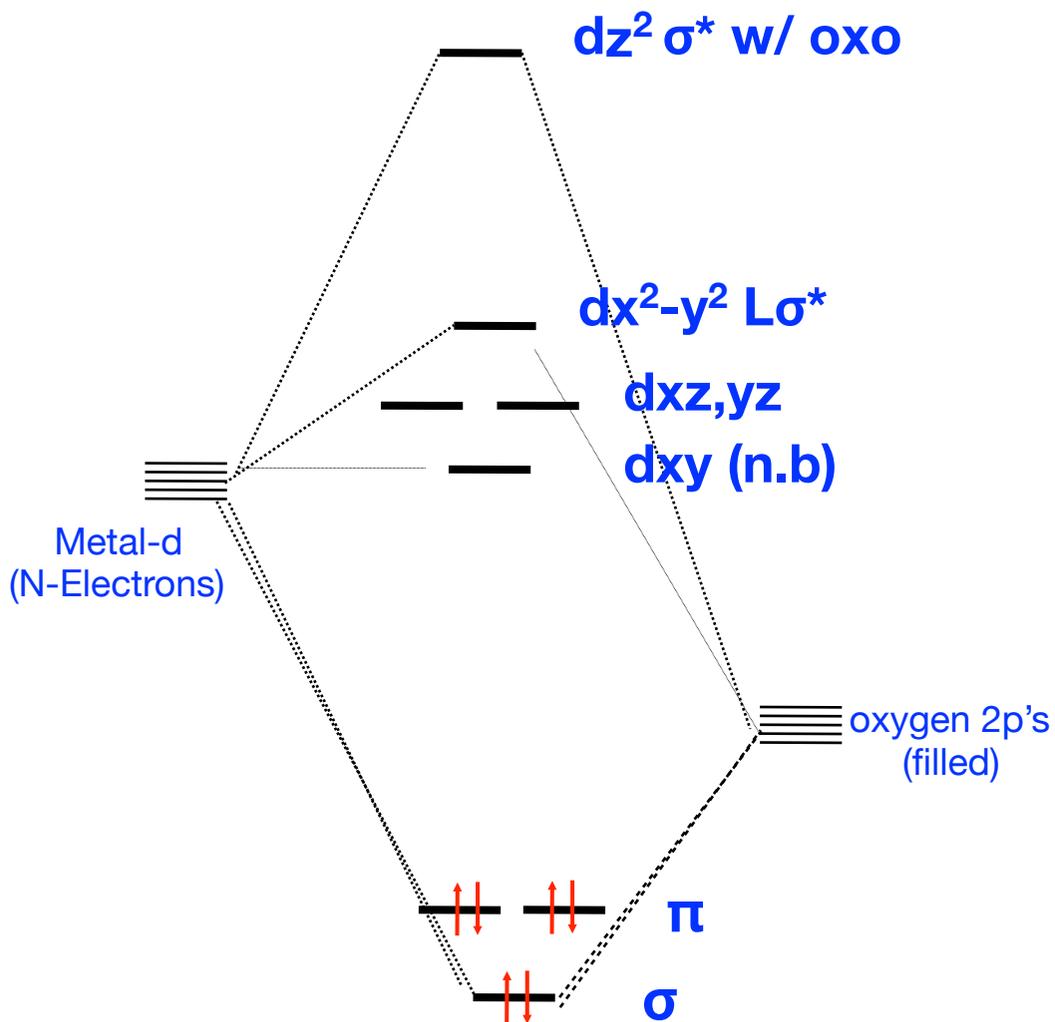


ANSWER: The Balance of Ligand Field Splitting and Electron Repulsion (,Spin-Pairing Energy'  $P=f(B)$ )



# The Utility of the MO-Based Picture

## MO diagram for $d^0$ TM-oxo complex in $C_{4v}$ Symmetry



- for  $d^1$  and  $d^2$  systems electrons occupy n.b. MO
- for  $d^3$  and beyond electron occupy a.b. orbitals
- $d^6$  - no net bond!
- *What effect does this have on the metal oxo complexes we observe and their reactivity?*

# What is spectroscopy?

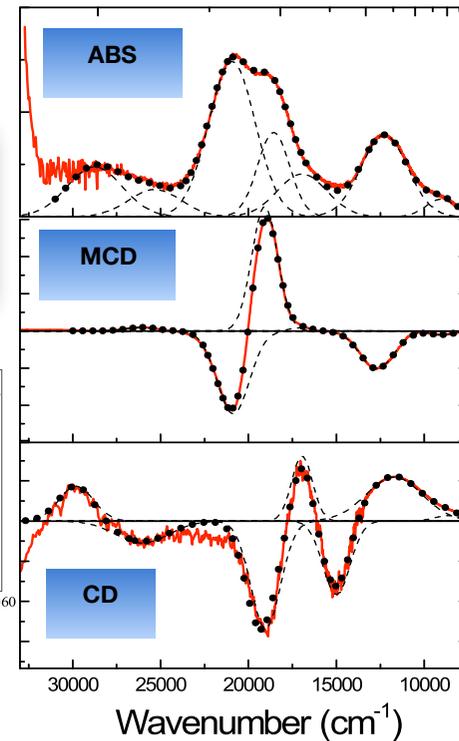
*spectroscopy involves transitions between STATES...*

	Gamma	X-Ray	UV/vis	Infrared	Microwave	Radiowave
eV	14000	8000	2000	4 - 1	0.1-0.01	10 <sup>-4</sup> -10 <sup>-5</sup>
					10 <sup>-4</sup> -10 <sup>-5</sup>	10 <sup>-6</sup> -10 <sup>-7</sup>

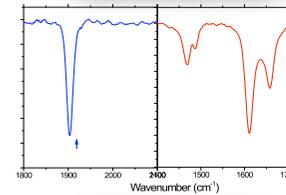


**Mössbauer**

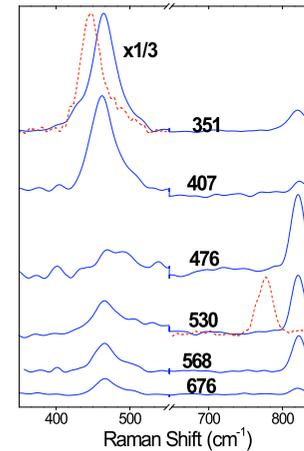
**XAS/ EXAFS  
XES**



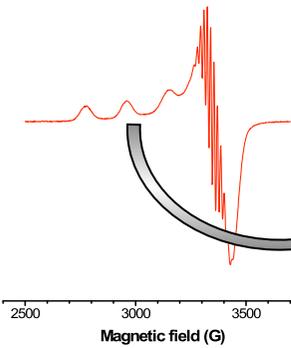
**IR**



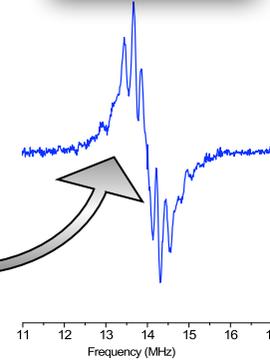
**Raman**



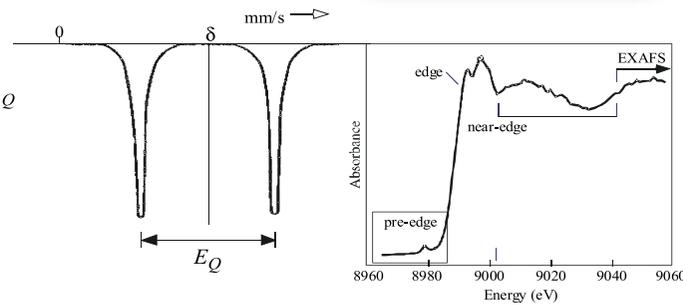
**EPR**

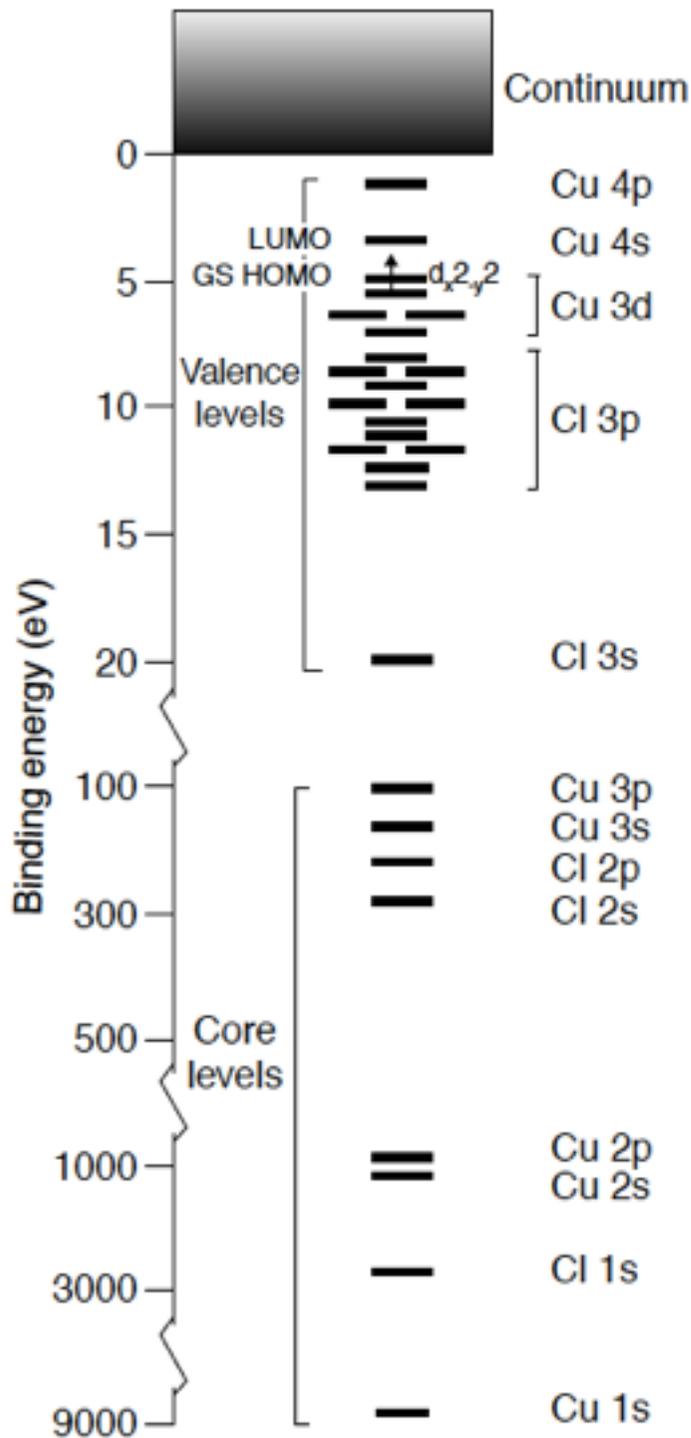


**ENDOR**



**NMR**





Energy Level Diagram for  $[\text{CuCl}_4]^{2-}$   
 adapted from Lehnert, DeBeer, and Solomon, COCB, 2001

- \* Energy level diagram spans ~10 orders of magnitude in photon energy
- \* Different spectroscopic methods probe different regions of this diagram
- \* Taken together different methods should provide a cohesive picture
- \* One of the strengths of bioinorganic chemistry community (application of multiple techniques)
- \* REMINDER: Though we will often relate spectroscopy to a molecular-orbital based picture: ORBITALS ARE NOT OBSERVABLES. Spectroscopically we observe states.
- \* ***We can probe ground or excited electronic states....***

# Ground State Methods

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\*Note by “ground” state, we mean the electronic ground state

\*Energy range  $10^{-3}$  -  $10^4$   $\text{cm}^{-1}$

\*Probing transitions that correspond to very small changes in energy

\*e.g. splitting of magnetic orbitals

\* $S=1/2$ ;  $m_s=-1/2$  to  $m_s=+1/2$

- 1) Electron Paramagnetic Resonance (EPR)
- 2) Electron Nuclear Double Resonance (ENDOR)
- 3) Electron Spin Echo Envelope Modulation (ESEEM)
- 4) Magnetic Susceptibility (low resolution)
- 5) Mössbauer (small changes in energy of nuclear spin states, but probed by a high energy source)

# Excited State Methods

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\*The rest of the electromagnetic spectrum - (0.01 eV to 100,000 eV!)

i) Near IR to Visible 0.01 to 1 eV

- electrons are excited from occupied to unoccupied valence orbitals
- ligand field or “d to d” transitions
- CD/ MCD

ii) Visible to UV 1 to 100 eV

- LMCT and MLCT
- Abs/ CD/ MCD
- Resonance Raman

ii) Core excited states (100+ eV)

- XAS
- XES

# States vs Orbitals

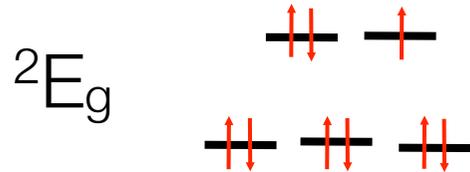
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- ★ Excited State methods involve electrons transitioning from an occupied to a semi-occupied or empty MO. As chemists we relate this to a simple MO based picture.
- ★ It is essential to understand that ORBITALS ARE NOT OBSERVABLES. You do NOT observe orbitals - you ALWAYS observe many electron states.
- ★ This is how you were probably taught UV-Vis.
- ★ “Ground State Methods” involve magnetic dipole transitions between nuclear or electronic spin states. Thus, in the orbital picture we remain in the electronic ground state.

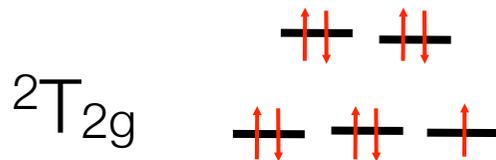
# Summary: Ground State vs Excited State Spectroscopy

---

Ex. Cu(II)  $d^9$



Ground State Methods = Many  
electron term symbol is  
unchanged  
 $2S+1 \Gamma \rightarrow 2S+1 \Gamma$



Excited State Methods = Many  
electron term symbol is  
changed  
 $2S+1 \Gamma \rightarrow 2S+n \Gamma'$

# Spectroscopic Selection Rules

---

❖ Most spectroscopy can be understood in terms of a few important selection rules

❖ Excited State Methods

-

- $\Delta S=0$  (spin selection rule)

-g to u or u to g (parity selection rule)

- $\Delta l = \pm 1$  (dipole selection rule)

❖ Ground State Methods (magnetic dipole transitions between nuclear or electronic spin states)

- $\Delta m_s = \pm 1$  (EPR)

- $\Delta m_l = 0, \pm 1$ ;  $\Delta l = \pm 1$  (Mössbauer)

★ *Spectroscopy has greatly influenced the development of bioinorganic chemistry. You will see this in lectures throughout the week.*

# Atoms: Atomic „Russell-Saunders“ Terms

Atomic Term Symbol:

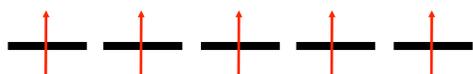
$$2S+1L$$

- ▶ Describes the orbital and spin degeneracy of a many electron state
- ▶  $L$  = Total angular momentum for the entire system  $L= 0,1,2,3,4\dots = S,P,D,F,G,\dots$
- ▶  $S$  = Total many electron spin angular momentum,  $2S+1$  = multiplicity
- ▶  $M_L= -L$  to  $L$ ;  $M_S = -S$  to  $S$ : describes the microstates that make up a many electron state

Examples for  $d^N$  Configurations:



$2S+1=2$ ;  
5 equivalent ways to put one  $e^-$   
into five degenerate orbitals



$2S+1=6$ ;  
1 equivalent ways to put five  $e^-$   
with parallel spin in five orbitals



$2S+1=3$ ;  
10 Ways to put two  $e^-$  with parallel  
spin in five orbitals



# Possible Microstates for a $p^2$ configuration

---

$\uparrow$	$\uparrow$		$M_L$	$M_S$	$\uparrow$		$\uparrow$	$M_L$	$M_S$		$\uparrow$	$\uparrow$	$M_L$	$M_S$
$\frac{\uparrow}{+1}$	$\frac{\uparrow}{0}$	$\frac{}{-1}$	1	1	$\frac{\uparrow}{+1}$	$\frac{}{0}$	$\frac{\uparrow}{-1}$	1	1	$\frac{}{+1}$	$\frac{\uparrow}{0}$	$\frac{\uparrow}{-1}$	-1	1
$\uparrow\downarrow$			2	0	$\uparrow\downarrow$			0	0	$\frac{}{+1}$	$\frac{}{0}$	$\uparrow\downarrow$	-2	0
$\frac{\uparrow}{+1}$	$\frac{\downarrow}{0}$	$\frac{}{-1}$	1	0	$\frac{\uparrow}{+1}$	$\frac{\downarrow}{0}$	$\frac{\downarrow}{-1}$	0	0	$\frac{}{+1}$	$\frac{\uparrow}{0}$	$\frac{\downarrow}{-1}$	-1	0
$\frac{\downarrow}{+1}$	$\frac{\downarrow}{0}$	$\frac{}{-1}$	1	-1	$\frac{\downarrow}{+1}$	$\frac{}{0}$	$\frac{\downarrow}{-1}$	0	-1	$\frac{}{+1}$	$\frac{\downarrow}{0}$	$\frac{\downarrow}{-1}$	-1	-1
$\frac{\downarrow}{+1}$	$\frac{\uparrow}{0}$	$\frac{}{-1}$	1	0	$\frac{\downarrow}{+1}$	$\frac{}{0}$	$\frac{\uparrow}{-1}$	0	0	$\frac{}{+1}$	$\frac{\downarrow}{0}$	$\frac{\uparrow}{-1}$	-1	0

15 possible micro states

# Possible Microstates for a $p^2$ configuration

---

$M_L \downarrow \backslash M_S \rightarrow$	-1	0	+1
D      +2		X	
P      +1	X	XX	X
S      0	X	XXX	X
P      -1	X	XX	X
D      -2		X	

Choose highest  $M_S$  &  $M_L$  for parent microstate:

$$M_S = 1; M_L = 1$$

$$L = 1; S = 1$$

$$M_S = 1 \text{ to } -1; M_L = 1 \text{ to } -1$$

# Possible Microstates for a $p^2$ configuration

$M_L \downarrow \backslash M_S \rightarrow$	-1	0	+1
D +2		X	
P +1	▲	▲X	▲
S 0	▲	▲XX	▲
P -1	▲	▲X	▲
D -2		X	

Choose highest  $M_S$  &  $M_L$  for parent microstate:

$$M_S = 1; M_L = 1$$

$$L = 1; S = 1$$

$$M_S = 1 \text{ to } -1; M_L = 1 \text{ to } -1$$

9 micro states  **$^3P$**

# Possible Microstates for a $p^2$ configuration

$M_L \downarrow \backslash M_S \rightarrow$	-1	0	+1
D +2		▲	
P +1	▲	▲ ▲	▲
S 0	▲	▲ ▲ ▲	▲
P -1	▲	▲ ▲	▲
D -2		▲	

9 microstates  **$^3P$**

5 microstates ( $M_S=0$ );  $M_L=2$  to  $-2$   **$^1D$**

1 microstate  $M_S=0$ ;  $M_L=0$   **$^1S$**

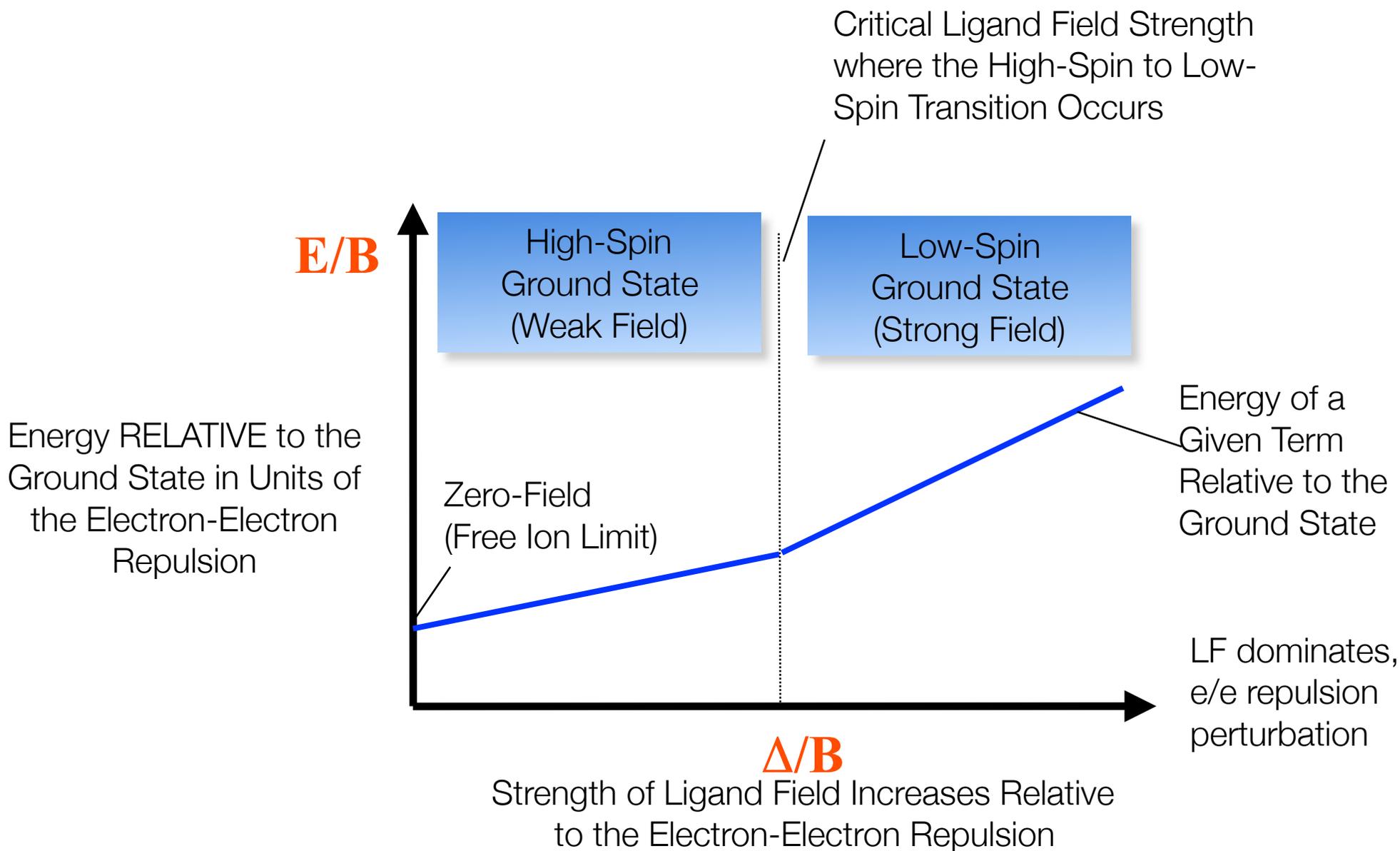


Different steps with different energies ordered by Hund's rules....

- I. Terms of a given configuration with higher S are lower in energy
- II. Terms with given configuration and equal spin have the higher L lower in energy

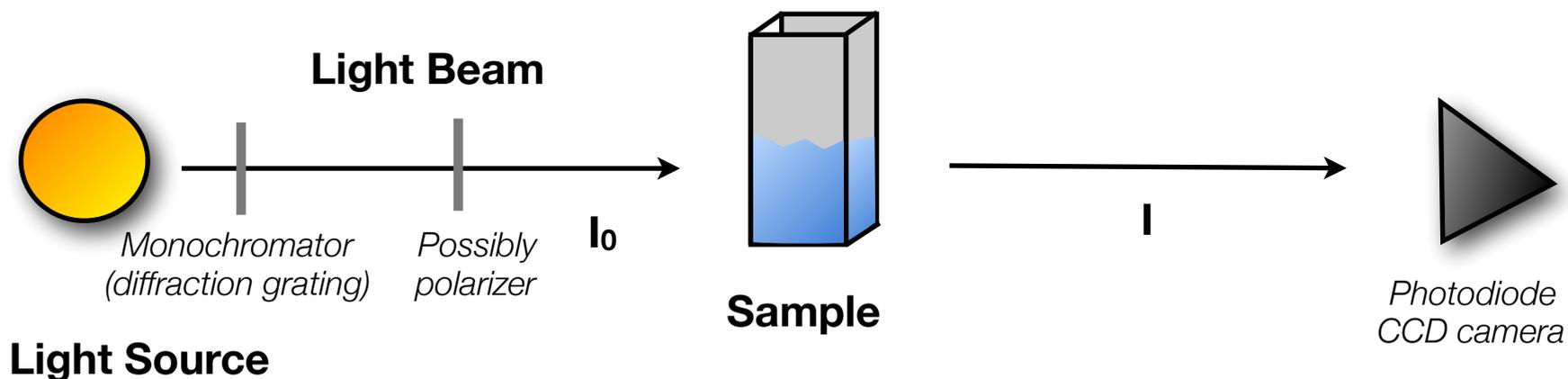
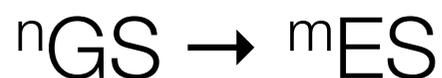


# Inside Ligand Field Theory: Tanabe-Sugano Diagrams



# Absorption Spectroscopy

*Absorption of light results in a transition from a lower energy state to a higher energy state*



*Beer-Lambert Law*

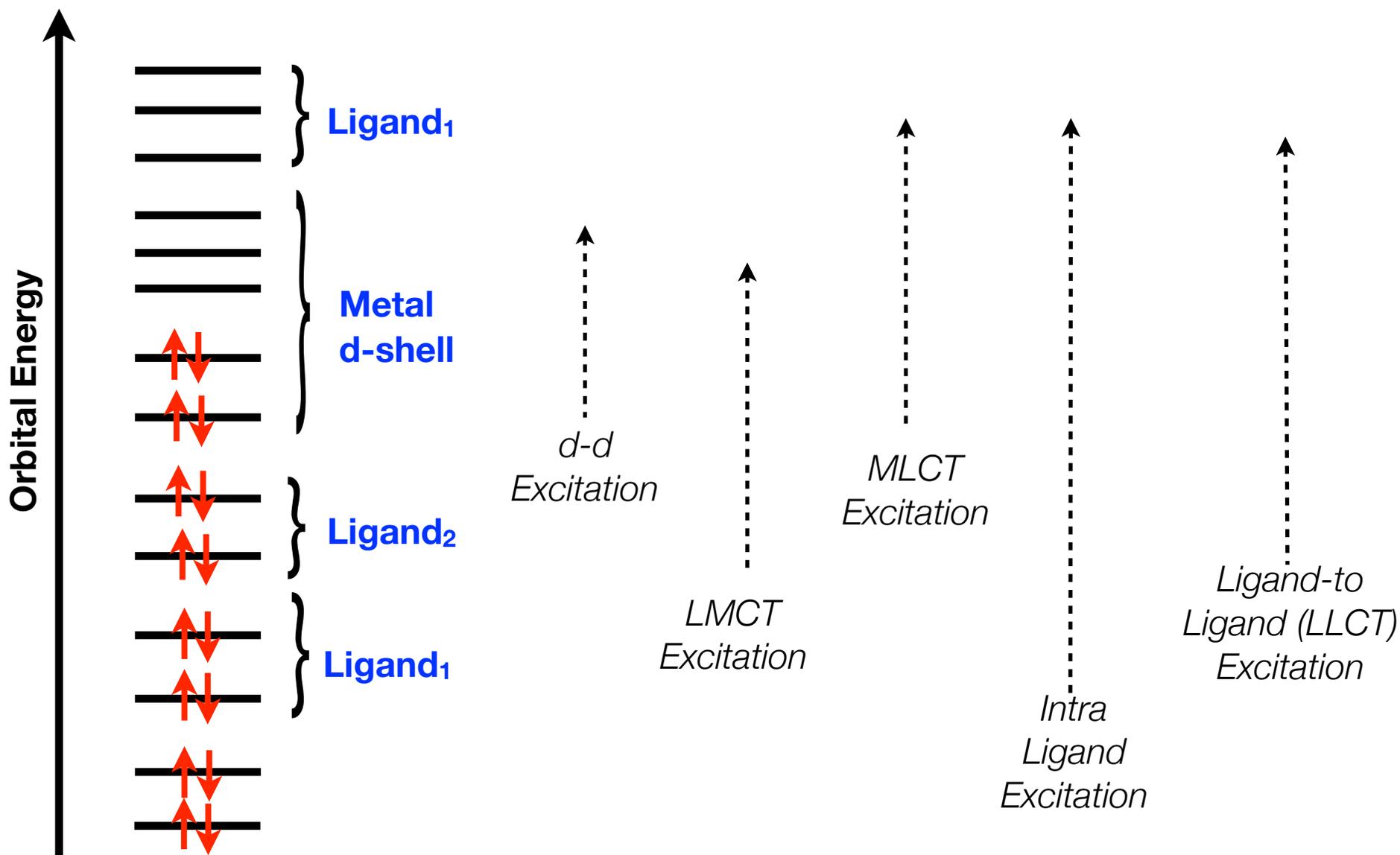
$$A = \epsilon \ell c = \log(I_0/I)$$

$\epsilon$  = molar absorptivity ( $\text{l mol}^{-1} \text{cm}^{-1}$ ) or extinction coeff

$\ell$  = path length

$c$  = concentration

# Types of Transitions in Transition Metal Complexes



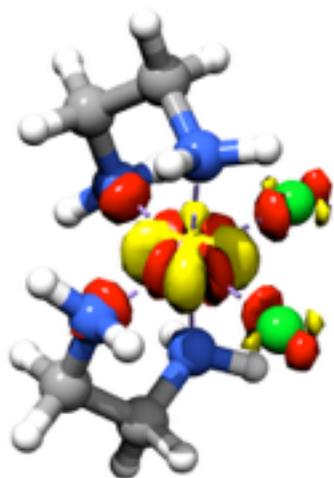
# Visualizing Possible Transitions

---

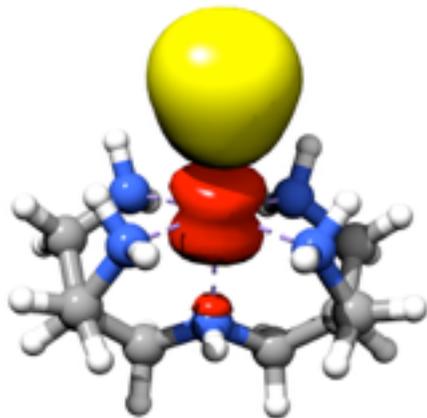
## Electronic Difference Densities

*Red = Electron Gain      Yellow = Electron Loss*

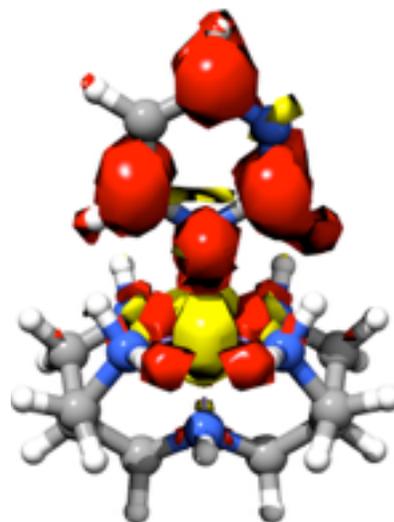
**d-d Transition**



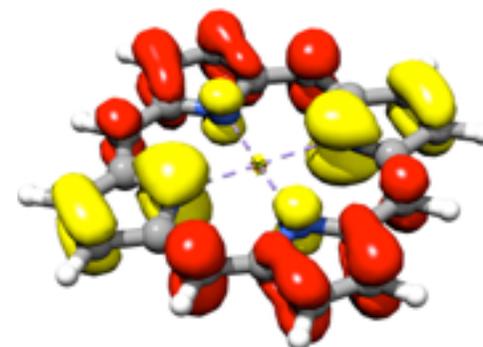
**LMCT Transition**



**MLCT Transition**



**$\pi \rightarrow \pi^*$  Transition**



***But how do we know what can happen and when?***

***Group Theory and Selection Rules...***

# Assigning Molecular Term Symbols

- ❖ The total symmetry of the state follows from the **direct product of the singly occupied MOs** (closed shells are always totally symmetric!)
- ❖ We need to be able to assign a term symbol for a given many electron ground or excited state

## ❖ Example: $d^4$ configuration $D_{2h}$

*Singly occupied MOs:*  $a_g, b_{1g}, b_{2u}, a_u$ :

*State Symmetry:*  $a_g \otimes b_{1g} = b_{1g}$

$$b_{1g} \otimes b_{2u} = b_{3u}$$

$$b_{3u} \otimes a_u = b_{3g} \Rightarrow {}^5\mathbf{B}_{3g}$$

Normal:

$$a \otimes a = a, \quad b \otimes b = a, \quad a \otimes b = b$$

$D_{2h}$ :

$$b_1 \otimes b_2 = b_3$$

Always:

$$g \otimes g = g, \quad u \otimes u = g, \quad g \otimes u = u$$

## ❖ Example: $d^5$ configuration in $O_h$

*Singly occupied MOs:*  $(t_{2g})^3(e_g)^2$  and  $S=5/2$

*State Symmetry:*  $t_{2g} \otimes t_{2g} \otimes t_{2g} = a_{2g}$

$$e_g \otimes e_g = a_{2g}$$

$$a_{2g} \otimes a_{2g} = a_{1g} \Rightarrow {}^6\mathbf{A}_{1g}$$

$$t_i \otimes t_i = a_1 \oplus e \oplus [t_1] \oplus t_2 \quad (i=1,2)$$

$$t_1 \otimes t_2 = a_2 \oplus e \oplus t_1 \oplus t_2$$

$$t_i \otimes e = t_1 \oplus t_2 \quad (i=1,2)$$

$$e_i \otimes e_i = e \oplus a_1 [\oplus a_2] \quad (i=1,2)$$

$$e_1 \otimes e_2 = e \oplus b_1 \oplus b_2$$

# Ground and Excited State Term Symbols

Example:  $D_{2d}$ -[CuCl<sub>4</sub>]<sup>2-</sup>

Character table for  $D_{2d}$  point group

	E	2S <sub>4</sub>	C <sub>2</sub> (z)	2C' <sub>2</sub>	2σ <sub>d</sub>	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	1		x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	1	-1	-1	R <sub>z</sub>	
B <sub>1</sub>	1	-1	1	1	-1		x <sup>2</sup> -y <sup>2</sup>
B <sub>2</sub>	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(x, y) (R <sub>x</sub> , R <sub>y</sub> )	(xz, yz)

 xy (b<sub>2</sub>)

 xz, yz (e)

 x<sup>2</sup>-y<sup>2</sup> (b<sub>1</sub>)

 z<sup>2</sup> (a<sub>1</sub>)

ground state

**<sup>2</sup>B<sub>2</sub>**

 xy (b<sub>2</sub>)

 xz, yz (e)

 x<sup>2</sup>-y<sup>2</sup> (b<sub>1</sub>)

 z<sup>2</sup> (a<sub>1</sub>)

1st excited state

state

**<sup>2</sup>E**

2nd excited state <sup>2</sup>B<sub>1</sub>

3rd excited state <sup>2</sup>A<sub>1</sub>

**which states will we observe transitions between?...**

**This depends on selection rules...**

# Experimental Observable: The Oscillator Strength

---

- ❖ Theory and experiment are correlated through the oscillator strength

$$f \propto \int \epsilon(\nu) d\nu \quad f \propto \left[ \int \psi_{g.s.} M(x, y, z) \psi_{e.s.} d\tau \right]^2$$

- ❖ For a transition to be observed

$$f > 0 \quad \therefore f \propto \int \psi_{g.s.} M(x, y, z) \psi_{e.s.} d\tau \neq 0$$

- ❖ Recall that a wavefunction has an orbital and spin component:

$$\psi_{g.s.} = \psi_{g.s.}^{orbital} \psi_{g.s.}^{spin} \quad M(x, y, z) \text{ operates only on the electron coordinate, does not effect spin}$$

$$\psi_{e.s.} = \psi_{e.s.}^{orbital} \psi_{e.s.}^{spin}$$

- ❖ therefore, we can rewrite as:

$$f \propto \int \psi_{g.s.}^{orbital} M(x, y, z) \psi_{e.s.}^{orbital} d\tau \int \psi_{g.s.}^{spin} \psi_{e.s.}^{spin} d\tau \neq 0$$

- ❖ From here it is straightforward to derive the selection rules....

# Selection rules

---

## ★ Spin Selection Rule

$$\int \psi_{g.s.}^{spin} \psi_{e.s.}^{spin} d\tau \neq 0$$

$$\psi_{g.s.}^{spin} = \Gamma_{g.s.}^{spin}; \psi_{e.s.}^{spin} = \Gamma_{e.s.}^{spin}$$

$$\Gamma_{g.s.}^{spin} = \Gamma_{e.s.}^{spin} \therefore \Delta s = 0$$

*Spin allowed transitions will be:*

*singlet to singlet*

*triplet to triplet*

*singlet to triplet not allowed*

# Selection Rules (cont'd)

---

- ★ Orbital Selection Rule (Laporte Selection Rule) - like parity transitions (i.e. g to g or u to u) are forbidden

$$f \propto \int \psi_{g.s.}^{orbital} M(x,y,z) \psi_{e.s.}^{orbital} d\tau \neq 0$$

- ★ from GT triple direct product must be totally symmetric to be non-zero

$$\Gamma_{g.s.} \times \Gamma_{x,y,z} \times \Gamma_{e.s.} \neq 0$$

- ★ Example in Oh symmetry:  $\Gamma_{x,y,z} \rightarrow T_{1u}$

$$\chi(i) = -1$$

for any irreducible rep of u symmetry

$$\chi(i) = 1$$

for any irreducible rep of g symmetry

$$\therefore g \times u \times u = g; u \times u \times g = g \quad \text{in order to be totally symmetric}$$

**therefore transition between states of like parity are forbidden!**

# Spectroscopic Selection Rules

---

- ★ The information about the allowedness of a transition is contained in:

- ★ **Spin-Selection rule:**  $\left| \left\langle \Psi_{initial} \mid \vec{\mu} \mid \Psi_{final} \right\rangle \right|^2$

- ➔ **The initial and final states must have the same total spin (the operators are spin-free!)**

- ➔ This is a *strong* selection rule up to the end of the first transition row. Beyond this, strong spin-orbit coupling leads to deviations

- ★ **Orbital-Selection rule, Laporte Selection Rule:**

- ➔ **The direct product of  $\Psi_i$ ,  $\Psi_f$ , and  $\mu$  must contain the totally symmetric irreducible representation**

- ➔ This is a *weak* selection rule: something breaks the symmetry all the time (environment, vibronic coupling, spin-orbit coupling, etc.)

**Electric Dipole:** Transforms as  $x, y, z$

**Magnetic Dipole:** Transforms as  $R_x, R_y, R_z$

**Electric Quadrupole:** Transforms as  $x^2, y^2, z^2, xy, xz, yz$

If there is a center of inversion only  $g \rightarrow u$  or  $u \rightarrow g$  transitions are allowed, e.g. d-d transitions are said to be „Laporte forbidden“

} If there is a center of inversion only  $g \rightarrow g$  or  $u \rightarrow u$  transitions are allowed

# Selection Rules (cont'd)

---

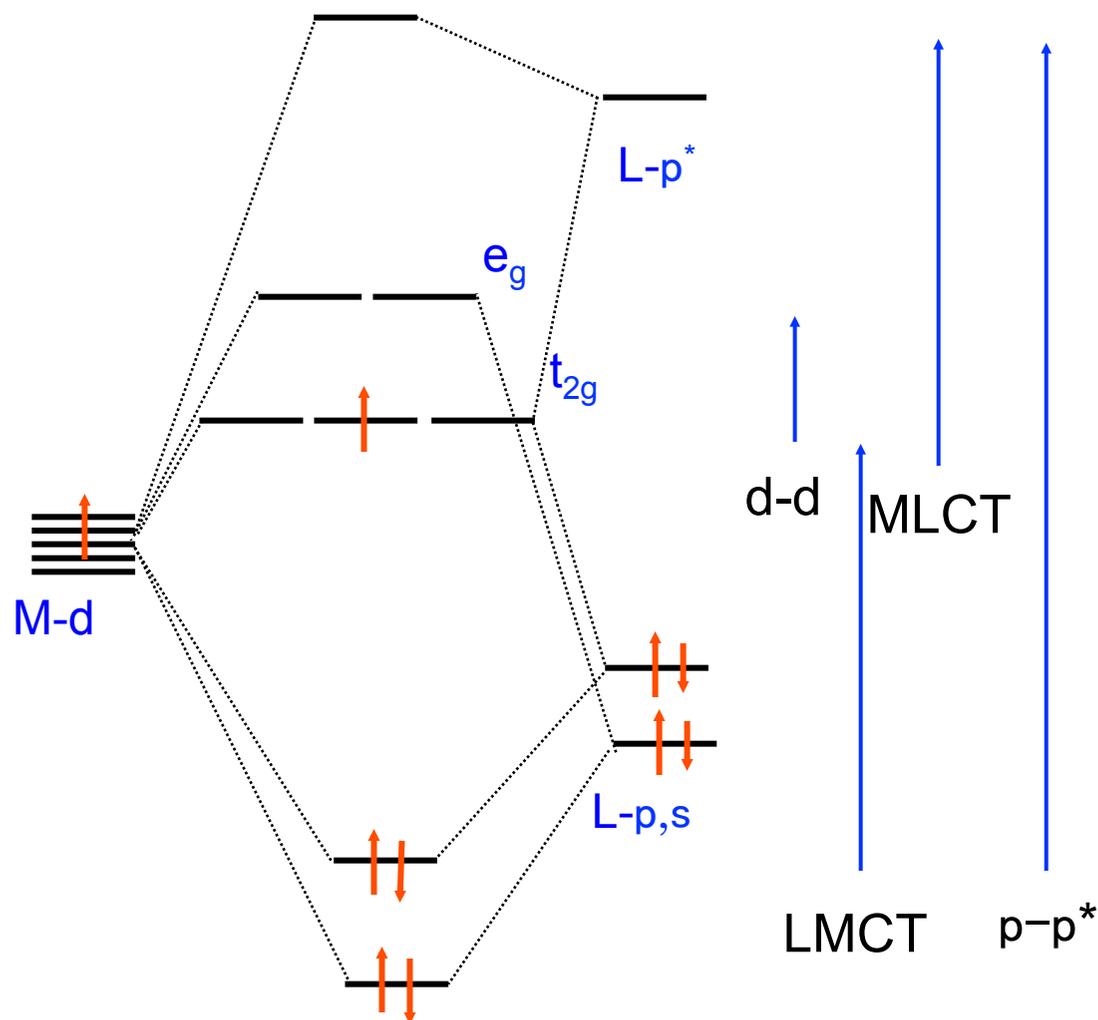
★ **Dipole-Selection rule:**

$$\Delta l = \pm 1$$

- ➔ transitioning electron must change by one orbital quantum number
- ➔ s to p or p to d is possible
- ➔ d to d; s to s; or s to d are all dipole forbidden
- ➔ comes from QM and Wigner-Eckart Thm.

# Optical Transition Intensities

★ *Just because transitions are “forbidden” does not mean we don’t see them.*



## Typical Intensities:

e- dipole allowed LMCT/MLCT:  
~500-15,000 M<sup>-1</sup>cm<sup>-1</sup>

parity forbidden, d to d:  
0-500 M<sup>-1</sup>cm<sup>-1</sup>

spin forbidden: 0.01 M<sup>-1</sup>cm<sup>-1</sup>

# Ground and Excited State Term Symbols

Example:  $D_{2d}$ -[CuCl<sub>4</sub>]<sup>2-</sup>

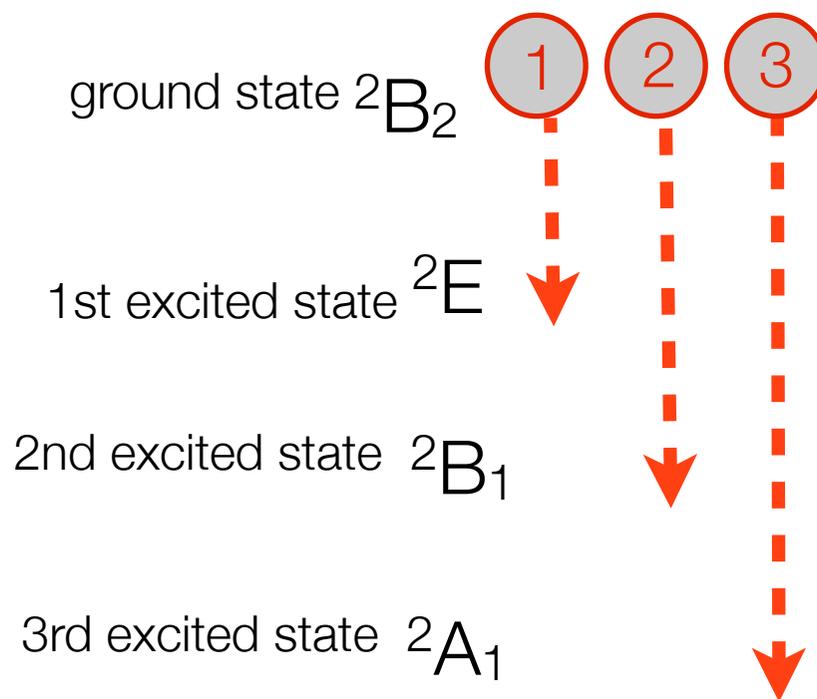
Character table for  $D_{2d}$  point group

	E	2S <sub>4</sub>	C <sub>2</sub> (z)	2C' <sub>2</sub>	2σ <sub>d</sub>	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	1		x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	1	-1	-1	R <sub>z</sub>	
B <sub>1</sub>	1	-1	1	1	-1		x <sup>2</sup> -y <sup>2</sup>
B <sub>2</sub>	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(x, y) (R <sub>x</sub> , R <sub>y</sub> )	(xz, yz)

$$\Gamma(M(x, y)) \rightarrow E$$

$$\Gamma(M(z)) \rightarrow B_2$$

**Predict two intense peaks with different polarizations**



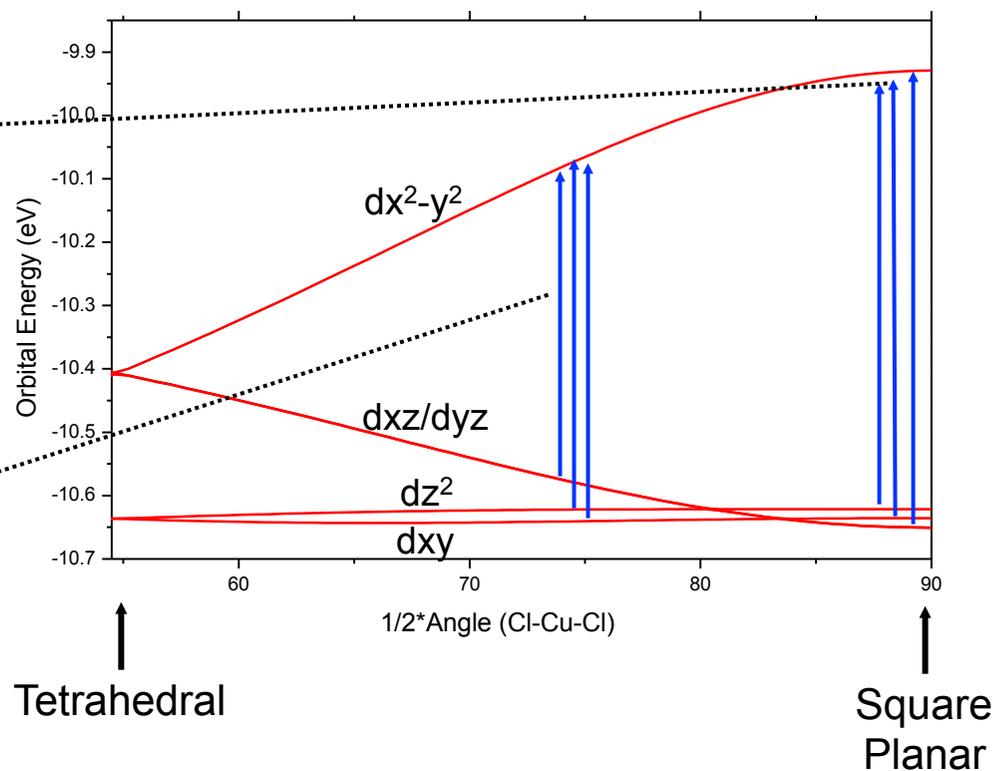
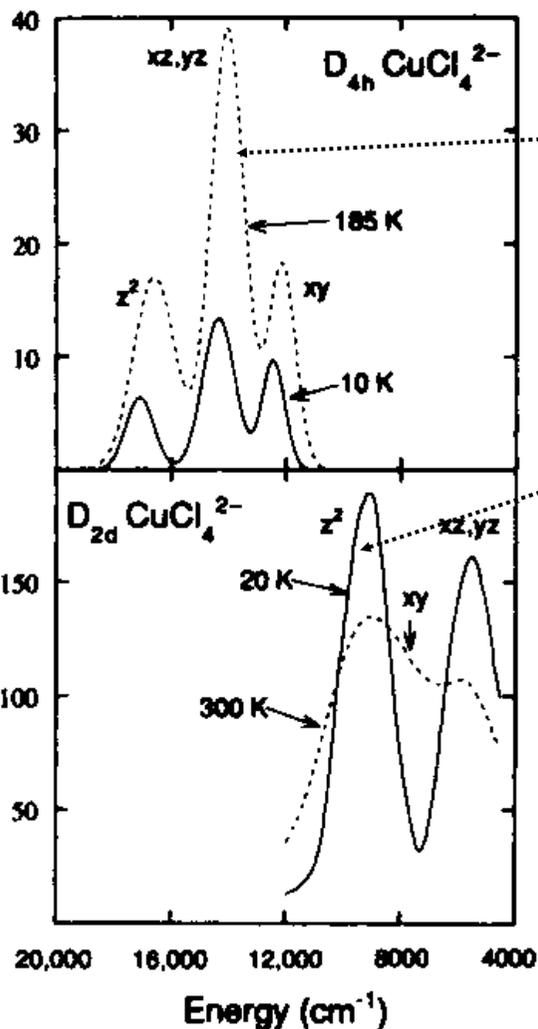
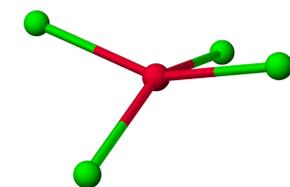
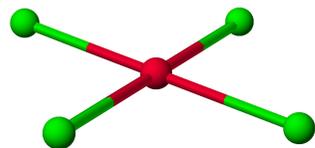
- 1
- 2
- 3

$B_2 \times E = E$  (x,y)-polarized

$B_2 \times B_1 = A_2$  forbidden

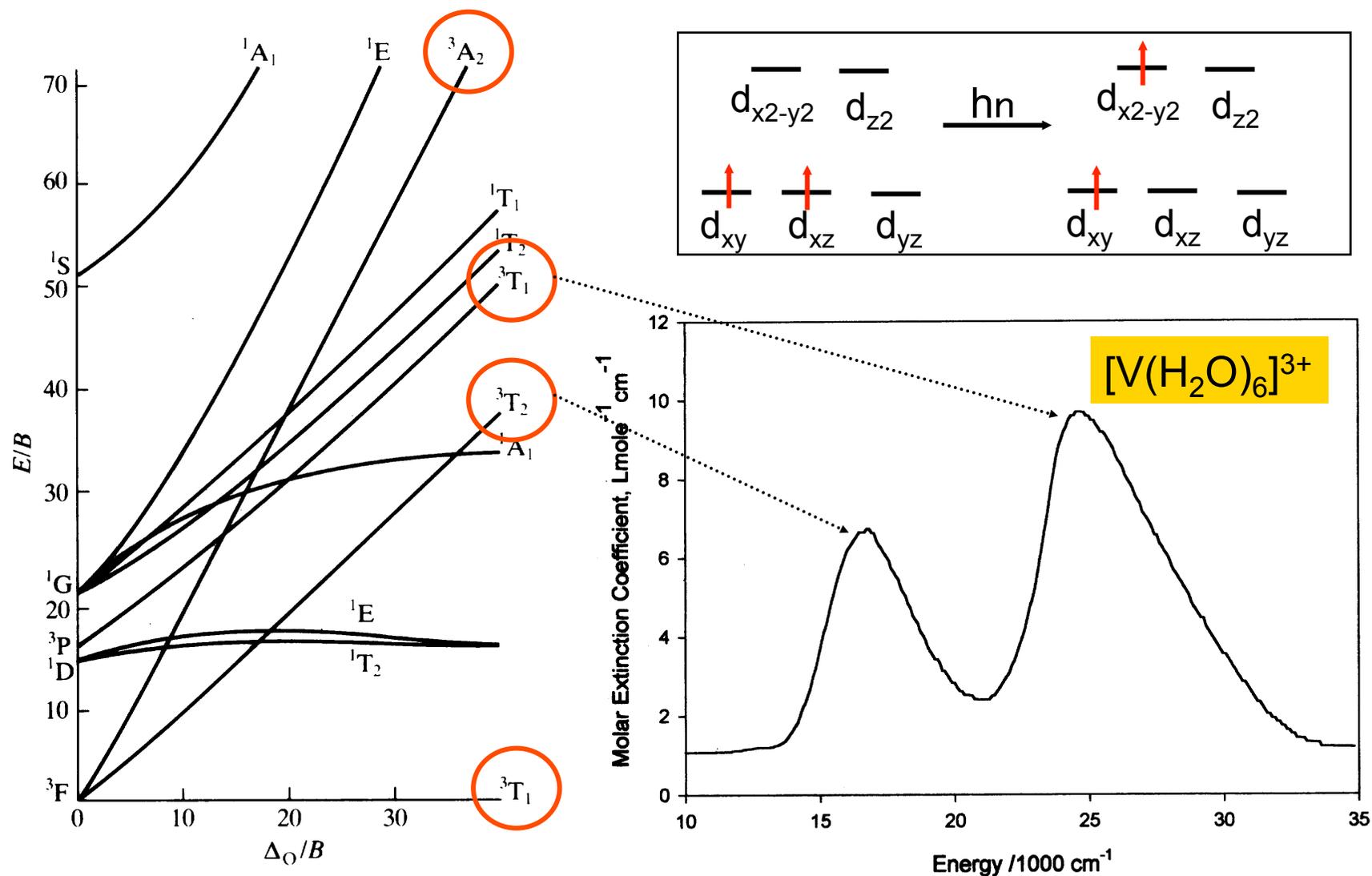
$B_2 \times A_1 = B_2$  z-polarized

# UV-Vis of $D_{4h}$ and $D_{2d}$ $[\text{CuCl}_4]^{2-}$



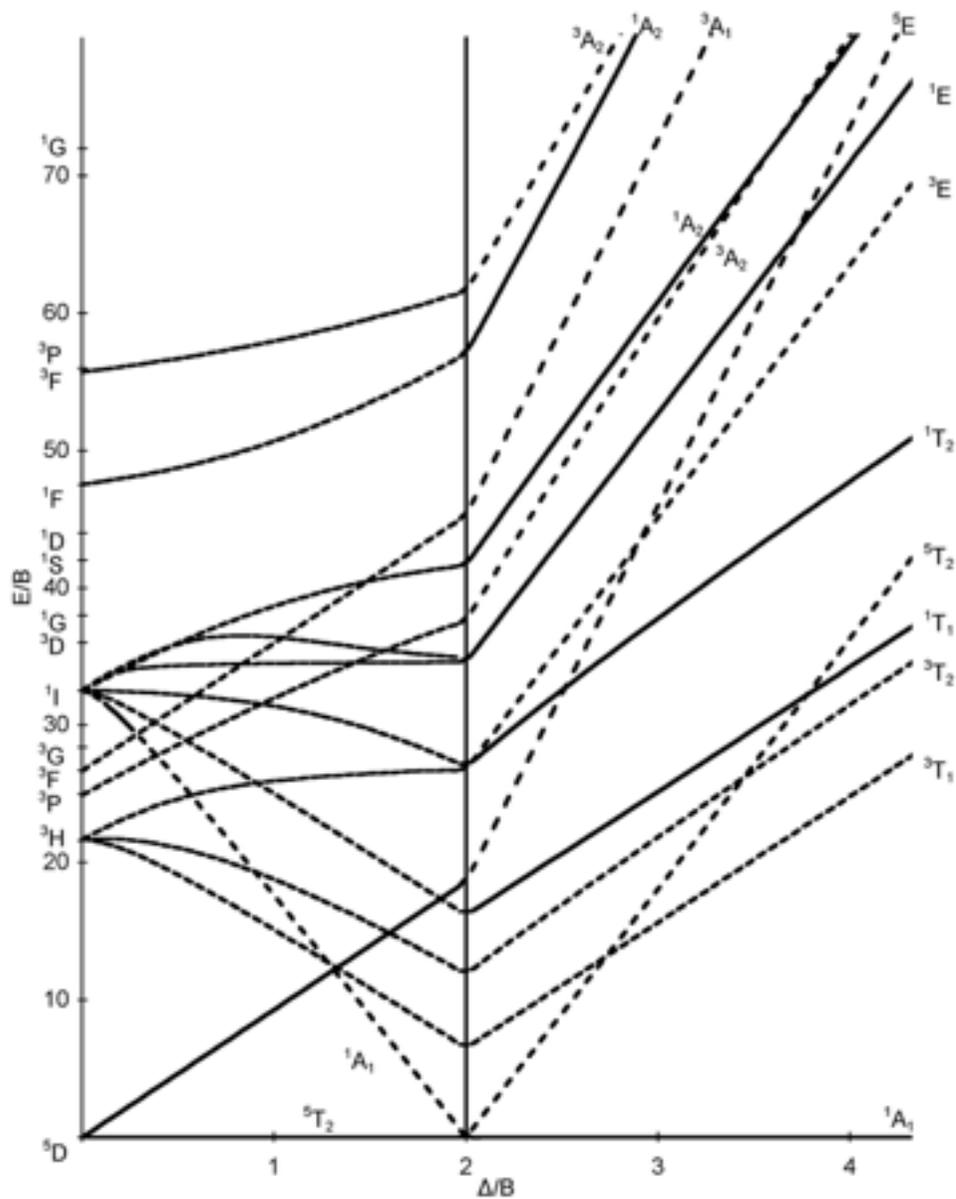
*What about more complicated system than  $d^9$ ?*

# More complex UV-Vis spectra...

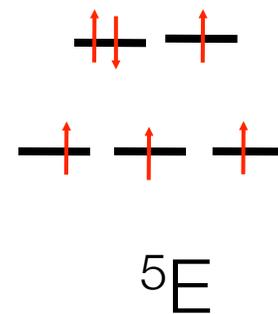
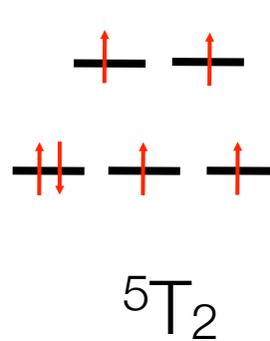


Also works for XAS. Use  $d^{n+1}$ !

# d<sup>6</sup> Tanabe-Sugano Diagrams...

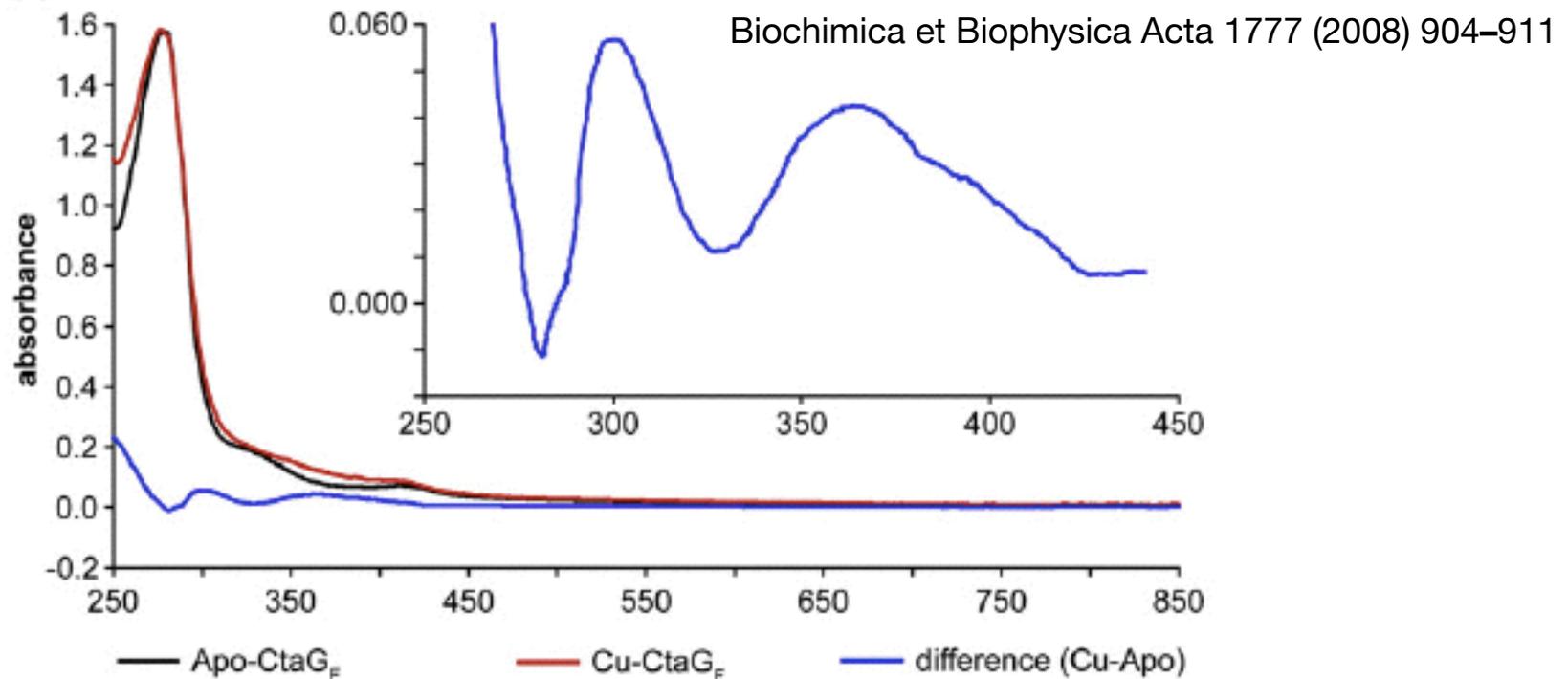


➔ Lowest energy 5T<sub>2</sub> to 5E spin allowed



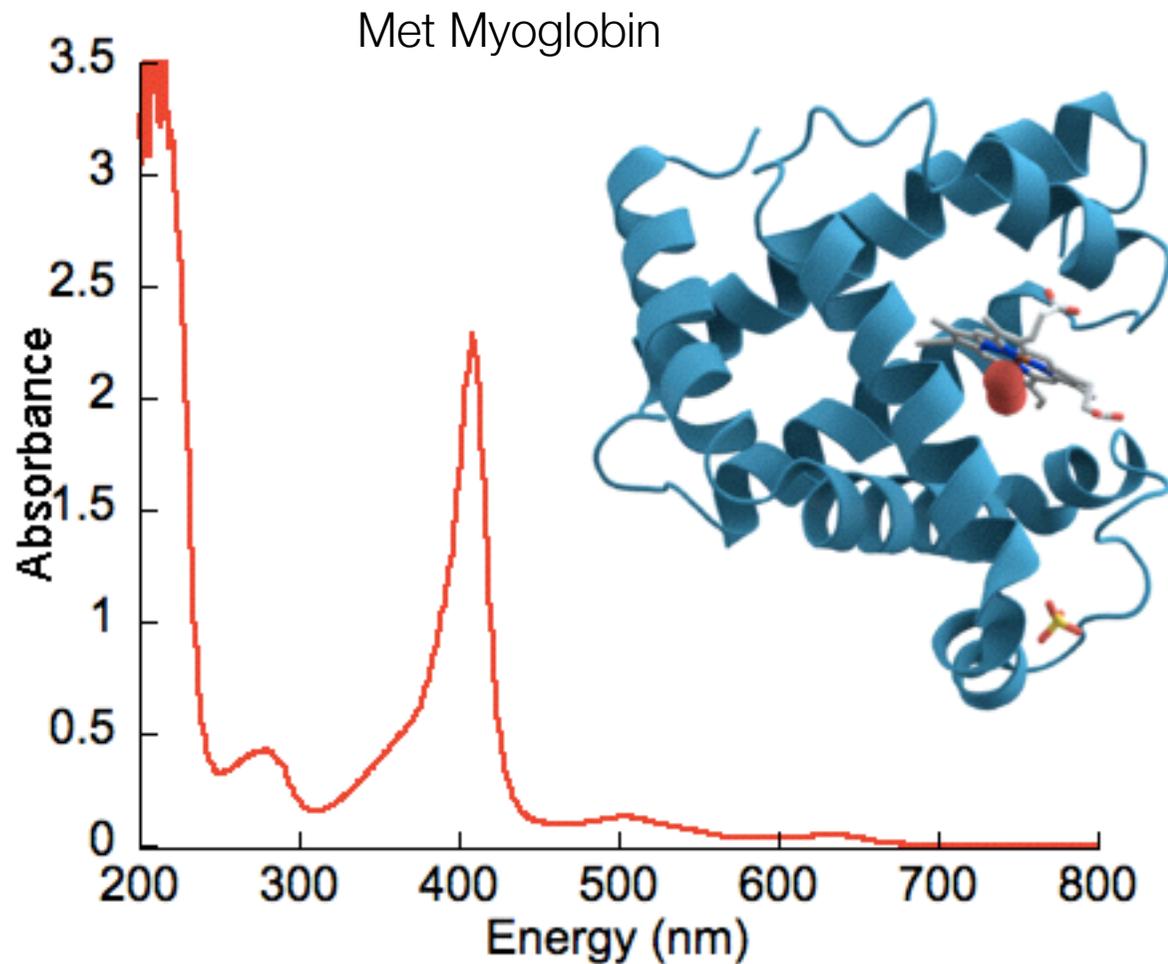


# Challenges with Protein UV-Vis...



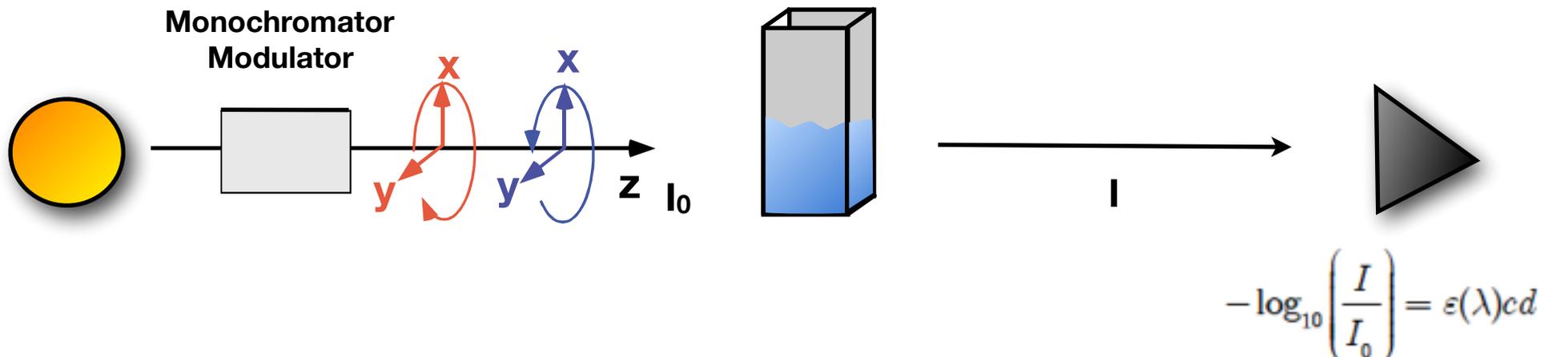
- ✓ Apoprotein will exhibit intense ~280 nm (~35,000 cm<sup>-1</sup>) absorbance.
- ✓ Contributions from aromatic amino acids (TYR, TRP) dominate spectrum of metalloproteins.
- ✓ Other means often desirable to find out what is happening around the metal.

# Challenges with Hemes...



- Intense “Soret” band resulting from porphyrin  $\pi$ - $\pi^*$  obscures d to d transitions
- What else can be done to resolve absorption features?

# Circular Dichroism Spectroscopy



## Light Source

*Tungsten, Xenon,  
Deuterium, Diode,...*

## Sample

**Requires a chiral substance!**

## Detector

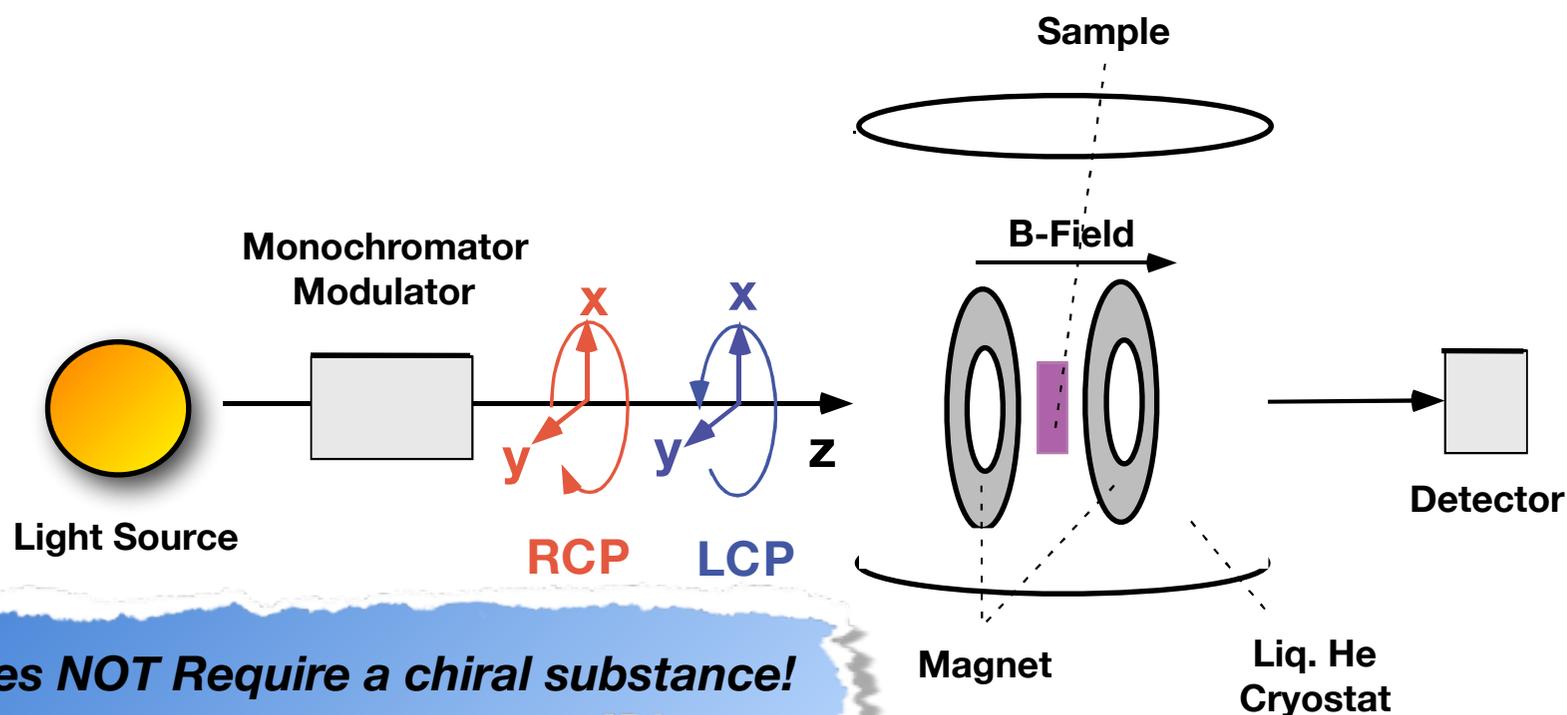
*Phase Sensitive Detector  
Detects difference between  
LCP and RCP absorption*

**Recall the Magnetic dipole operator transforms as  $R_x, R_y, R_z$**

Intensity Mechanism: **Electric/Magnetic Dipole**

$$R = \Re e \left( \left\langle \Psi_i \mid \vec{\mu}_{ED} \mid \Psi_f \right\rangle \left\langle \Psi_f \mid \vec{\mu}_{MD} \mid \Psi_i \right\rangle \right)$$

# Magnetic Circular Dichroism Spectroscopy

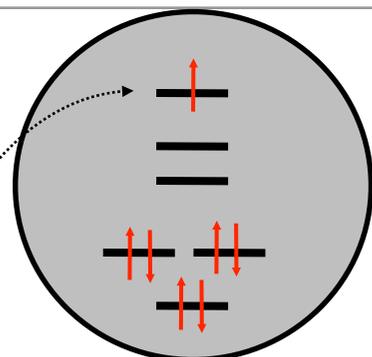


**Does NOT Require a chiral substance!**

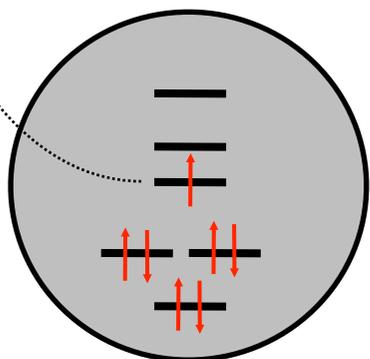
$$MCD = A_{LOP}(B, T) - A_{RCP}(B, T) - \underbrace{\left[ A_{LOP} - A_{RCP} \right]_{B=0}}_{\text{Natural CD}}$$

$$\propto cd(E_f - E_i) \sum_{\text{initial states}} N_j(B, T) \sum_{\text{final states}} \left\{ \left| \langle \Psi_j | \vec{\mu}_{ED,LOP} | \Psi_f \rangle \right|^2 - \left| \langle \Psi_j | \vec{\mu}_{ED,RCP} | \Psi_f \rangle \right|^2 \right\}$$

# EPR versus Optical Spectroscopy



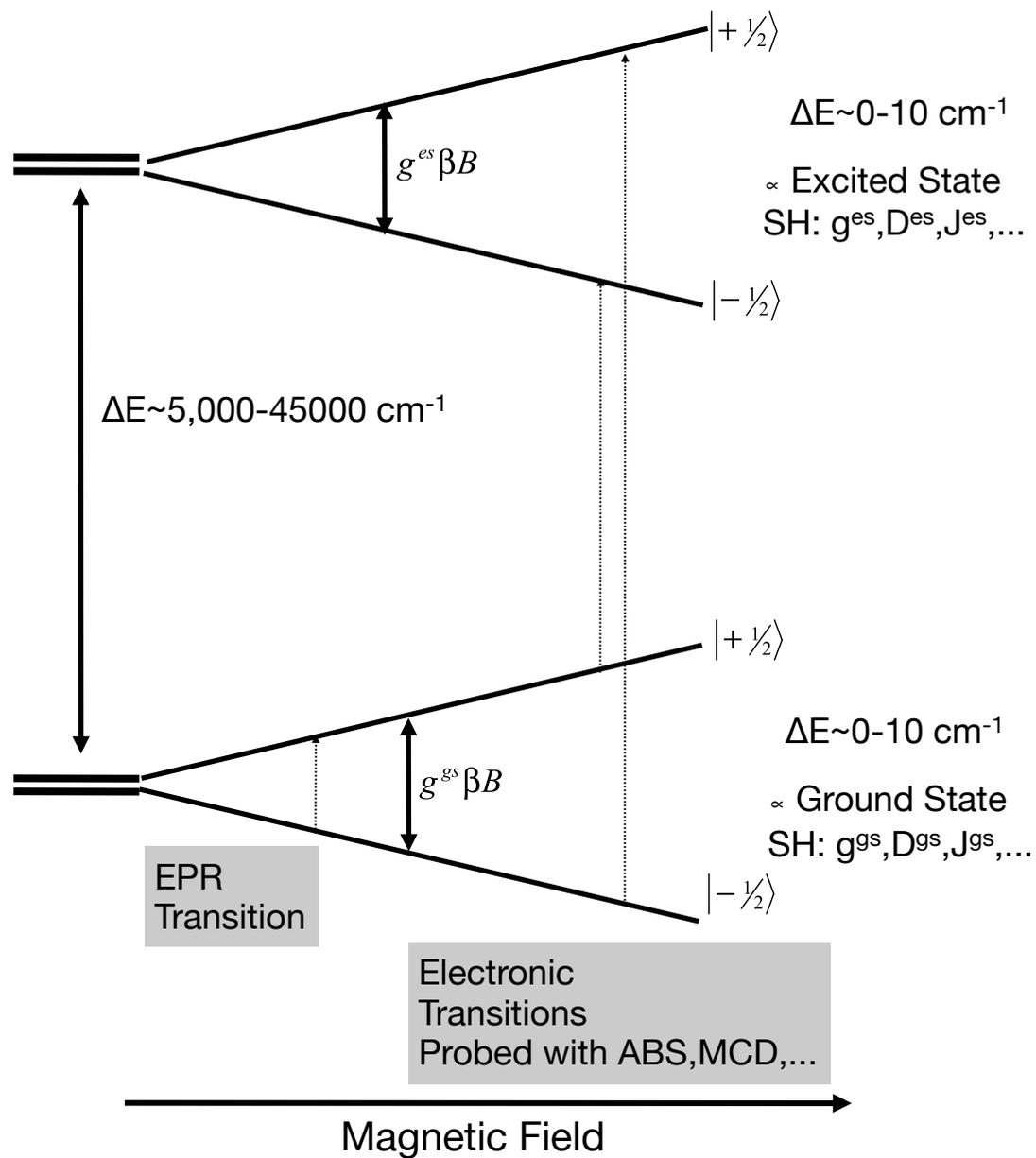
Electronically  
Excited State  
Multiplet



Electronic  
Ground State  
Multiplet

Total Spin  $S'$   
 $\downarrow$   
 $2S'+1$  Components  
 $M'_S = S', S'-1, \dots, -S'$

Total Spin  $S$   
 $\downarrow$   
 $2S+1$  Components  
 $M_S = S, S-1, \dots, -S$



# What is spectroscopy?

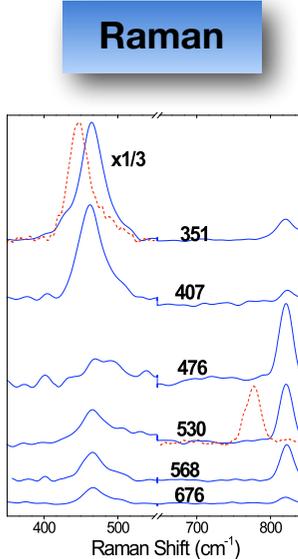
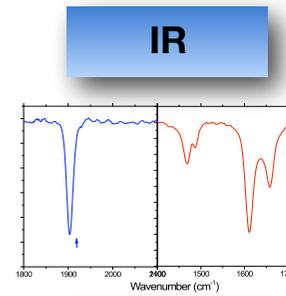
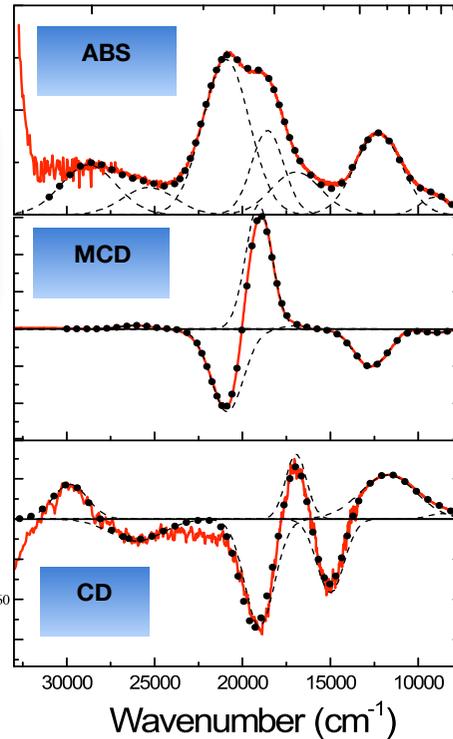
*spectroscopy involves transitions between STATES...*

	Gamma	X-Ray	UV/vis	Infrared	Microwave	Radiowave
eV	14000	8000	2000	4 - 1	0.1-0.01	10 <sup>-4</sup> -10 <sup>-5</sup>
					10 <sup>-4</sup> -10 <sup>-5</sup>	10 <sup>-6</sup> -10 <sup>-7</sup>



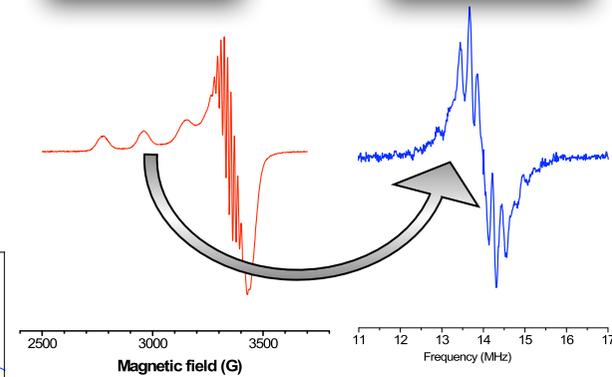
**Mössbauer**

**XAS/ EXAFS  
XES**

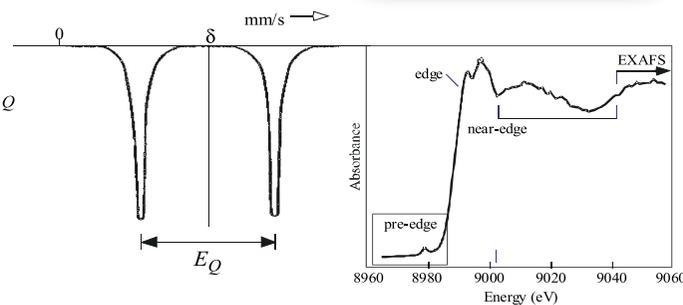


**EPR**

**ENDOR**



**NMR**



# Summary

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❖ Most spectroscopy can be understood in terms of a few important selection rules

❖ Excited State Methods

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- $\Delta S=0$  (spin selection rule)

-g to u or u to g (parity selection rule)

- $\Delta l = \pm 1$

❖ Ground State Methods (magnetic dipole transitions between nuclear or electronic spin states)

- $\Delta m_s = \pm 1$  (EPR)

- $\Delta m_l = 0, \pm 1$  (Mössbauer)

- $\Delta l = \pm 1$

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Thank you for your attention!

Special thanks to Frank Neese (and also various  
online teaching sources for borrowed slides/  
images :-))