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Ligand Field Theory

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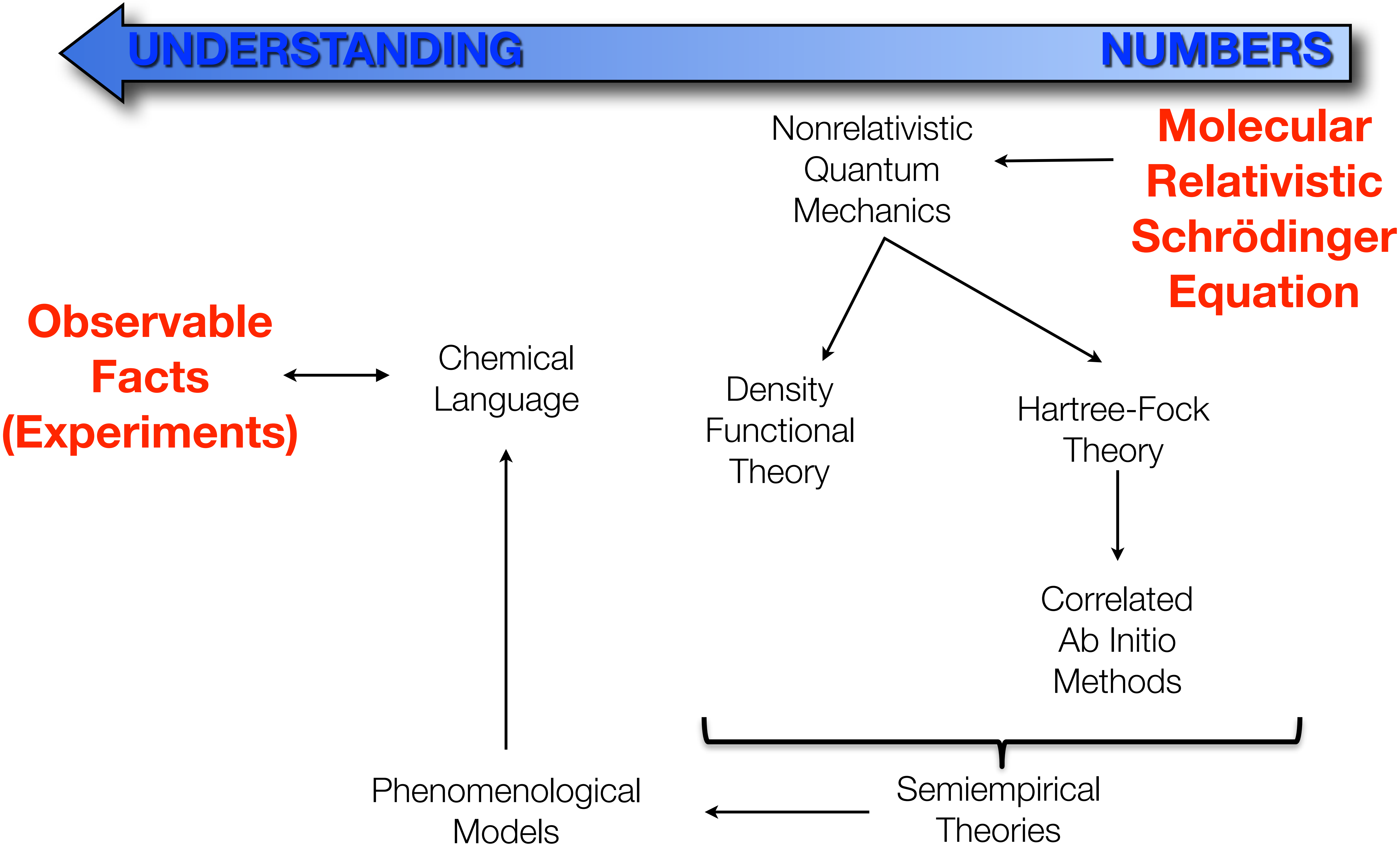
Theory in Chemistry



UNDERSTANDING

NUMBERS

Molecular
Relativistic
Schrödinger
Equation

Nonrelativistic
Quantum
Mechanics

Density
Functional
Theory

Hartree-Fock
Theory

Correlated
Ab Initio
Methods

Semiempirical
Theories

Phenomenological
Models

Chemical
Language

Observable
Facts
(Experiments)

What is Ligand Field Theory ?

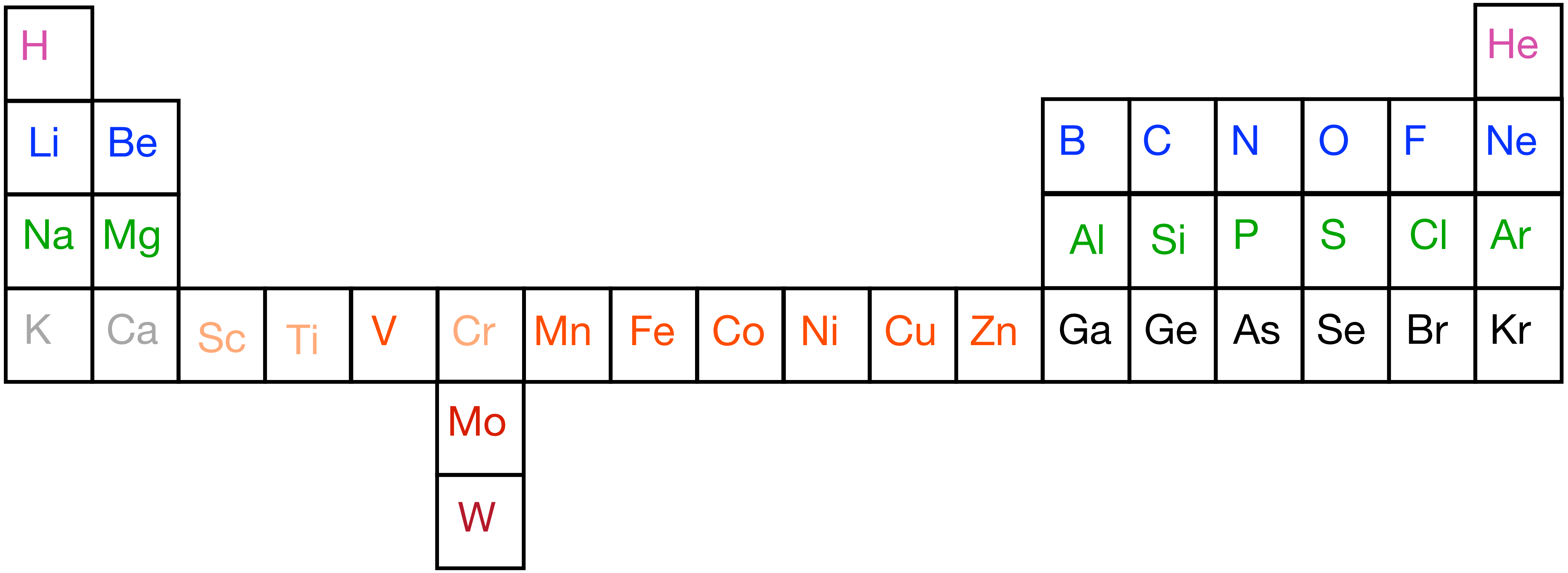
★ **Ligand Field Theory is:**

- A semi-empirical theory that applies to a **CLASS** of substances (transition metal complexes).
- A **LANGUAGE** in which a vast number of experimental facts can be rationalized and discussed.
- A **MODEL** that applies only to a restricted part of reality.

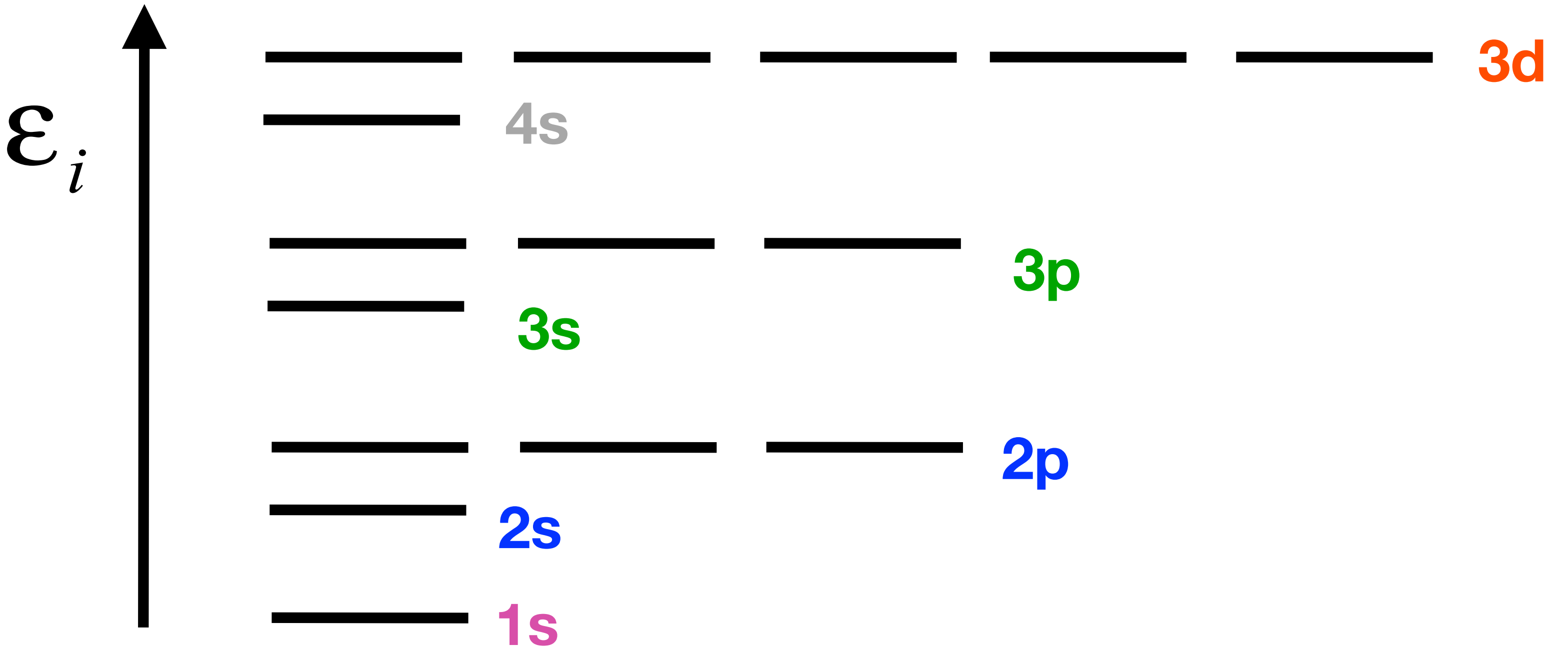
★ **Ligand Field Theory is NOT:**

- An ***ab initio* theory** that lets one predict the properties of a compound ‚from scratch'
- A physically rigorous treatment of transition metal electronic structure

Many Electron Atoms and the ‚Aufbau‘ Principle



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
					Mo												
					W												



States of Atoms and Molecules

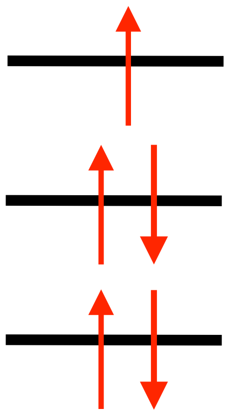
- Atoms and Molecule exist in **STATES**
- **ORBITALS** can NEVER be observed in many electron systems !!!
- A **STATE** of an atom or molecule may be characterized by four criteria:
  1. The distribution of the electrons among the available orbitals (the electron **CONFIGURATION**) (A set of occupation numbers)
  2. The overall **SYMMETRY** of the STATE (Γ Quantum Number)
  3. The **TOTAL SPIN** of the STATE (S-Quantum Number)
  4. The **PROJECTION** of the Spin onto the Z-axis (M_S Quantum Number)

⇨ $|\mathbf{n}S_kM\Gamma M_\Gamma>$

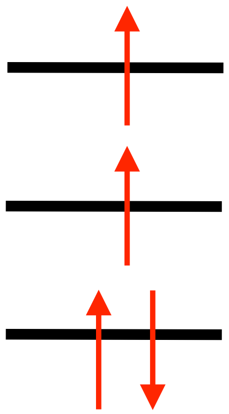
The Total Spin

For the **Total Spin** of an atom or molecule the rules apply:

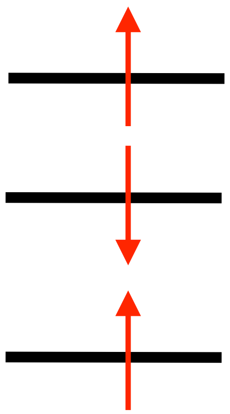
1. Doubly occupied orbitals do NOT contribute to the total Spin
2. Singly occupied orbitals can be occupied with either spin-up or spin-down electrons
3. Unpaired electrons can be coupled parallel or antiparallel to produce a final total spin S
4. For a state with total spin S there are 2S+1 ‚components‘ with M=S,S-1,...,-S
5. The M_S quantum number is always the sum of all individual m_s quantum numbers



$S=1/2$
$M_S=1/2$



$S=1$
$M_S=1$



$S=1/2$ AND $3/2$
$M_S=1/2$

Atoms: Atomic „Russel-Saunders“ Terms

Atomic Term Symbol: ^{2S+1}L

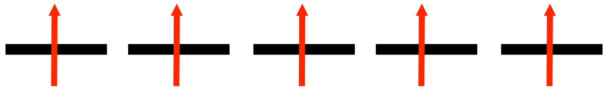
Rules:

- A L-Term is 2L+1 fold orbitally degenerate and (2S+1)(2L+1) fold degenerate in total
- L=0,1,2,3,4... terms are given the symbols S,P,D,F,G,...
- Terms of a given configuration with higher S are lower in energy (Hund I)
- Terms with given configuration and equal spin have the higher L lower in energy (Hund II)

Examples for d^N Configurations:

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

⇒ ^2D



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

⇒ ^6S

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

⇒ $^3F+^3P$

Molecules: Symmetry and Group Theory

- A Molecule can be classified according to the operations that turn the molecule into itself (=symmetry operations), i.e rotations, improper rotations, inversion, reflection.
- The precise mathematical formulation is part of „group theory“
- The results is that states can be classified according to their „irreducible representation“ („symmetry quantum number“)

Rules for naming „irreducible representations“:

- Small Letters : Reserved for **orbitals** (One-electron level)
- Capital Letters : Reserved for **states** (Many electron level)
- T,t : Triply degenerate level
- E,e : Doubly degenerate level
- A,B : Non-degenerate Levels

Term-Symbol: $\boxed{^{2S+1}\Gamma}$

2S+1 : „Multiplicity“ = Spin Degeneracy

Γ : „Irreducible Representation“

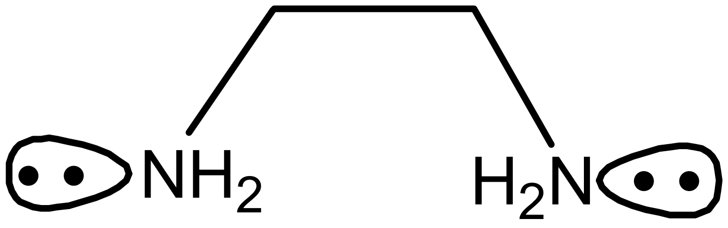
Principles of Ligand Field Theory

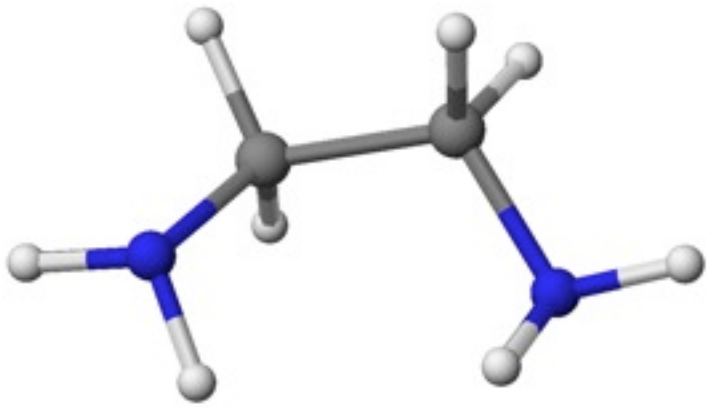
R-L| M

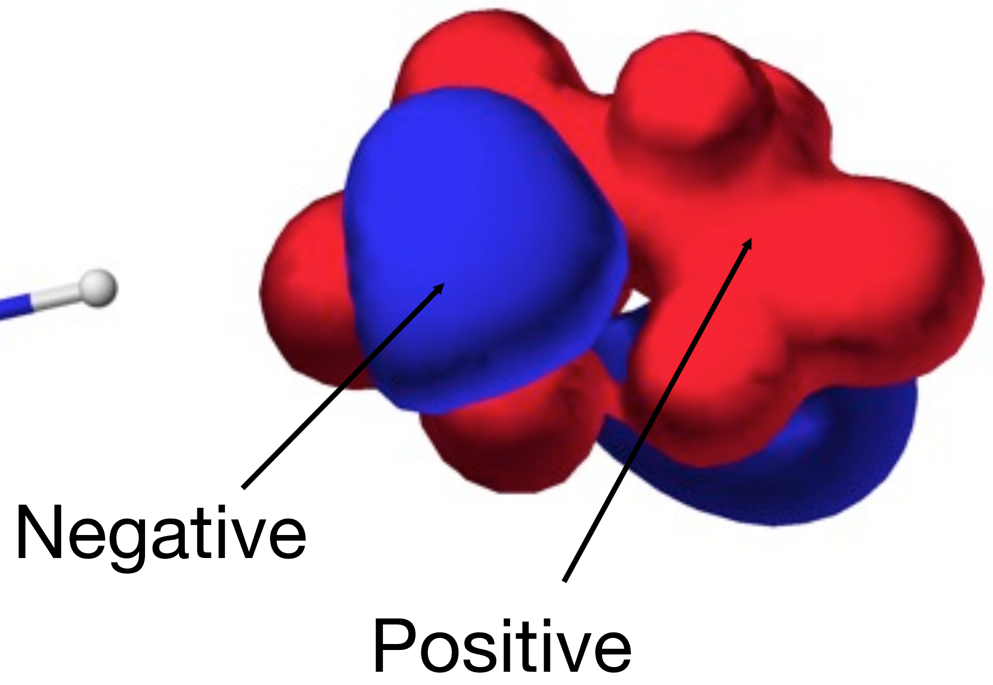
δ- δ+

Strong Attraction

Example:

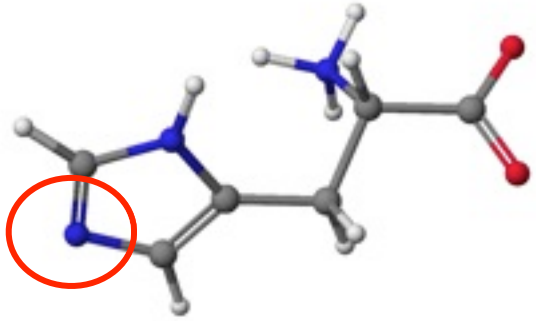




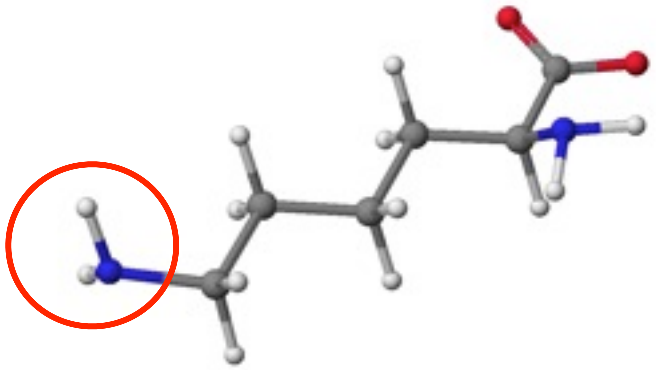

Electrostatic Potential

Protein Derived Ligands

N

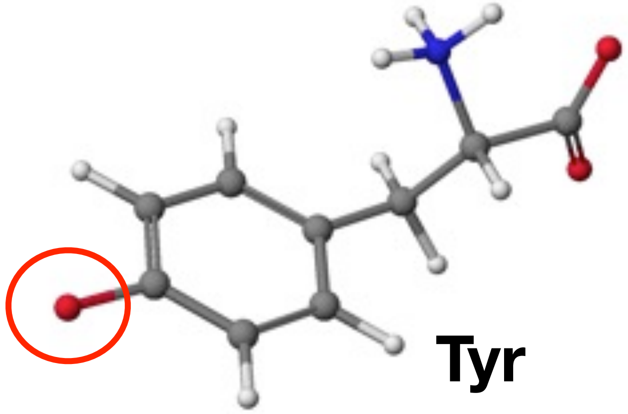


His

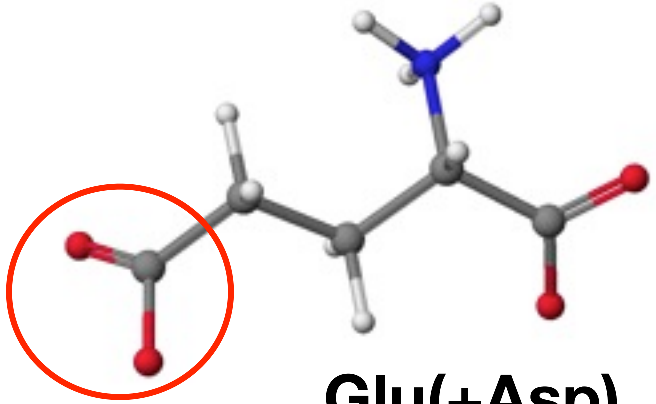


Lys

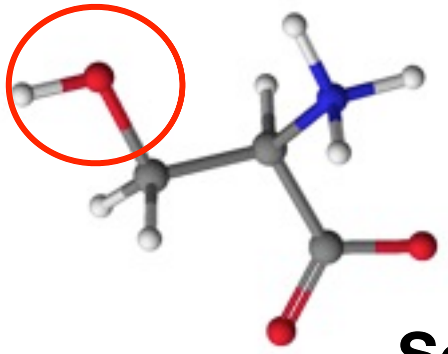
O



Tyr

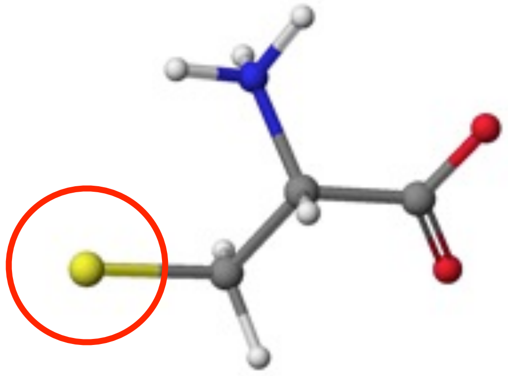


Glu(+Asp)

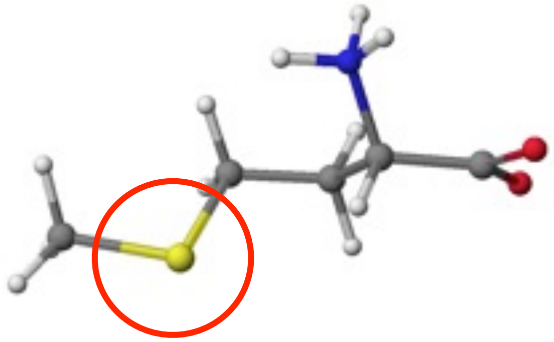


Ser

S



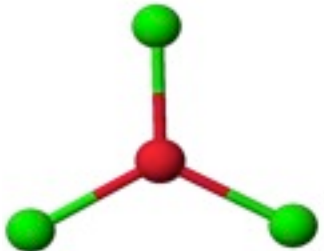
Cys



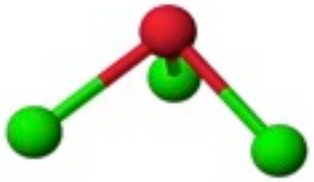
Met

Complex Geometries

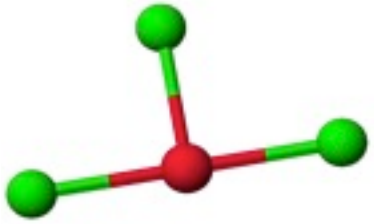
3



Trigonal

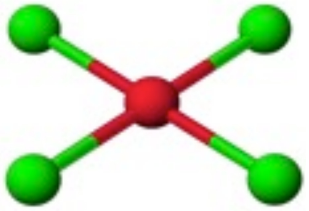


Trigonal Pyramidal

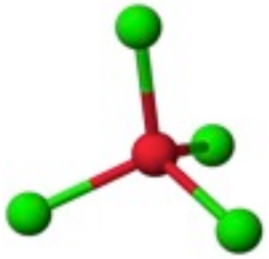


T-Shaped

4

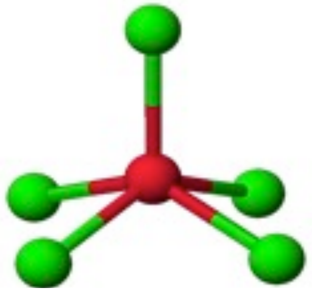


Quadratic Planar

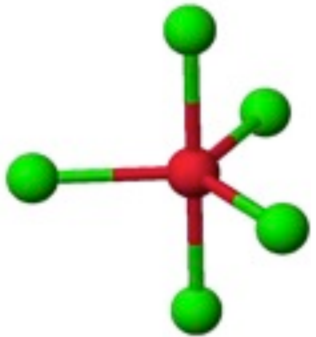


Tetrahedral

5

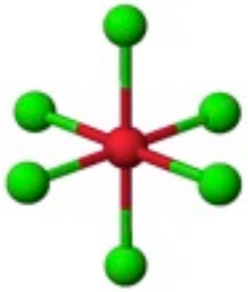


Quadratic Pyramidal



Trigonal Bipyramidal

6

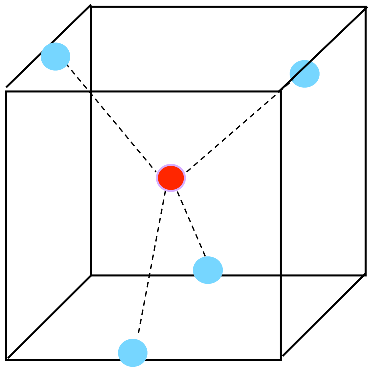


Octahedral

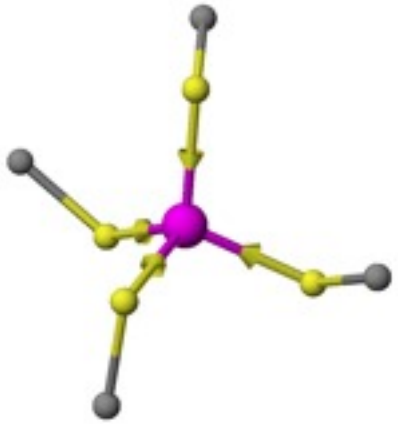
Coordination Geometries

- Approximate Symmetries Observed in Enzyme Active Sites -

Tetrahedral

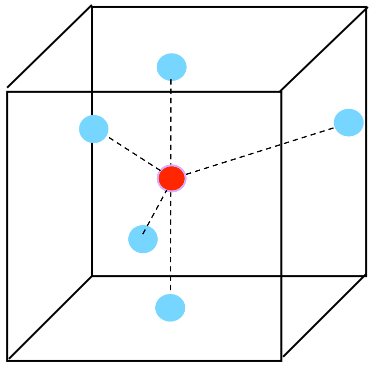


T_d

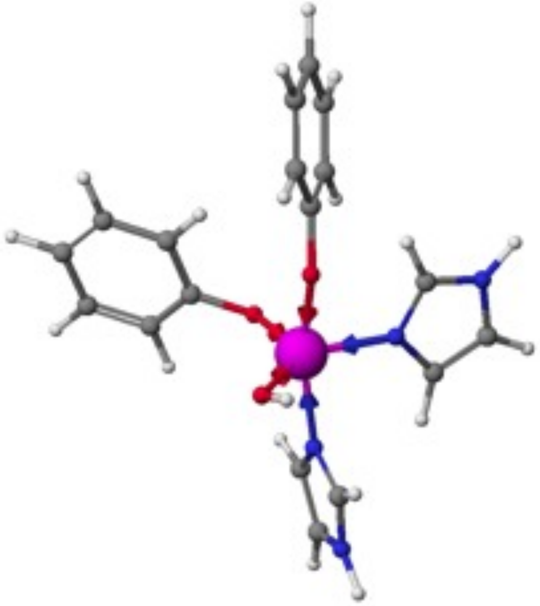


Rubredoxin

Trigonal Bipyramidal

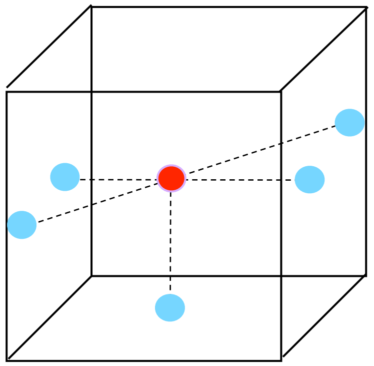


D_{3h}

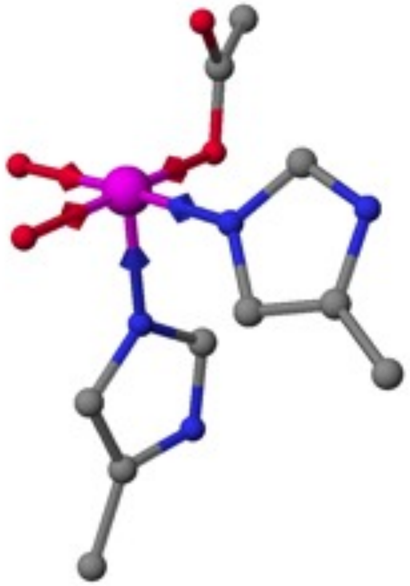


3,4-PCD

Tetragonal Pyramidal

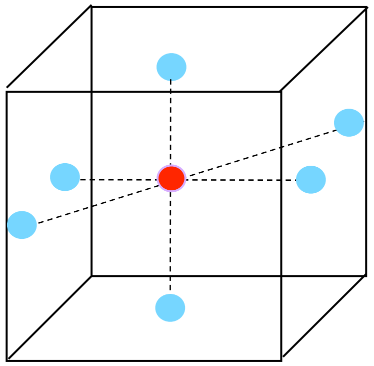


C_{4v}

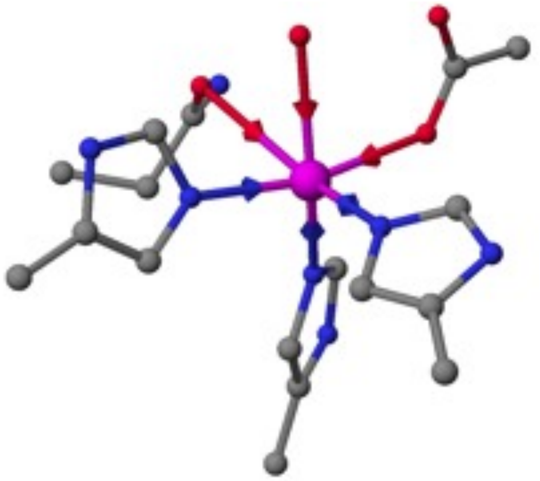


Tyrosine Hydroxylase

Octahedral

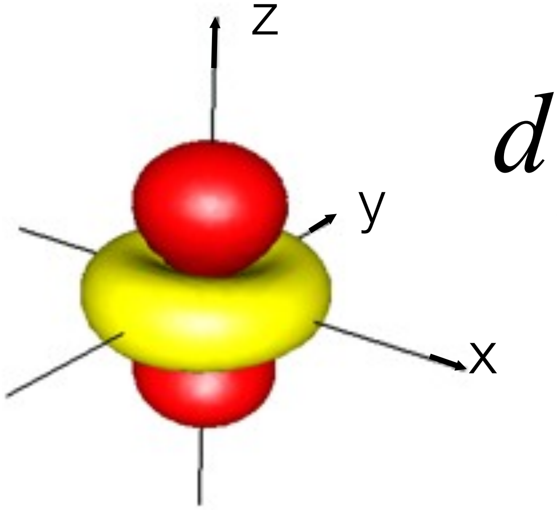


O_h



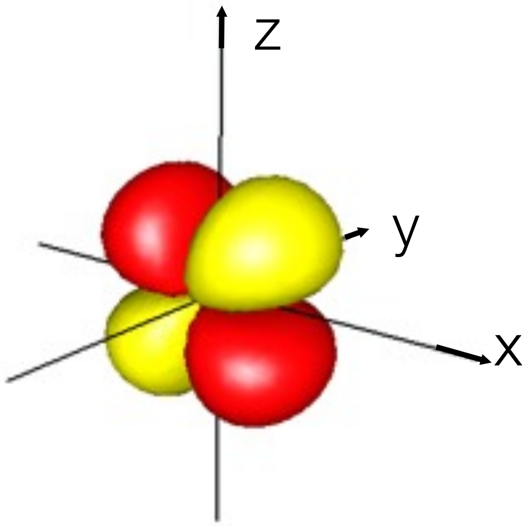
Lipoxygenase

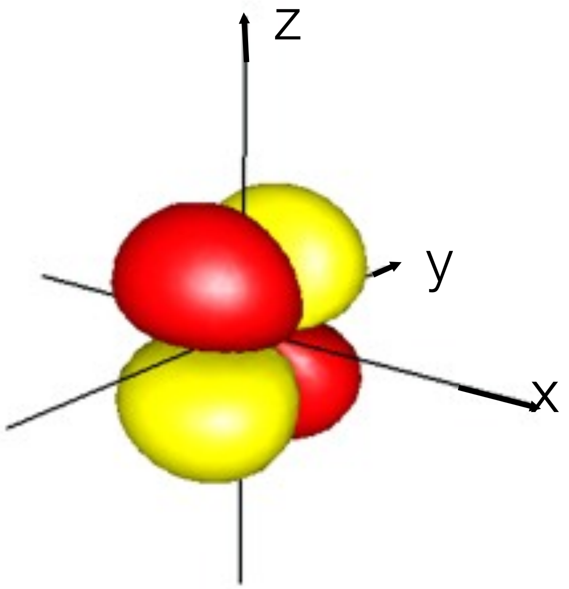
The Shape of Orbitals



$d_{z^2-r^2}$

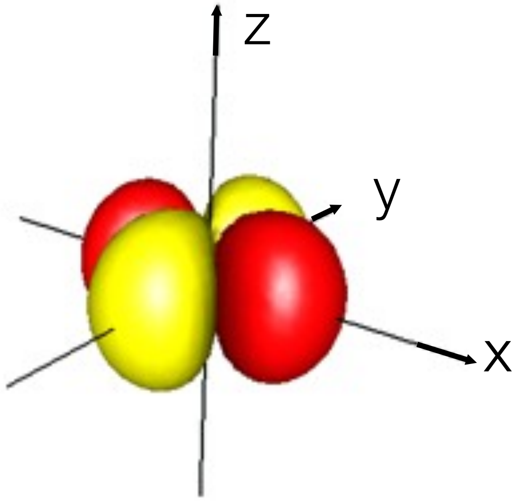
d_{xz}

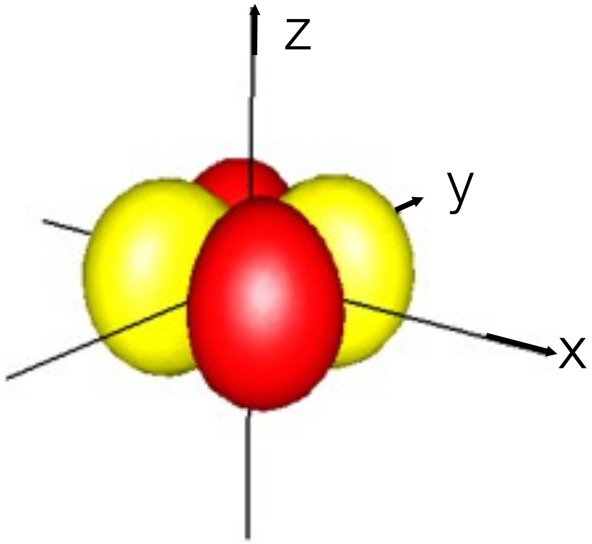




d_{yz}

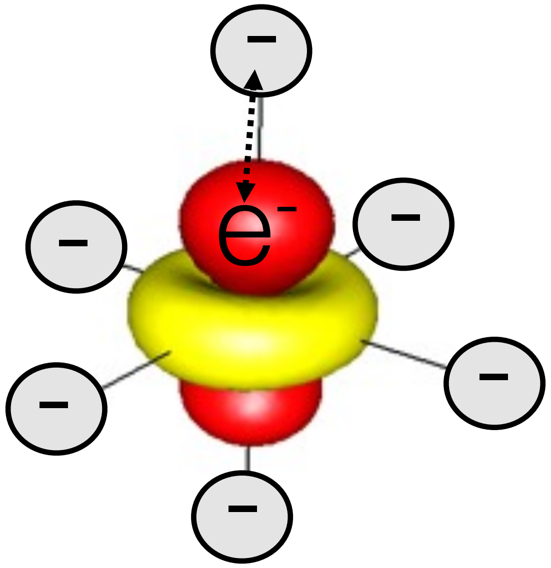
$d_{x^2-y^2}$



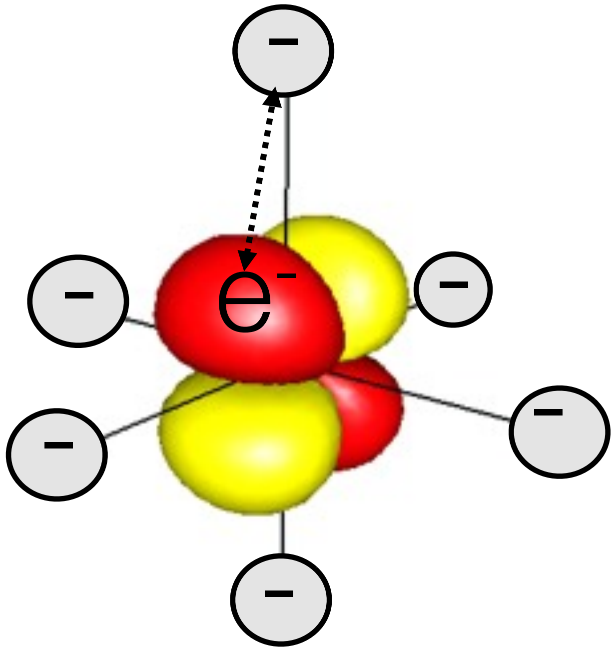


d_{xy}

A Single d-Electron in an Octahedral Field



d_{z2}



d_{yz}

The Negatively Charged Ligands Produce an Electric Field+Potential

⇩

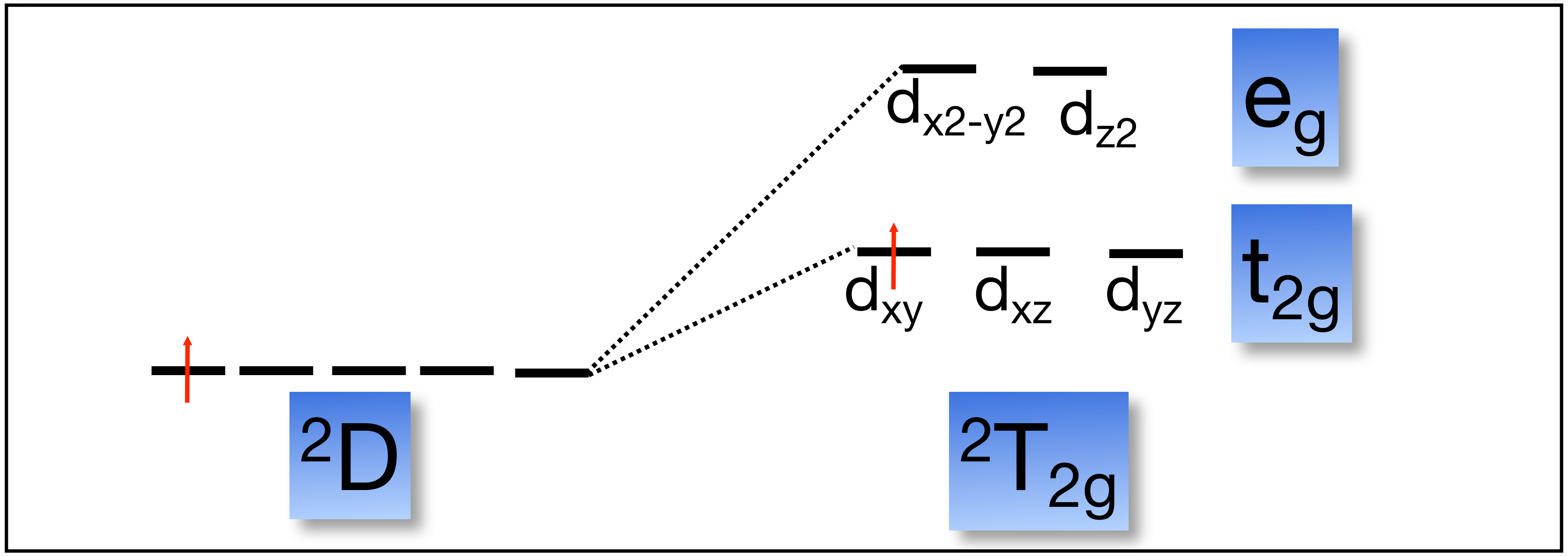
The Field Interacts with the d-Electrons on the Metal (Repulsion)

⇩

The Interaction is NOT Equal for All Five d-Orbitals

⇩

1. The Spherical Symmetry of the Free Ions is Lifted
2. The d-Orbitals Split in Energy
3. The Splitting Pattern Depends on the Arrangement of the Ligands



Making Ligand Field Theory Quantitative

Hans Bethe
1906-2005

Charge Distribution of Ligand Charges: $\rho(\mathbf{R}) = \sum_{i=1}^{N_L} q_i \delta\left(\mathbf{R} - \mathbf{R}_{L_i}\right)$

Ligand field potential: $V_{LF}(\mathbf{r}) = \int \frac{\rho(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} d\mathbf{R}$

q_i=charges

Expansion of inverse distance: $\frac{1}{|\mathbf{R} - \mathbf{r}|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} \sum_{m=-l}^{l} S_{lm}(\mathbf{R}) S_{lm}(\mathbf{r})$

S_l^m=real spherical harmonics
$r_{<,>}$ Smaller/Larger or r and R

Insertion into the potential: $V_{LF}(\mathbf{r}) = \sum_{l=0}^{\infty} r^l \sum_{m=-l}^{l} S_{lm}(\mathbf{r}) A_{lm}$

„Geometry factors“: $A_{lm} = \sum_{i=1}^{N_L} \frac{4\pi}{2l+1} \frac{q_i}{R_{L_i}^{l+1}} S_{lm}\left(\mathbf{R}_{L_i}\right)$

Ligand-field matrix elements: $\left\langle d_i \middle| V_{LF} \middle| d_j \right\rangle = -\sum_{l=0}^{\infty} \left\langle r^l \right\rangle \sum_{m=-l}^{l} A_{lm} \left(\begin{array}{cc|c} l_i & l_j & l \\ m_i & m_j & m \end{array}\right)$

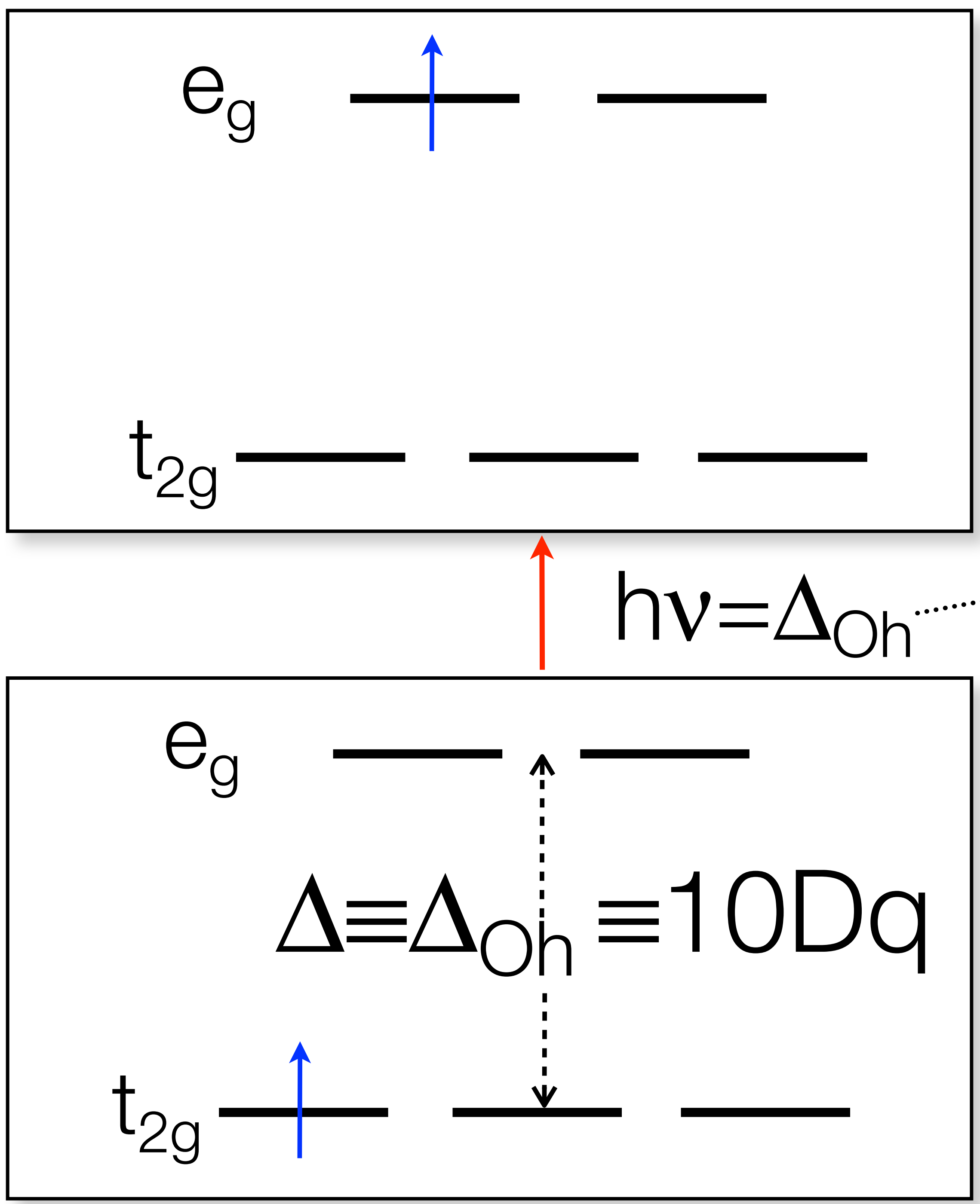
$\left(\begin{array}{cc|c} l_i & l_j & l \\ m_i & m_j & m \end{array}\right)$ =Gaunt Integral (tabulated)

Ligand-field splitting in O_h: $\boxed{\left\langle d_{e_g} \middle| V_{LF} \middle| d_{e_g} \right\rangle - \left\langle d_{t_{2g}} \middle| V_{LF} \middle| d_{t_{2g}} \right\rangle \equiv 10Dq = \frac{5}{3} \frac{q}{R^5} \left\langle d \middle| r^4 \middle| d \right\rangle}$

➡ Don‘t evaluate these integrals analytically, plug in and compare to experiment! LFT is not an ab initio theory (the numbers that you will get are ultimately absurd!). What we want is a parameterized model and thus we want to leave 10Dq as a fit parameter. The ligand field model just tells us how many and which parameters we need what their relationship is

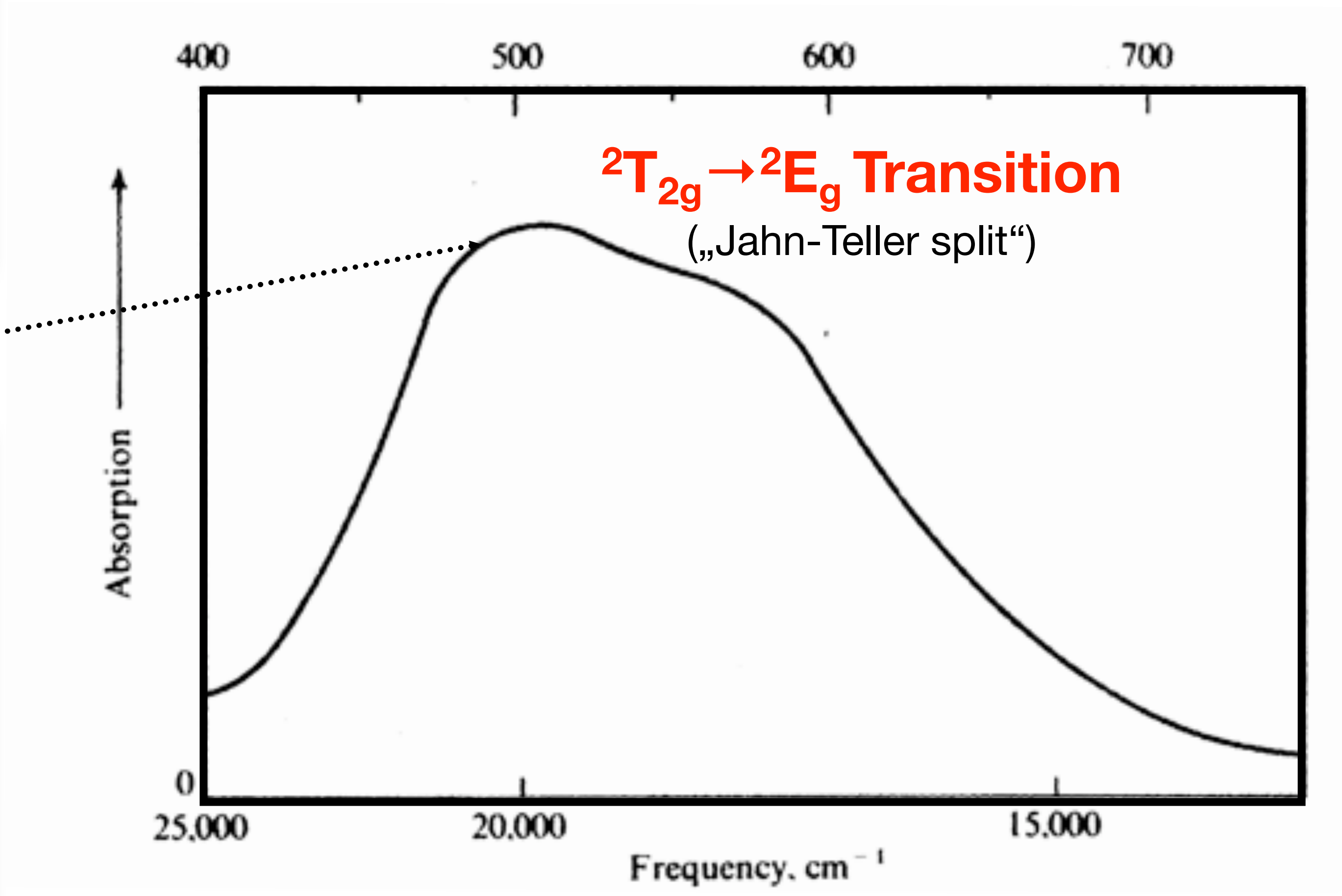
Optical Measurement of Δ: d-d Transitions

Excited State



Ground State

$[Ti(H_2O)_6]^{3+}$



$^2T_{2g}\rightarrow{}^2E_g$ Transition

(„Jahn-Teller split“)

The Spectrochemical Series

A „Chemical“ Spectrochemical Series

$I^- < S^{2-} < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO \sim NO < NO^+$

Δ SMALL

Δ LARGE

A „Biochemical“ Spectrochemical Series (A. Thomson)

Asp/Glu < Cys < Tyr < Met < His < Lys < His^-

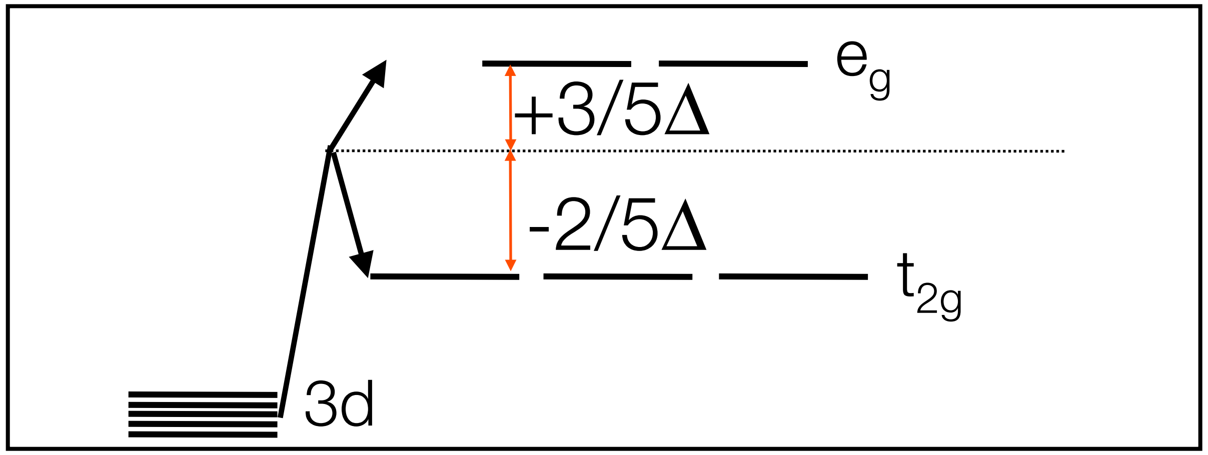
Δ SMALL

Δ LARGE

Ligand Field Stabilization Energies

Central Idea:

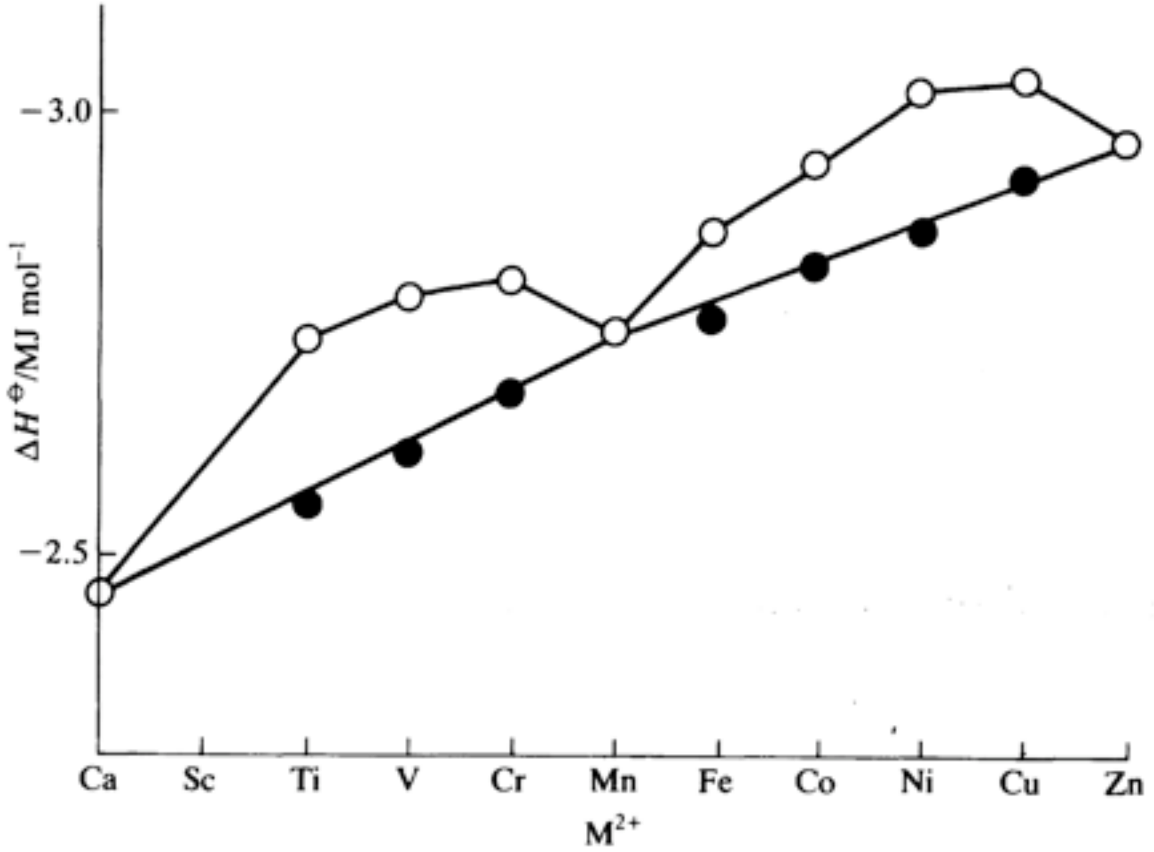
- ➡ Occupation of t_{2g} orbitals stabilizes the complex while occupation of e_g orbitals destabilizes it.
- ➡ Ligand Field Stabilization Energy (LSFE)



d^N	LSFE
1	$-2/5\Delta$
2	$-4/5\Delta$
3	$-6/5\Delta$
4	$-3/5\Delta$
5	**0**
6	$-2/5\Delta$
7	$-4/5\Delta$
8	$-6/5\Delta$
9	$-3/5\Delta$
10	**0**

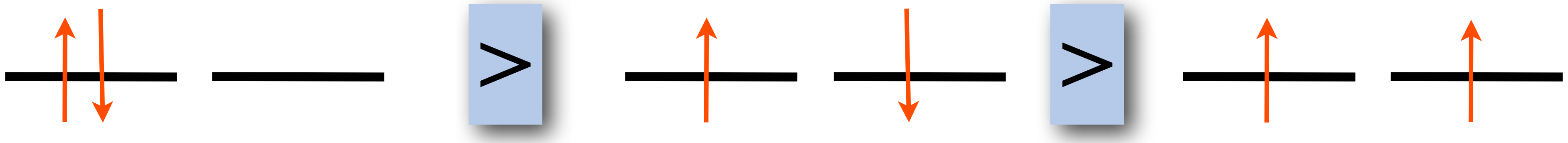
Experimental Test:

- ➡ Hydration energies of hexaquo M^{2+}



Many Electrons in a Ligand Field: Electron Repulsion

BASIC TRUTH: Electrons REPEL Each Other



Rules:

- Electrons in the SAME orbital repel each other most strongly.
- Electrons of oppsite spin repel each other more strongly than electrons of the same spin.

Consequences:

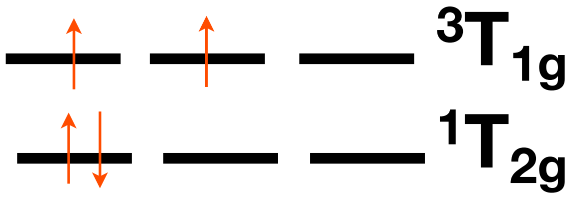
- In degenerate orbitals electrons enter first with the same spin in different orbitals (→Hund‘s Rules in atoms!)
- A given configuration produces several states with different energies

Ligand Field Theory:

- Electron repulsion can be taken care of by ONE PARAMETER: B (~1000 cm^{-1})

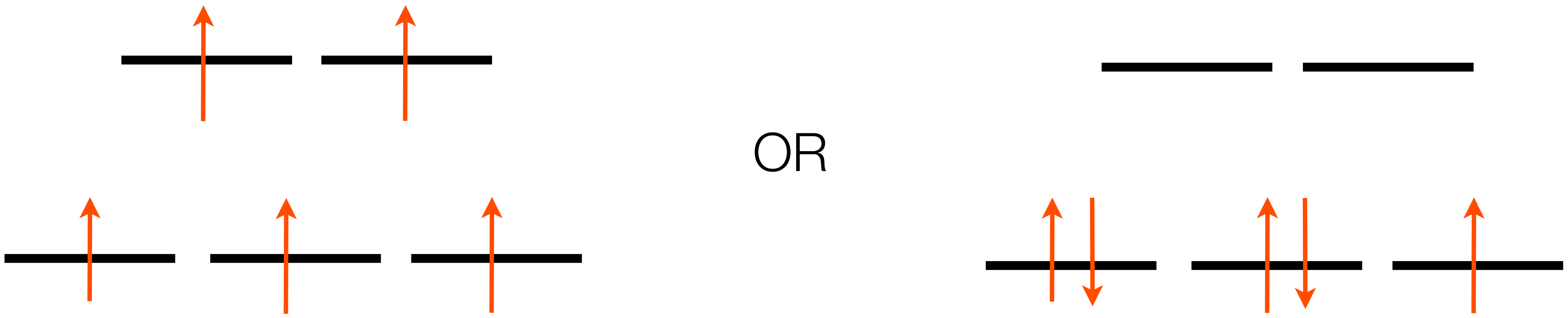
Example:

- d^2-Configuration: $\Delta E(^1T_{2g}-^3T_{1g})$ ~ 4B ~ 3,000-4,000 cm^{-1}



High-Spin and Low-Spin Complexes

QUESTION: What determines the electron configuration?

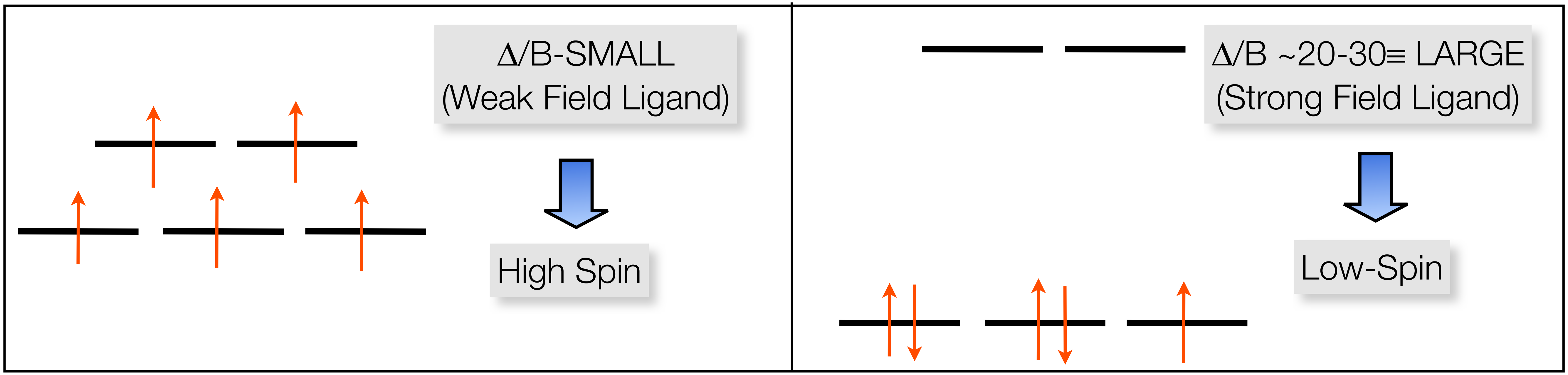


OR

High-Spin

Low-Spin

ANSWER: The balance of ligand field splitting and electron repulsion (‚**Spin-Pairing Energy**‘ P=f(B))



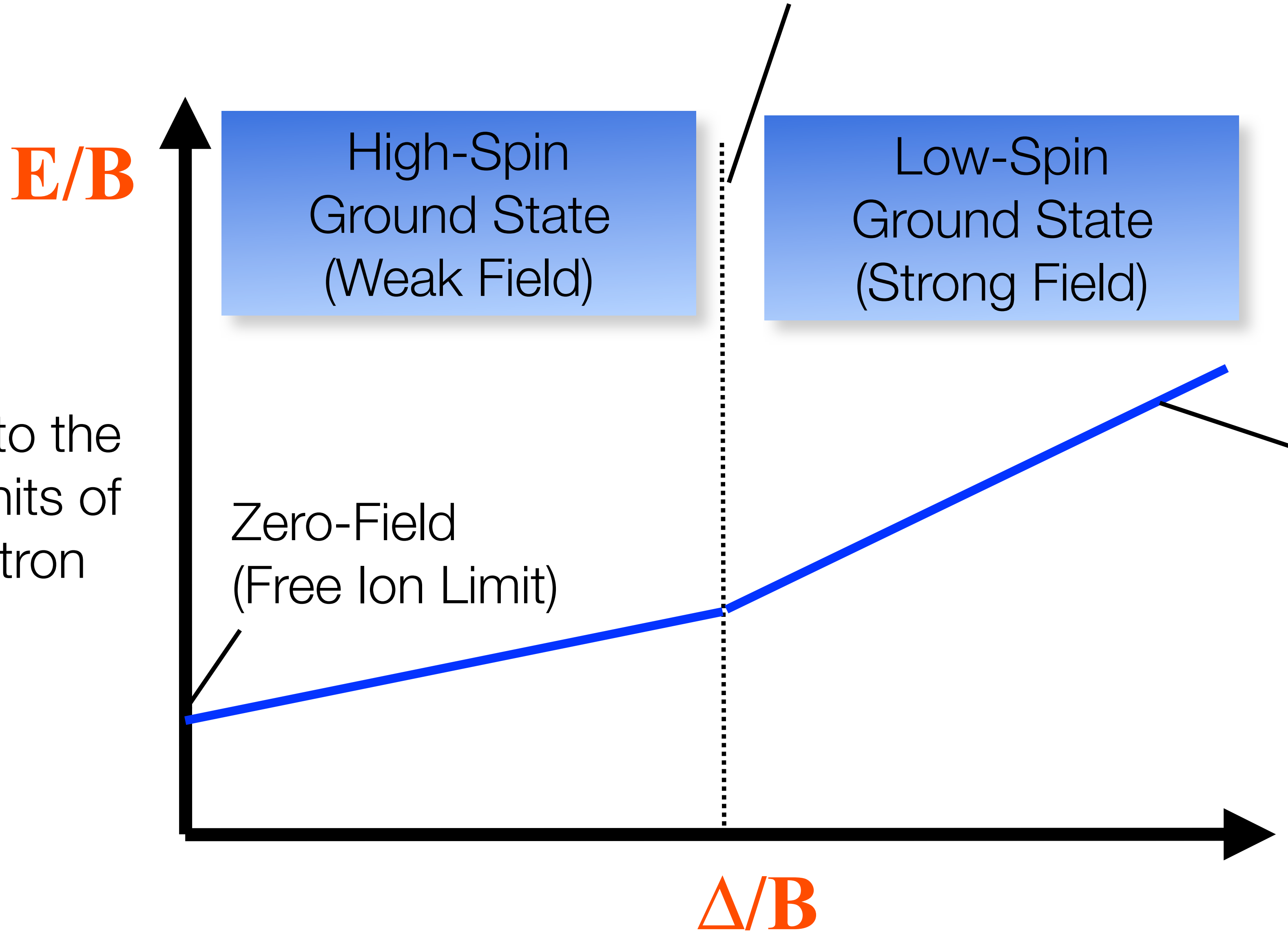
Δ/B-SMALL
(Weak Field Ligand)

High Spin

Δ/B ~20-30≡ LARGE
(Strong Field Ligand)

Low-Spin

Inside Ligand Field Theory:Tanabe-Sugano Diagrams



Critical Ligand Field Strength where the High-Spin to Low-Spin Transition Occurs

E/B

High-Spin
Ground State
(Weak Field)

Low-Spin
Ground State
(Strong Field)

Energy RELATIVE to the Ground State in Units of the Electron-Electron Repulsion

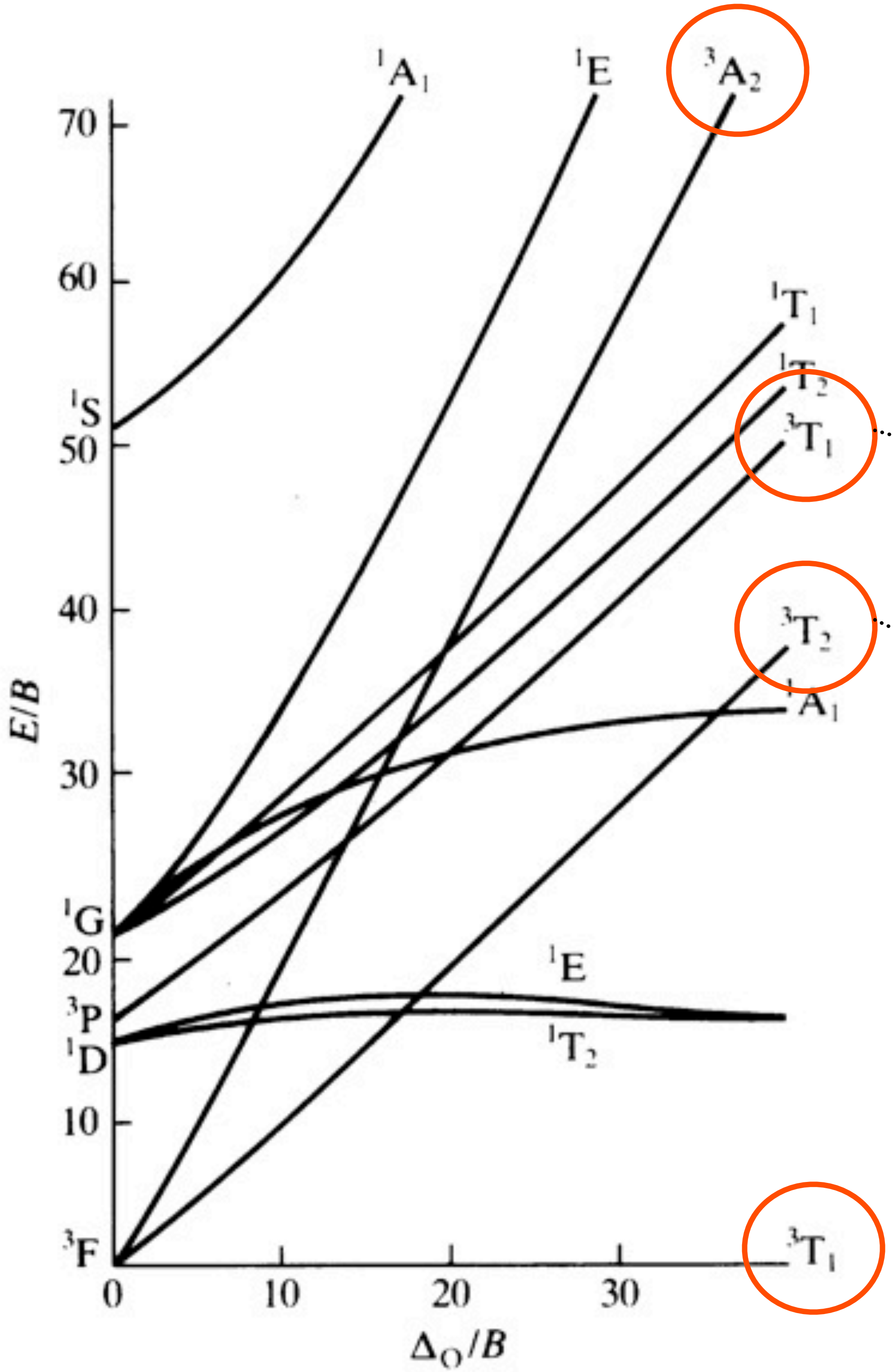
Zero-Field
(Free Ion Limit)

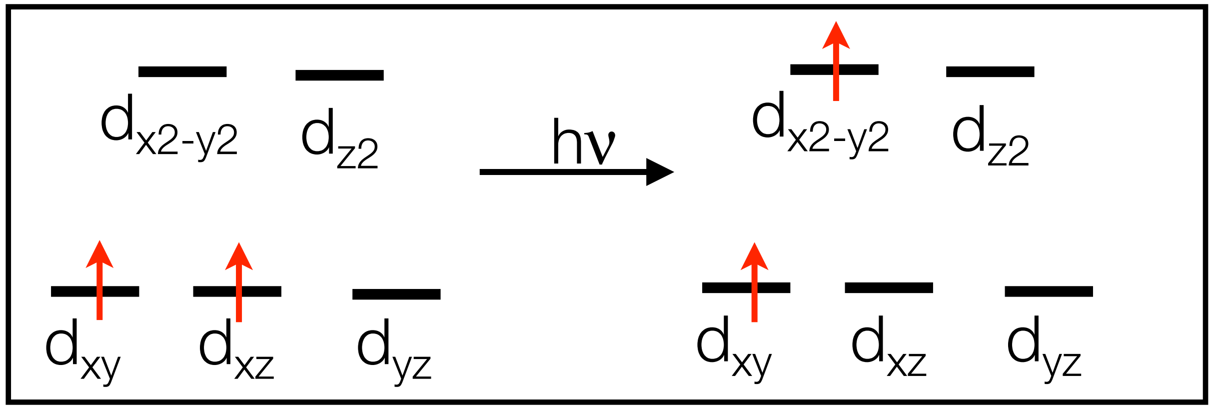
Energy of a Given Term Relative to the Ground State

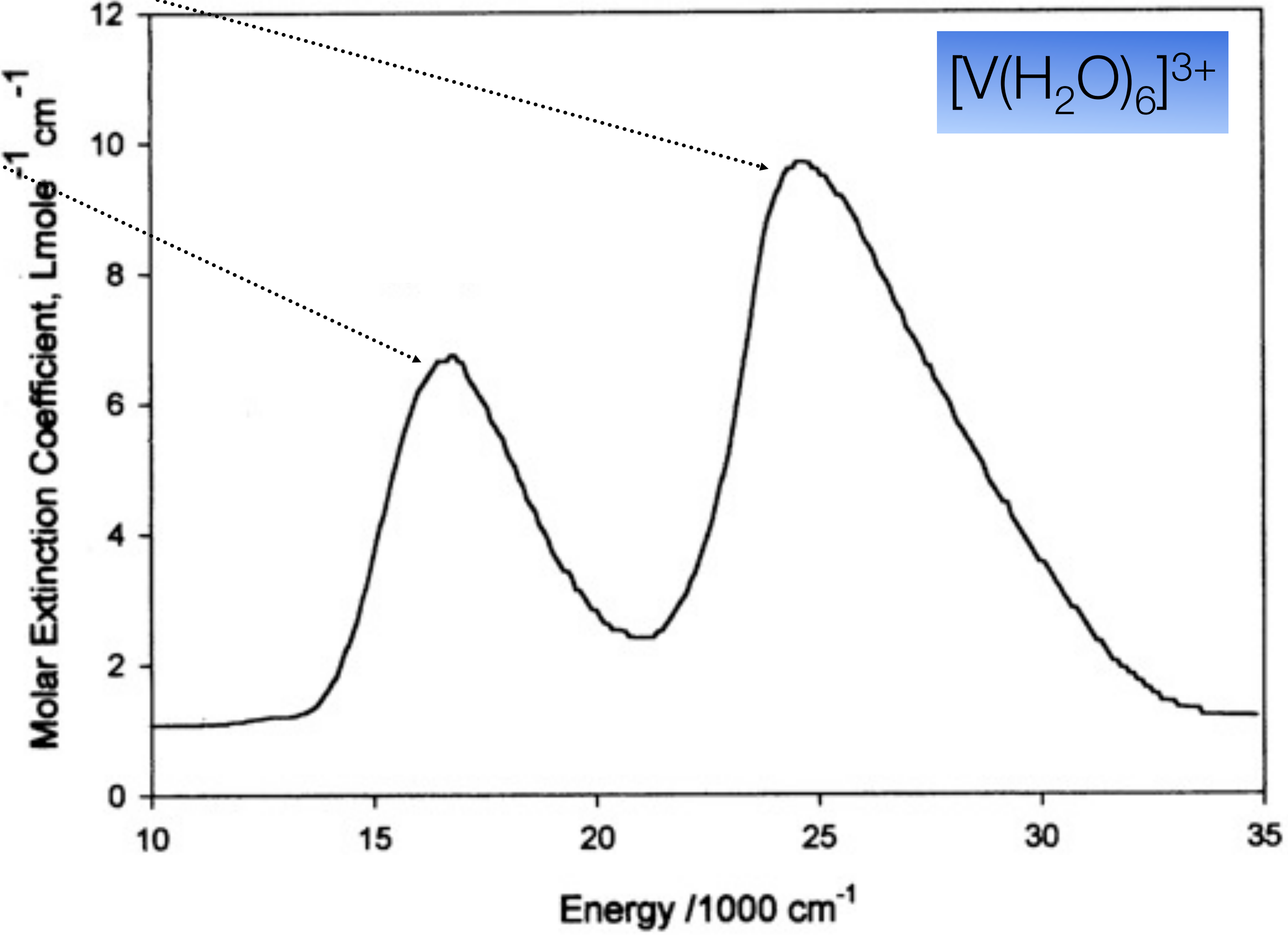
Δ/B

Strength of Ligand Field Increases Relative to the Electron-Electron Repulsion

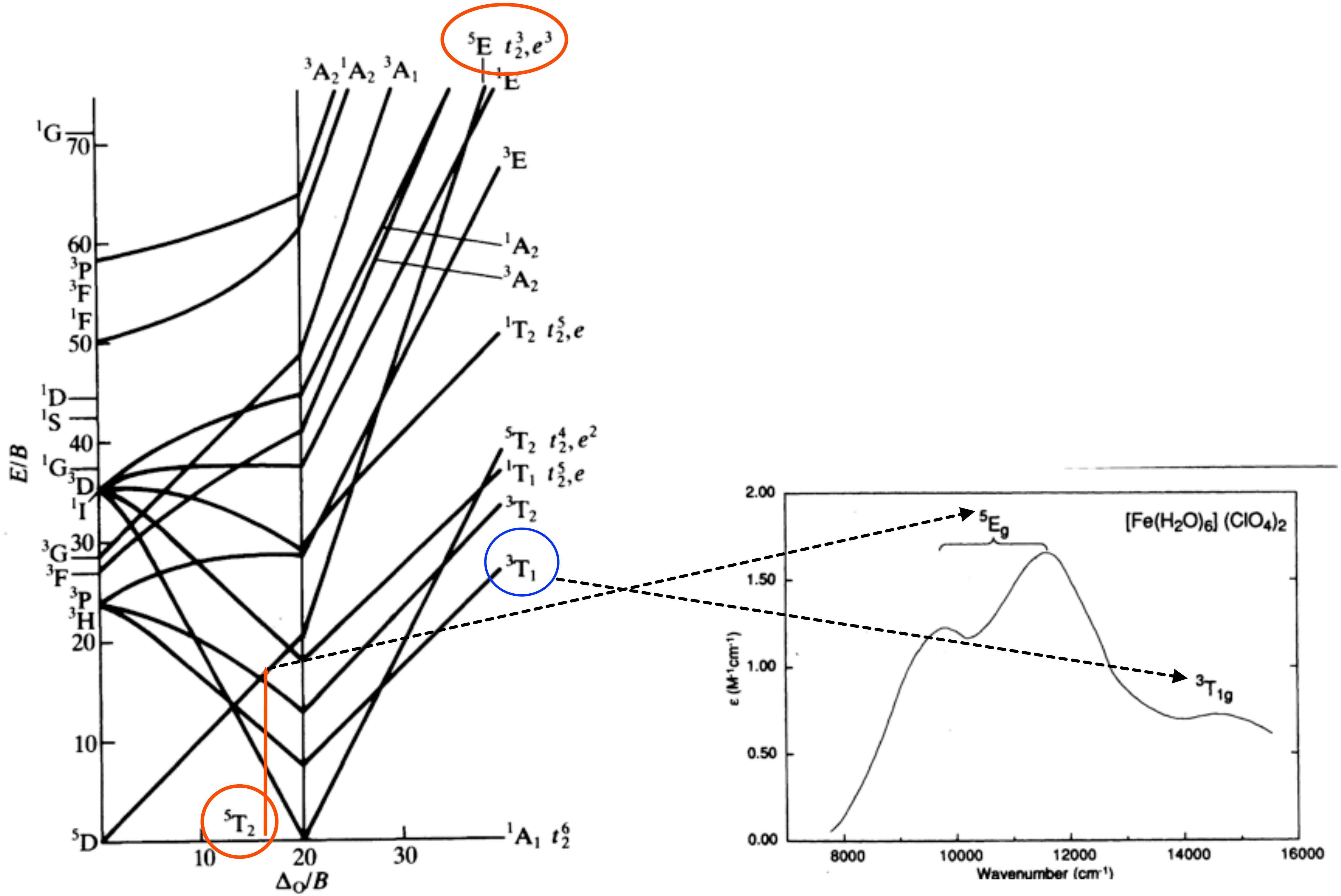
Optical Properties: d-d Spectra of d^2 Ions



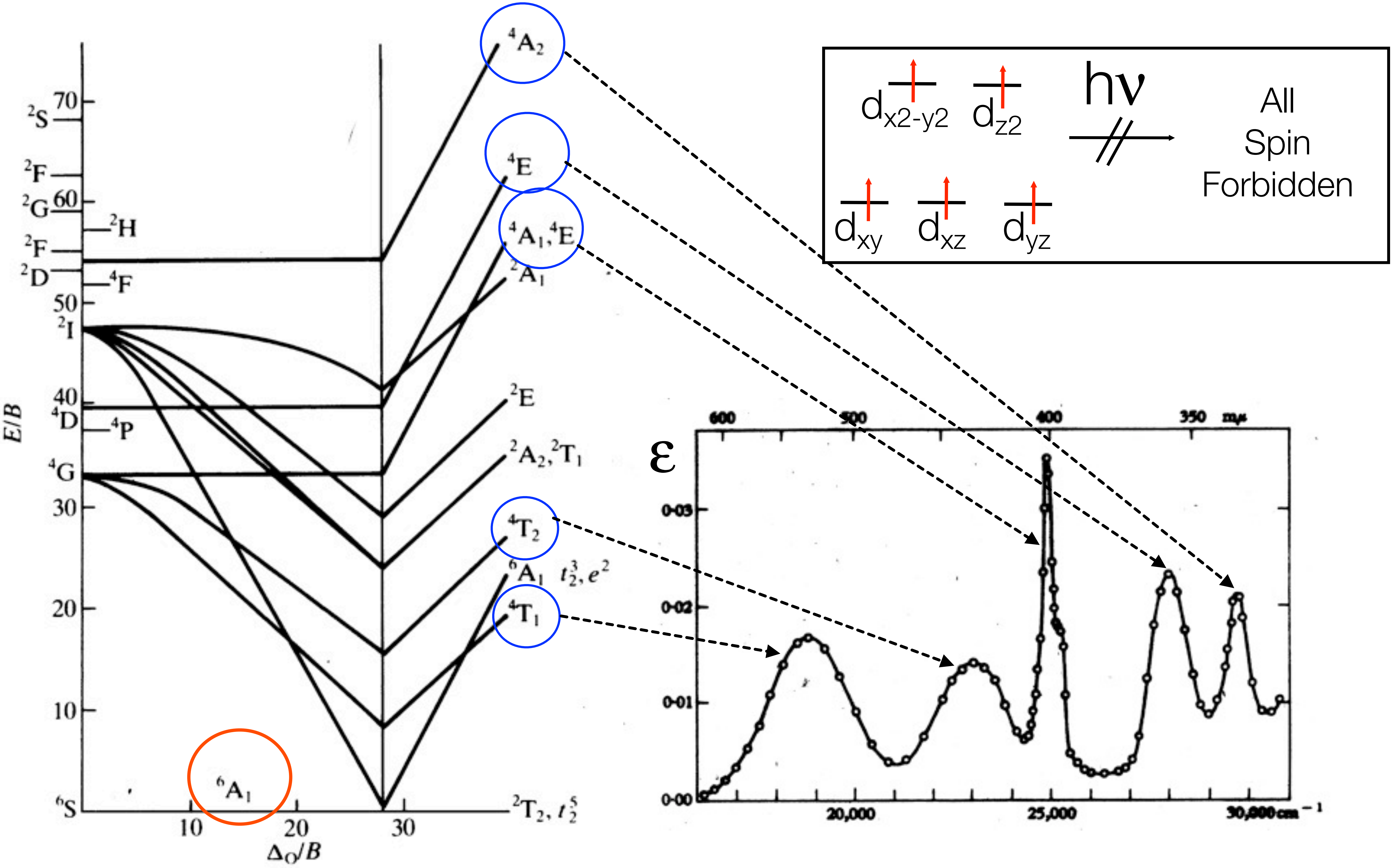




d-d Spectra of d^6 Ions (Fe^{II}, Co^{III})

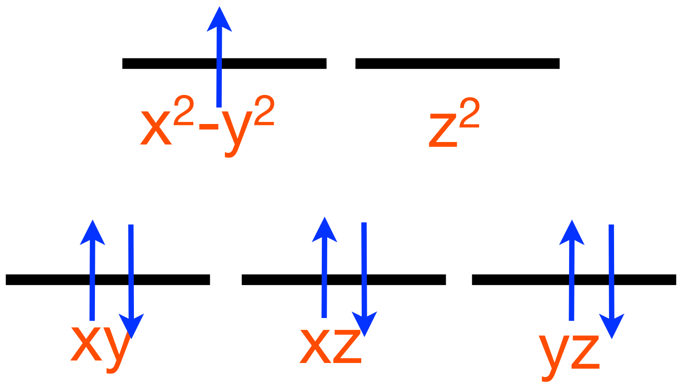


d-d Spectra of d^5 Ions (Fe^{III}, Mn^{II})

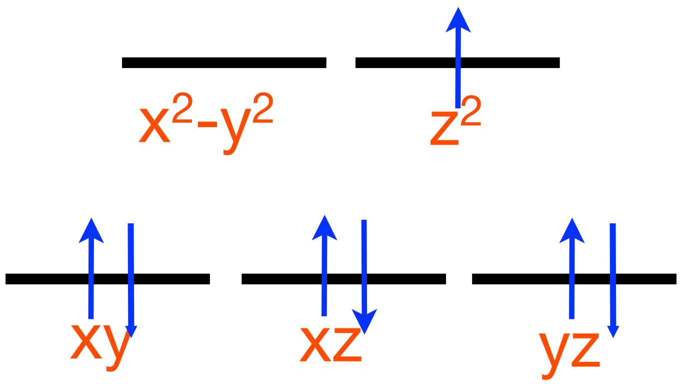


The Jahn-Teller Effect: Basic Concept

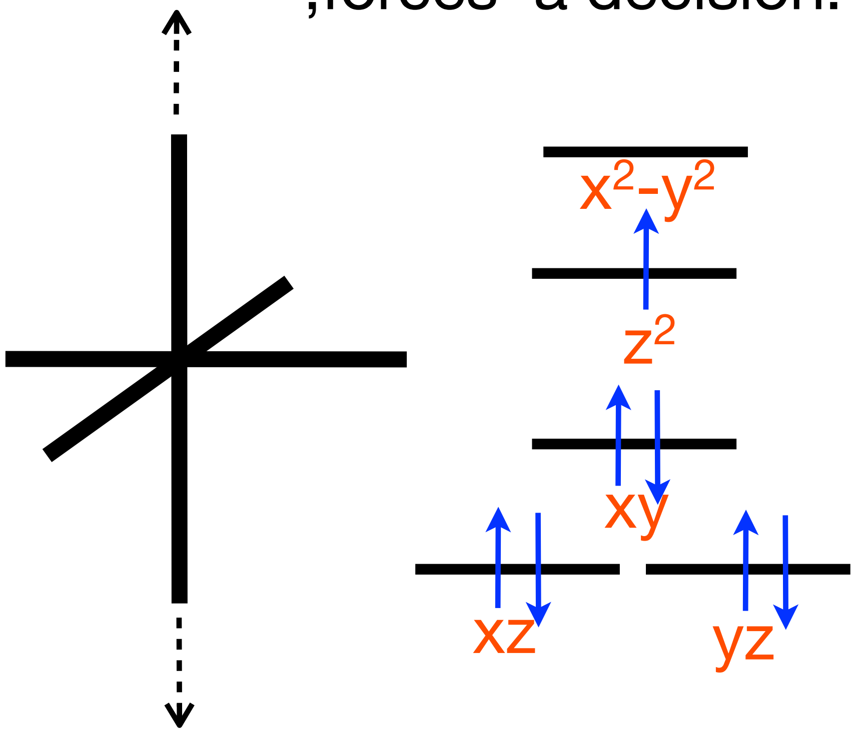
QUESTION: What happens if an electron can occupy one out of a couple of degenerate orbitals?



OR



ANSWER: There is **ALWAYS** a nuclear motion that removes the degeneracy and ‚forces‘ a decision! (JT-Theorem)



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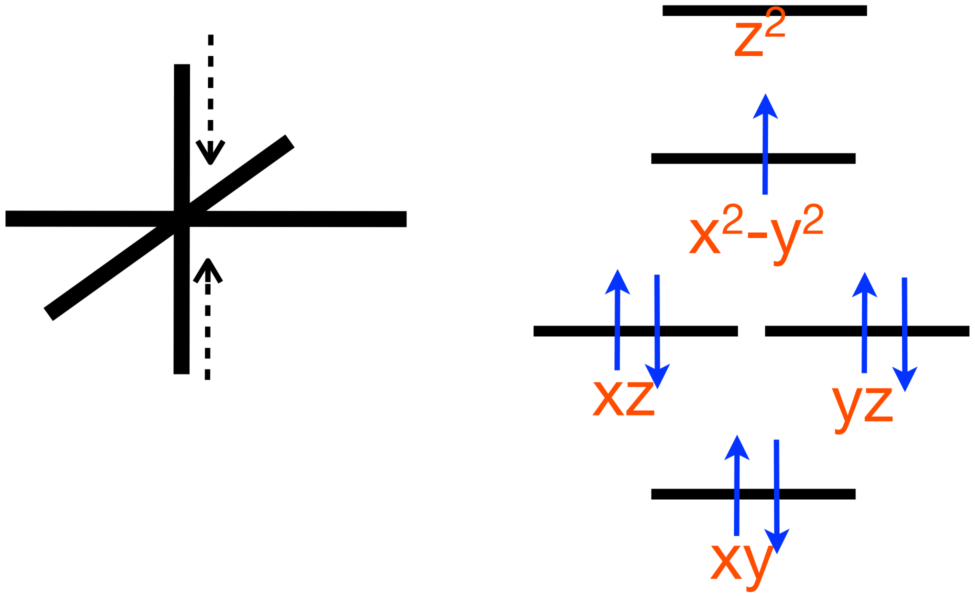
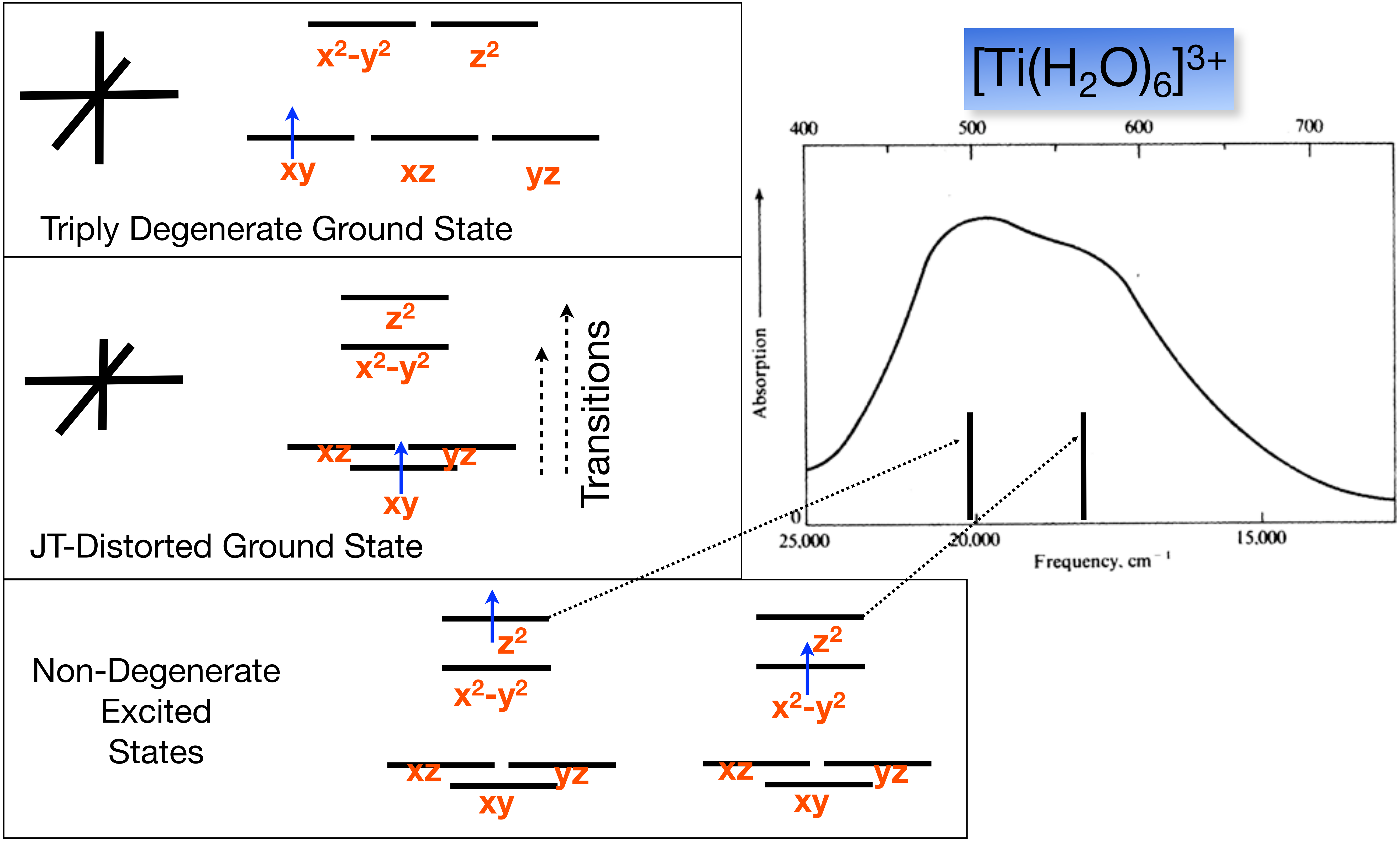


The Jahn-Teller Effect: An Example



$[Ti(H_2O)_6]^{3+}$

Triply Degenerate Ground State

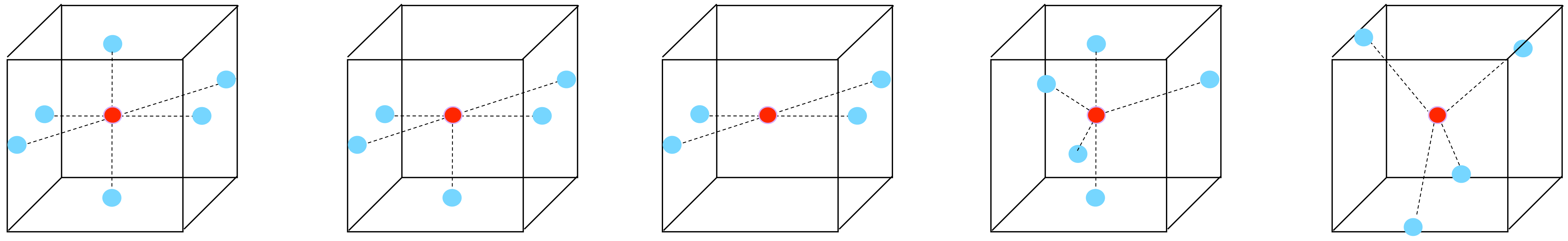
JT-Distorted Ground State

Transitions

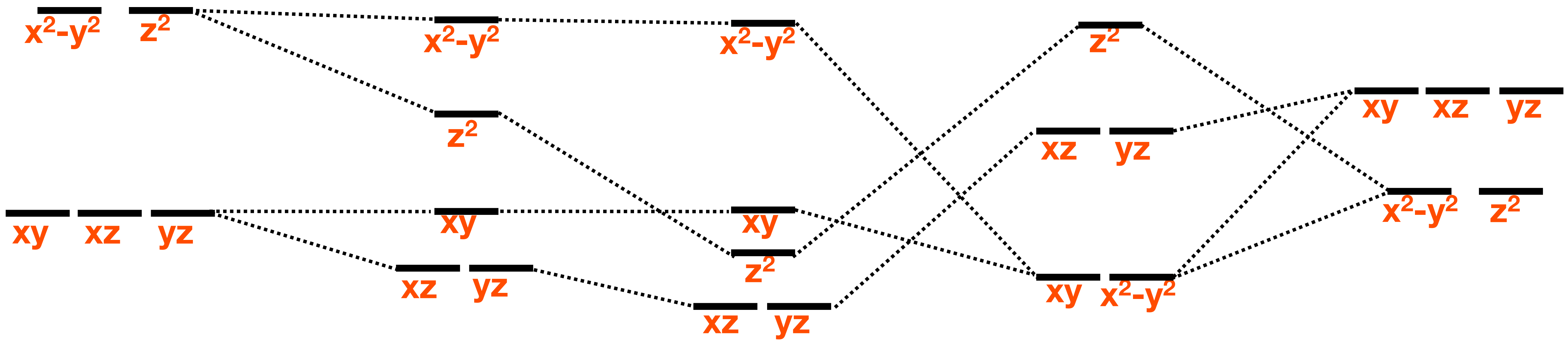
Non-Degenerate
Excited
States

Ligand Field Splittings in Different Coordination Geometries

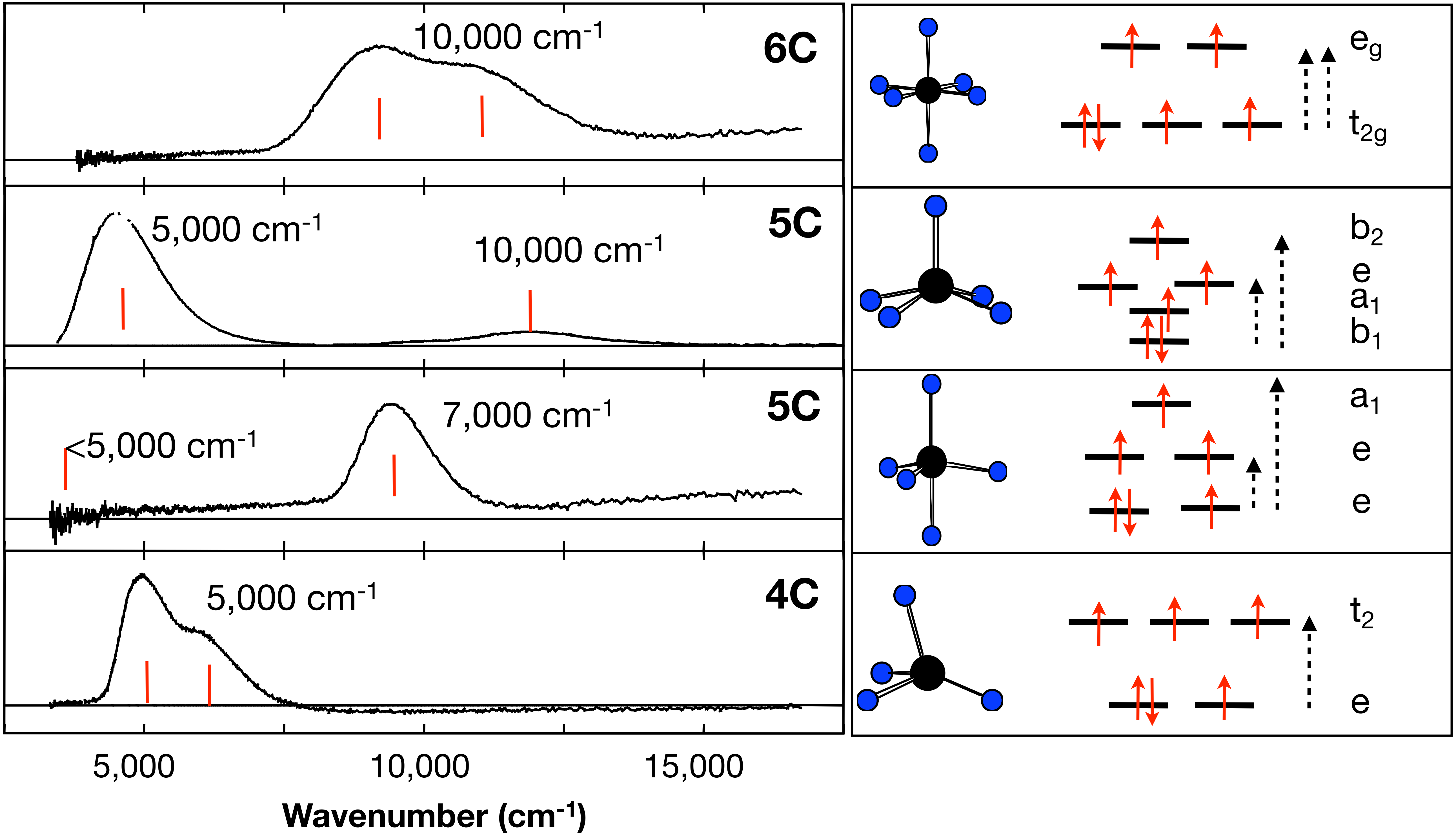
Octahedral | Tetragonal Pyramidal | Square Planar | Trigonal Bipyramidal | Tetrahedral



O_h | C_{4v} | D_{4h} | D_{3h} | T_d

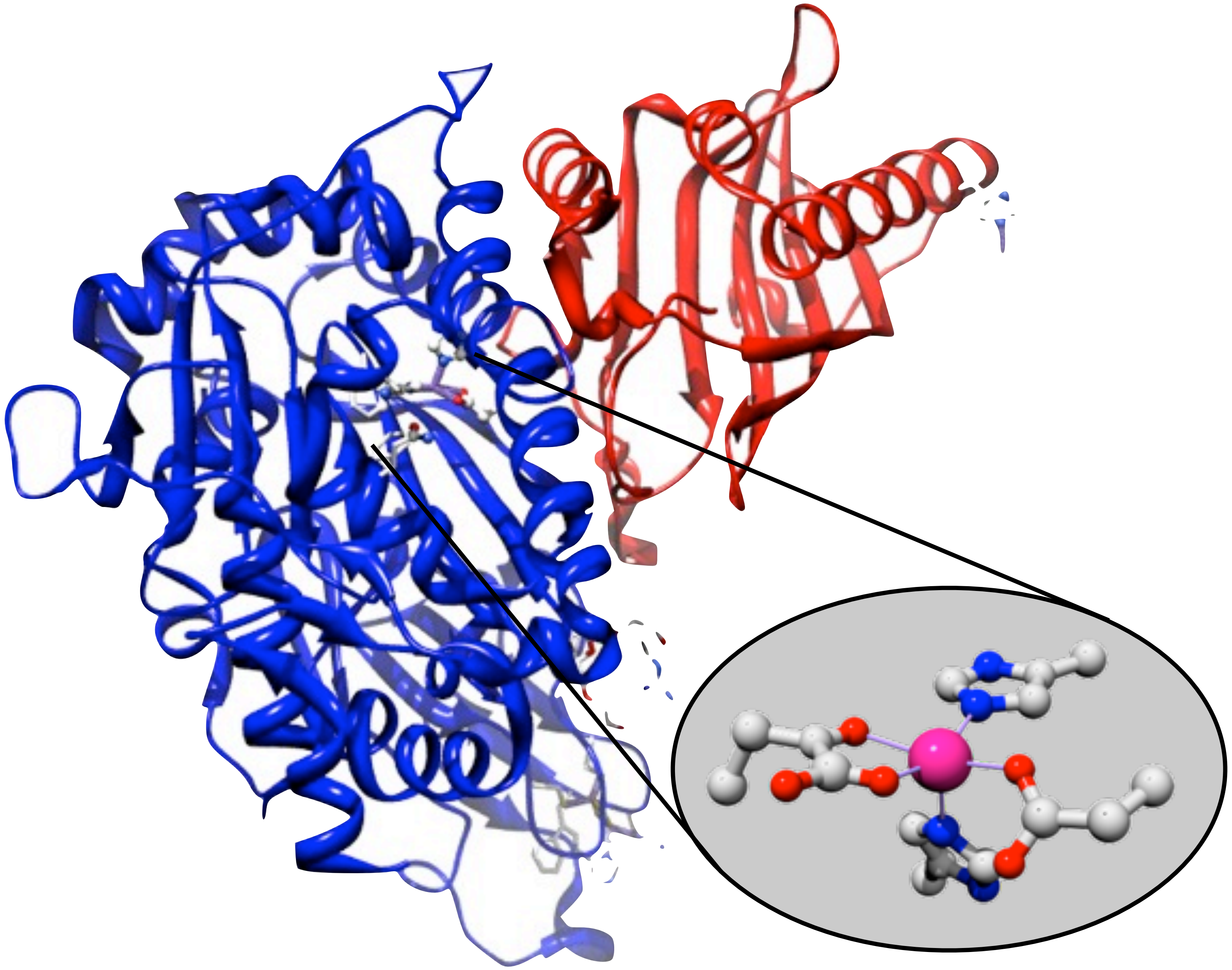


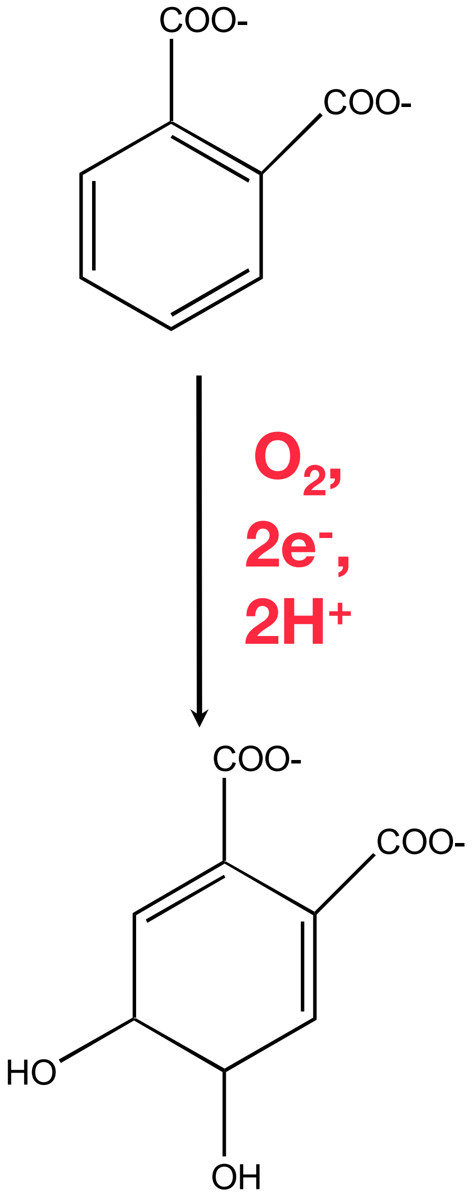
Coordnation Geometry and d-d Spectra: HS-Fe(II)



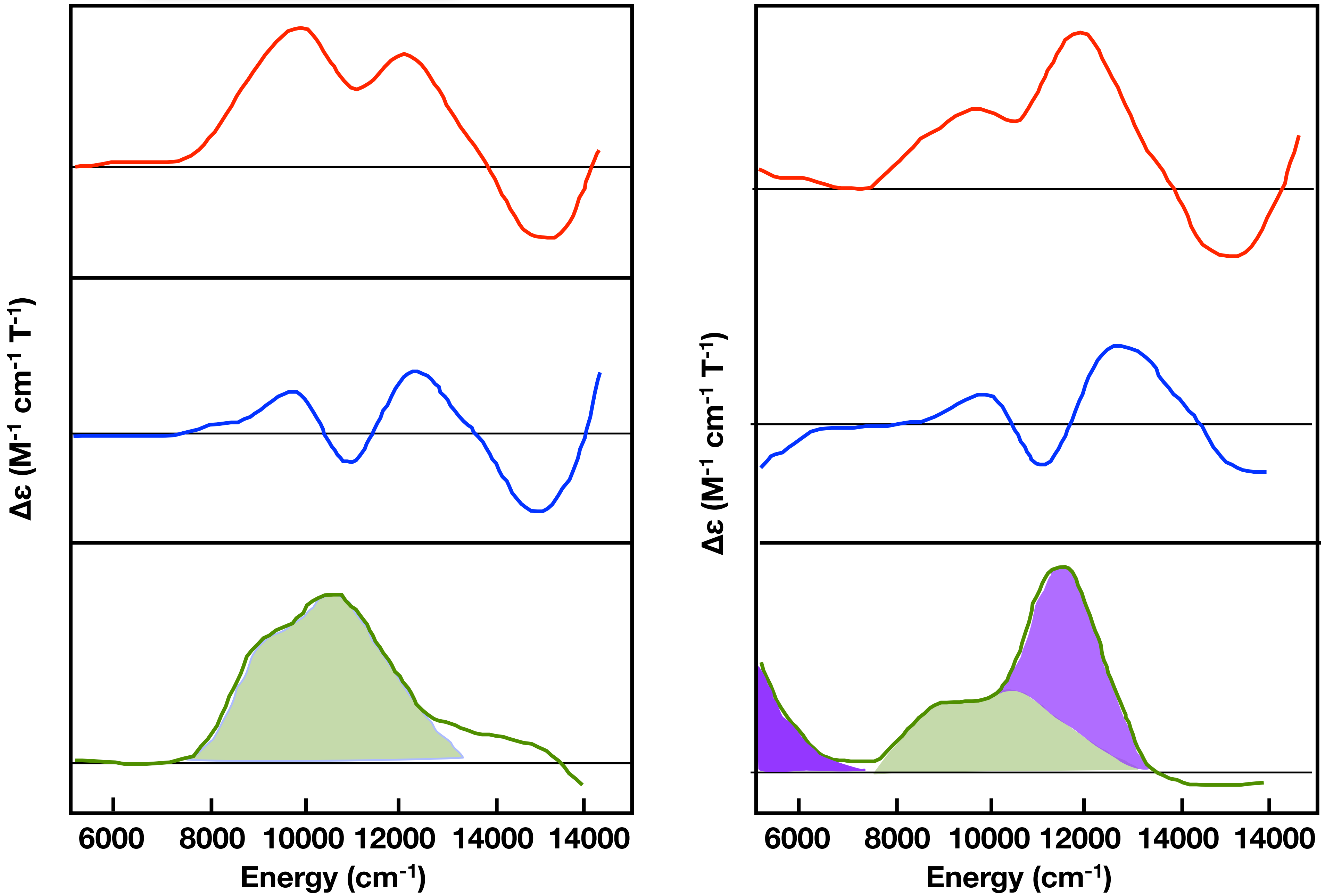
Studying Enzyme Mechanisms

Rieske-Dioxygenases





Active Site Geometry from d-d Spectra



-Substrate

+Substrate

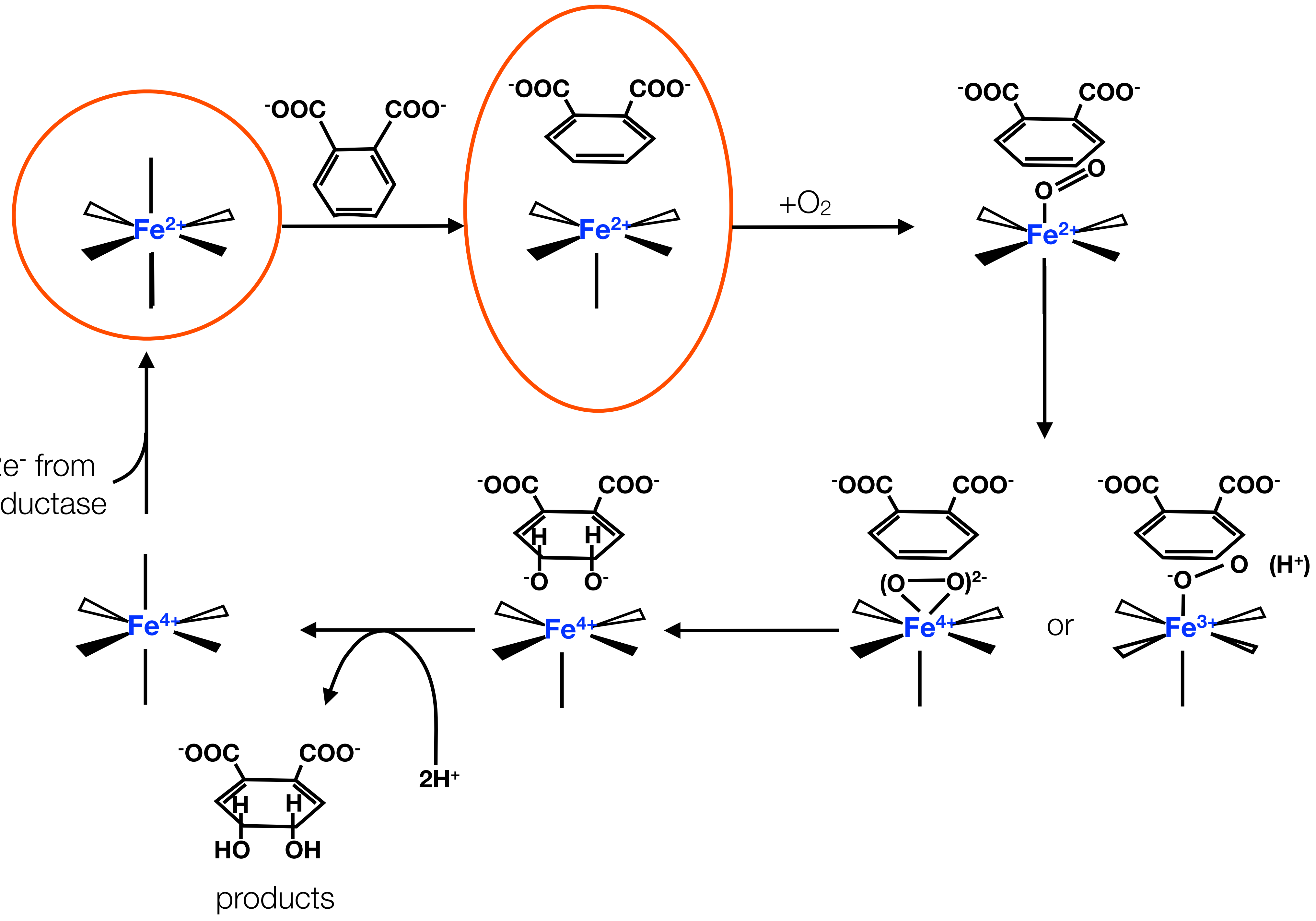
Holoenzyme

Rieske only

Difference

Solomon et al., (**2000**) *Chem. Rev.*, 100, 235-349

Mechanistic Ideas from Ligand Field Studies



products

Solomon et al., (**2000**) *Chem. Rev.*, 100, 235-349

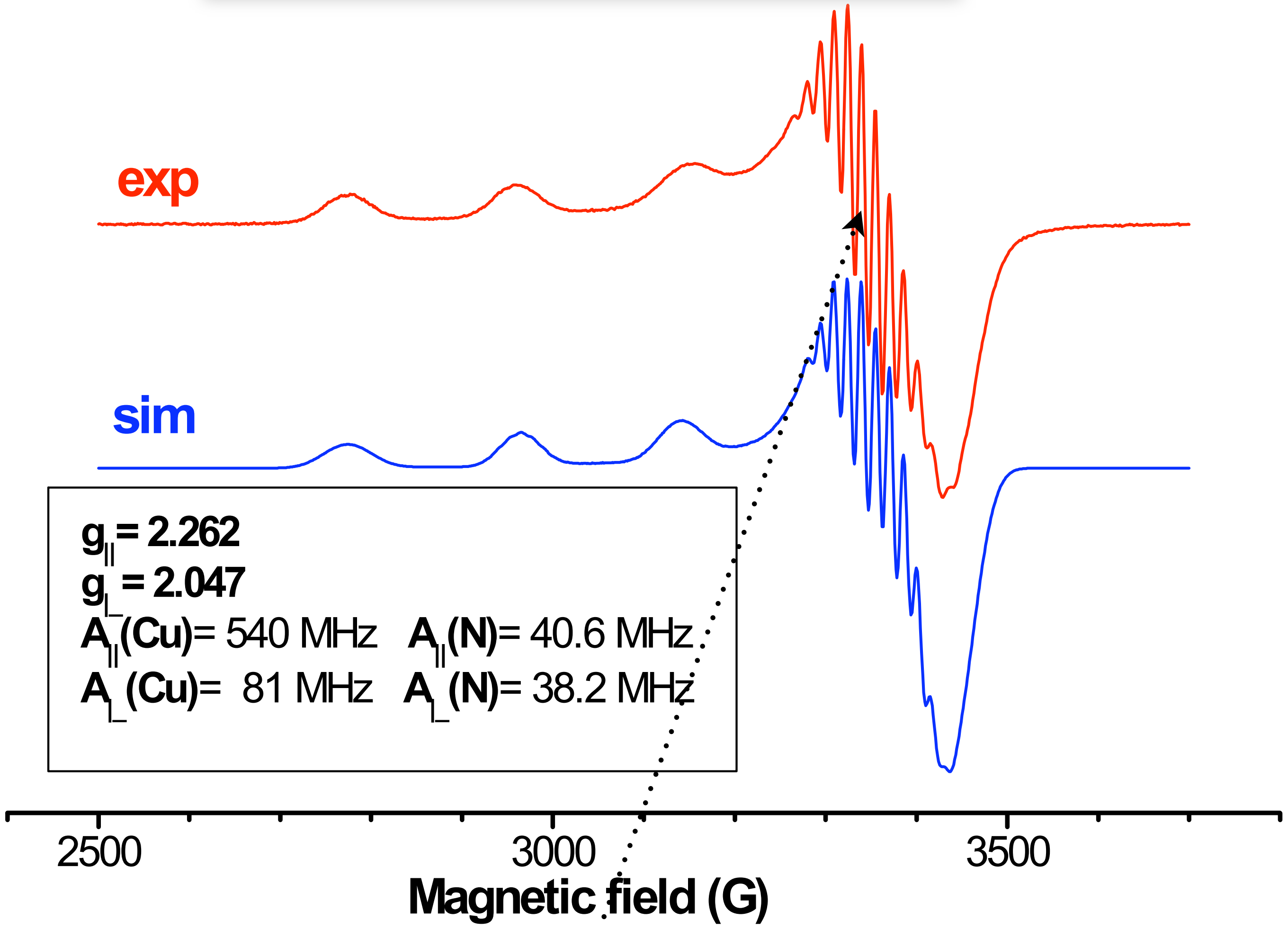
Beyond Ligand Field Theory

„Personally, I do not believe much of the electrostatic romantics, many of my collegues talked about“

(C.K. Jörgensen, **1966** *Recent Progress in Ligand Field Theory*)

Experimental Proof of the Inadequacy of LFT

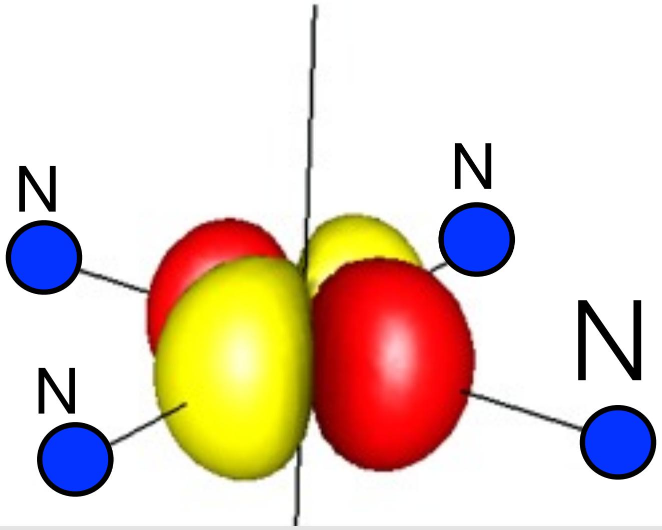
$[Cu(imidazole)_4]^{2+}$



$g_{\|}$ = 2.262
$g_{\perp}$ = 2.047
$A_{\|}$(Cu)= 540 MHz $A_{\|}$(N)= 40.6 MHz
$A_{\perp}$(Cu)= 81 MHz $A_{\perp}$(N)= 38.2 MHz

Clearly Observed Coupling Between The Unpaired Electron and the Nuclear Spin of Four ^{14}N Nitrogens (I=1)

Ligand Field Picture



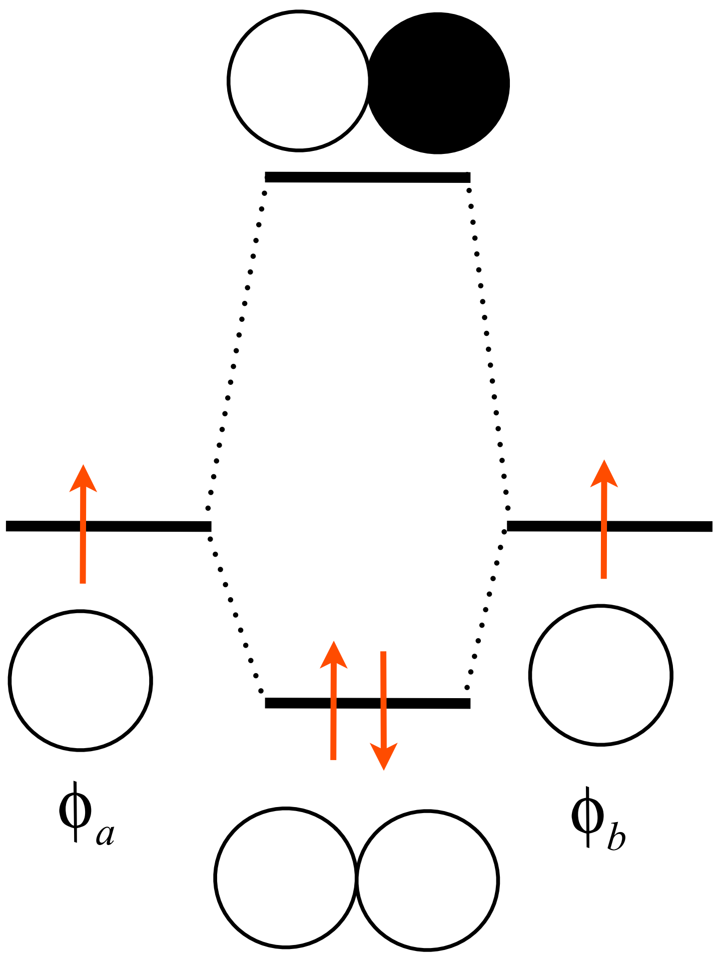
Wavefunction of the Unpaired Electron Exclusively Localized on the Metal

No Coupling Expected

Need a Refined Theory that Includes the Ligands Explicitly

Description of Bonds in MO Theory

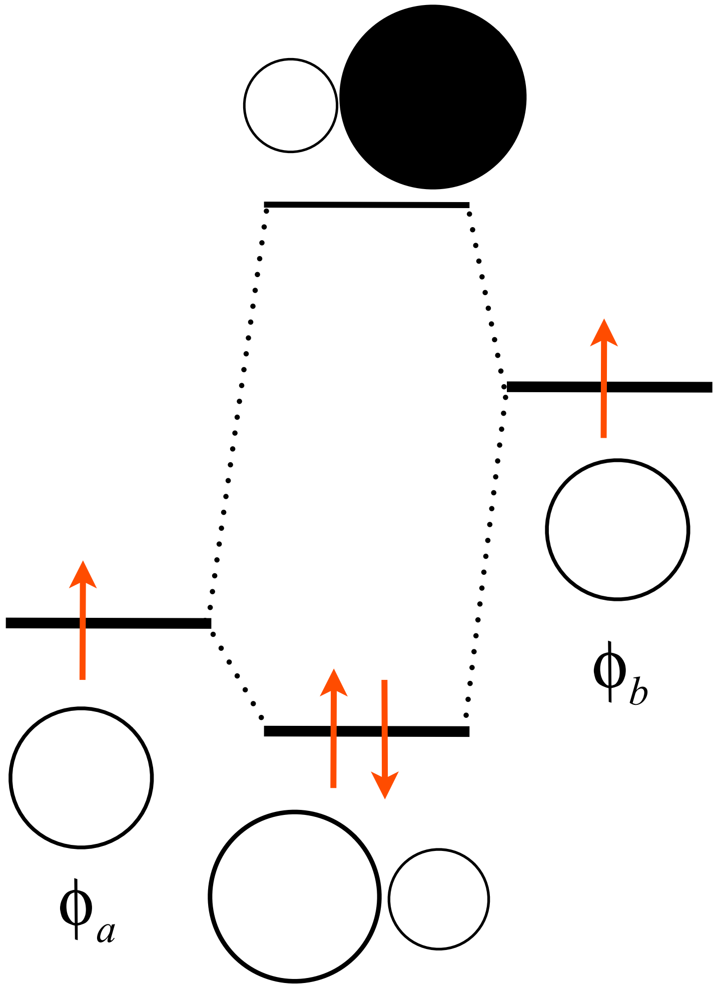
$$\frac{\phi_a - \phi_b}{\sqrt{2(1-S)}}$$



$$\frac{\phi_a + \phi_b}{\sqrt{2(1+S)}}$$

Homopolar Bond

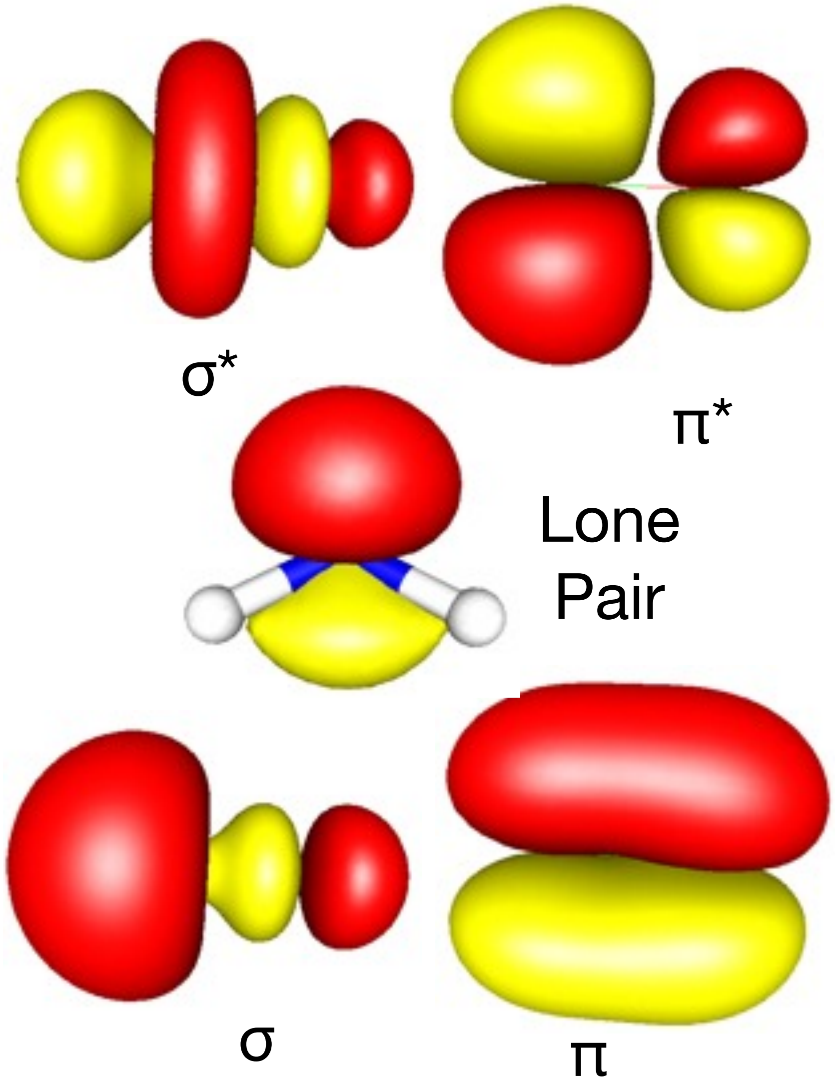
$$\frac{\lambda'\phi_a - \phi_b}{\sqrt{1+\lambda'(\lambda'-2S)}}$$



$$\frac{\phi_a + \lambda\phi_b}{\sqrt{1+\lambda(2S+\lambda)}}$$

Heteropolar Bond

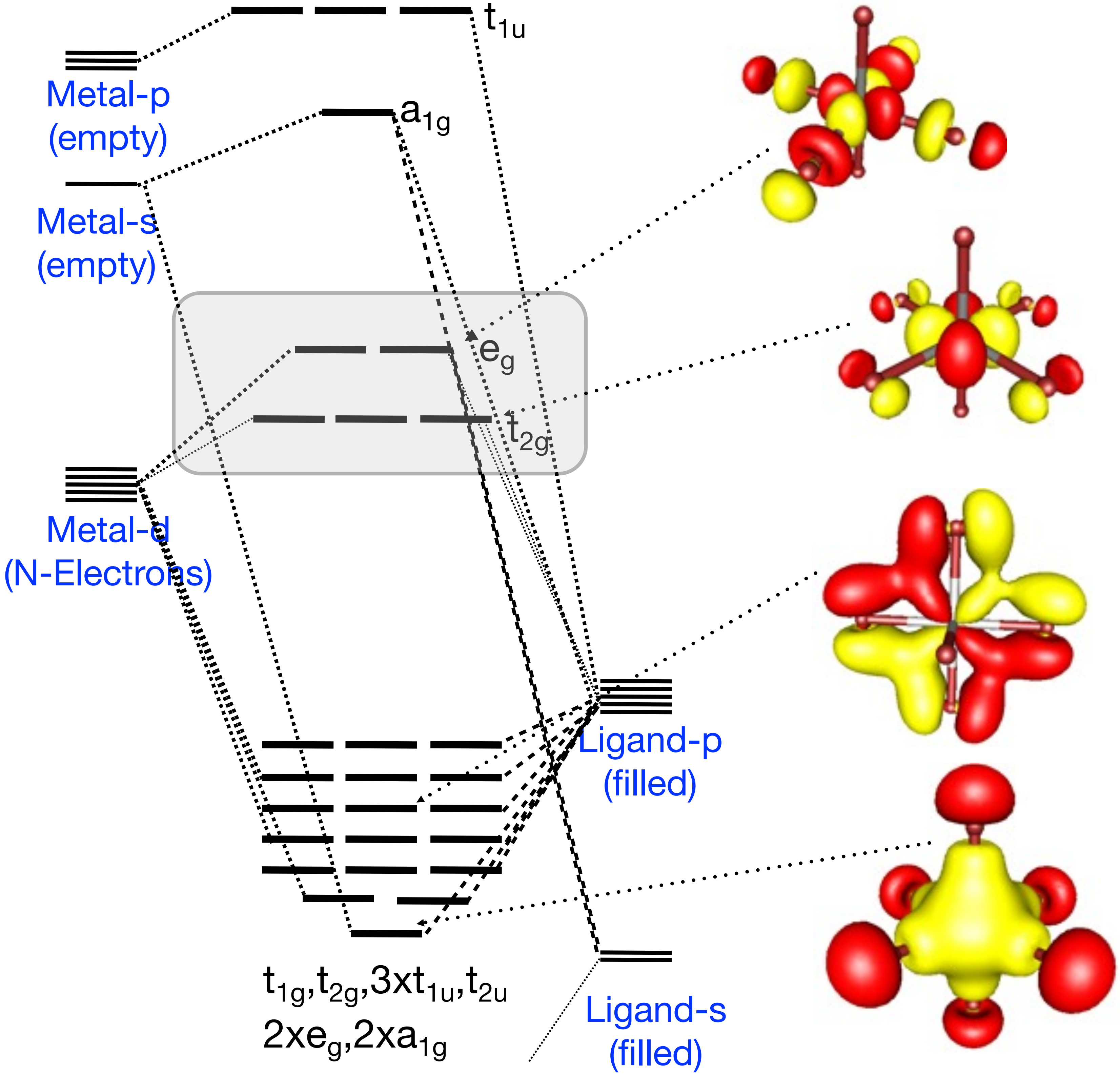
Types of MO's



Bond-Order:

$$B = \tfrac{1}{2}\left(N_B - N_A\right)$$

MO Theory of ML_6 Complexes

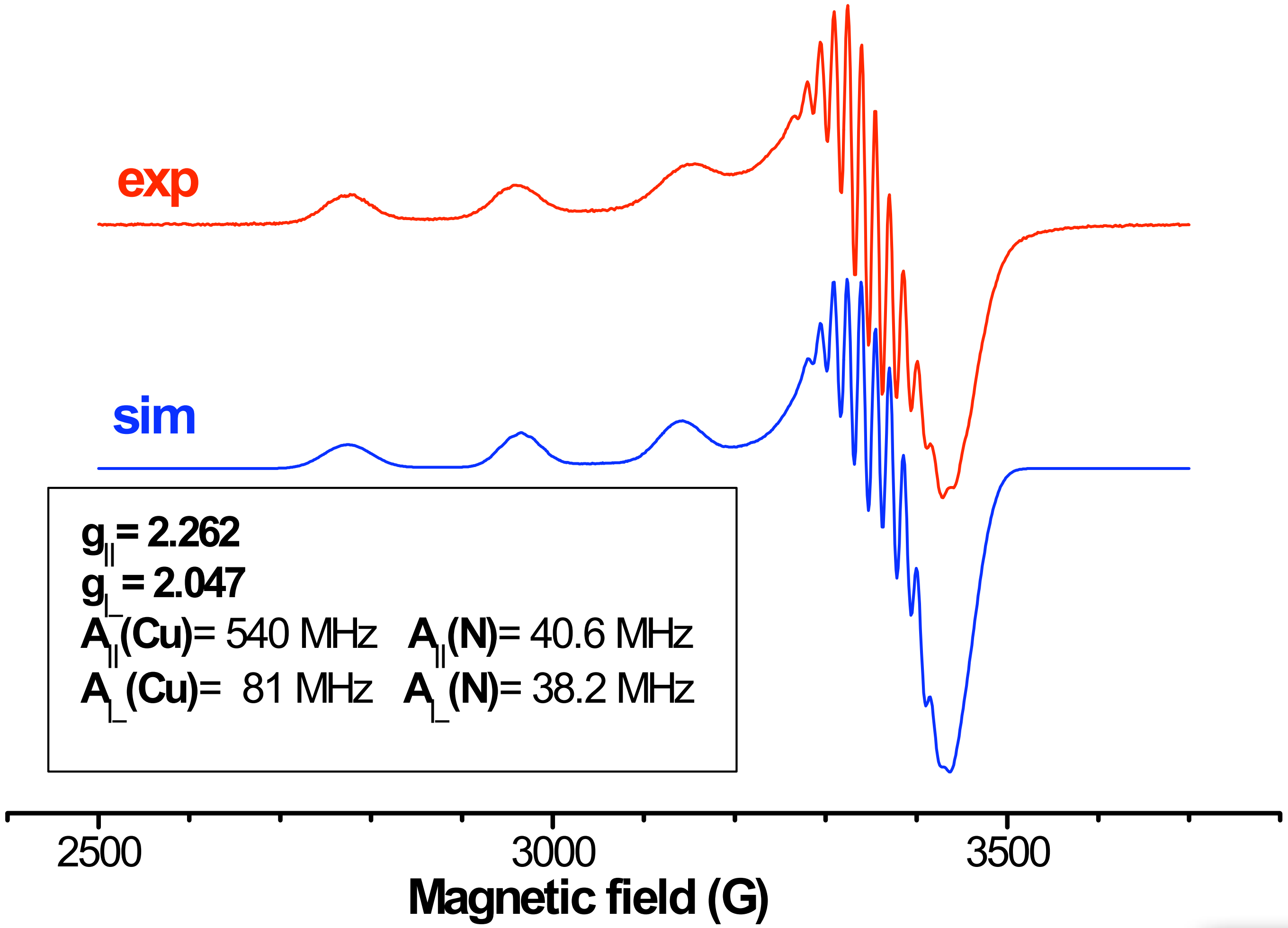


Key Points:

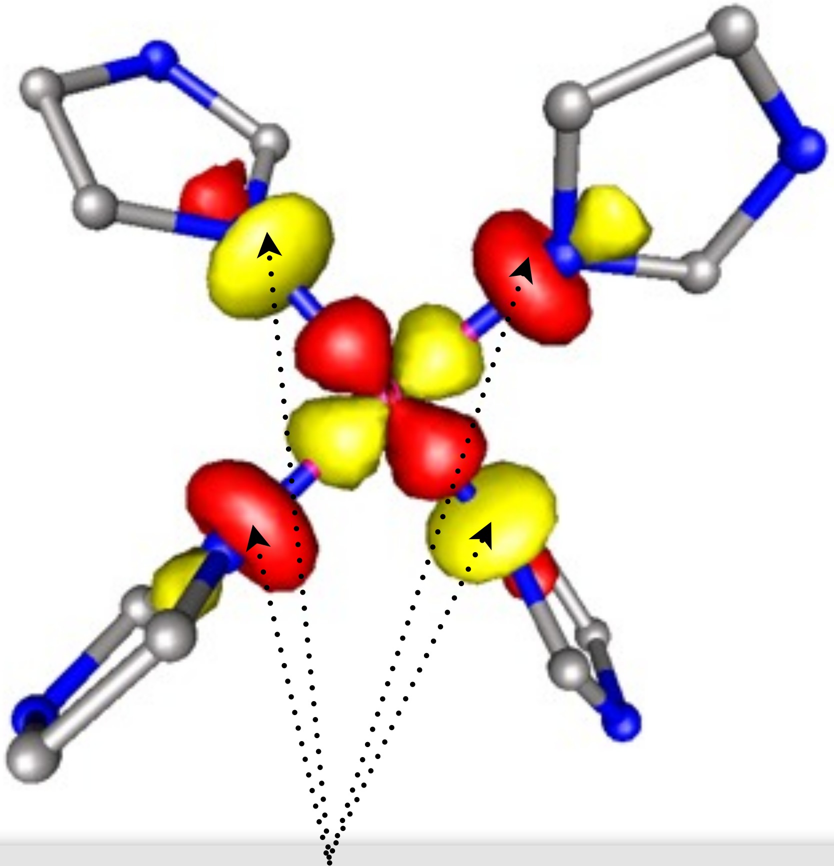
- Filled ligand orbitals are lower in energy than metal d-orbitals
- **The orbitals that are treated in LFT correspond to the anti-bonding metal-based orbitals in MO Theory**
- Through bonding some electron density is transferred from the ligand to the metal
- The extent to which this takes place defines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

MO Theory and Covalency

$[Cu(imidazole)_4]^{2+}$



$g_{||} = 2.262$
$g_{\perp} = 2.047$
$A_{||}(Cu) = 540$ MHz $A_{||}(N) = 40.6$ MHz
$A_{\perp}(Cu) = 81$ MHz $A_{\perp}(N) = 38.2$ MHz

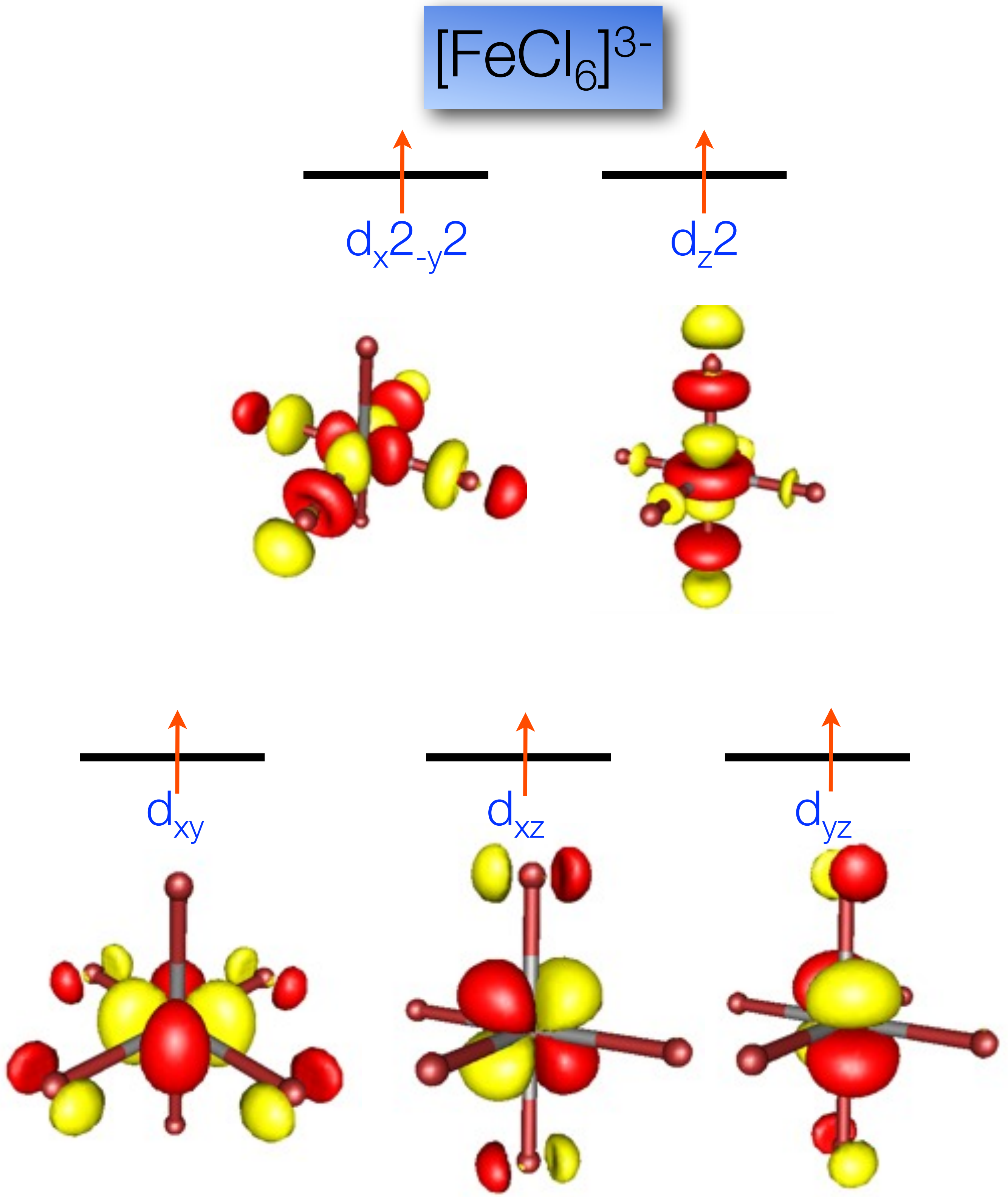


The Unpaired Electron is Partly Delocalized Onto the Ligands

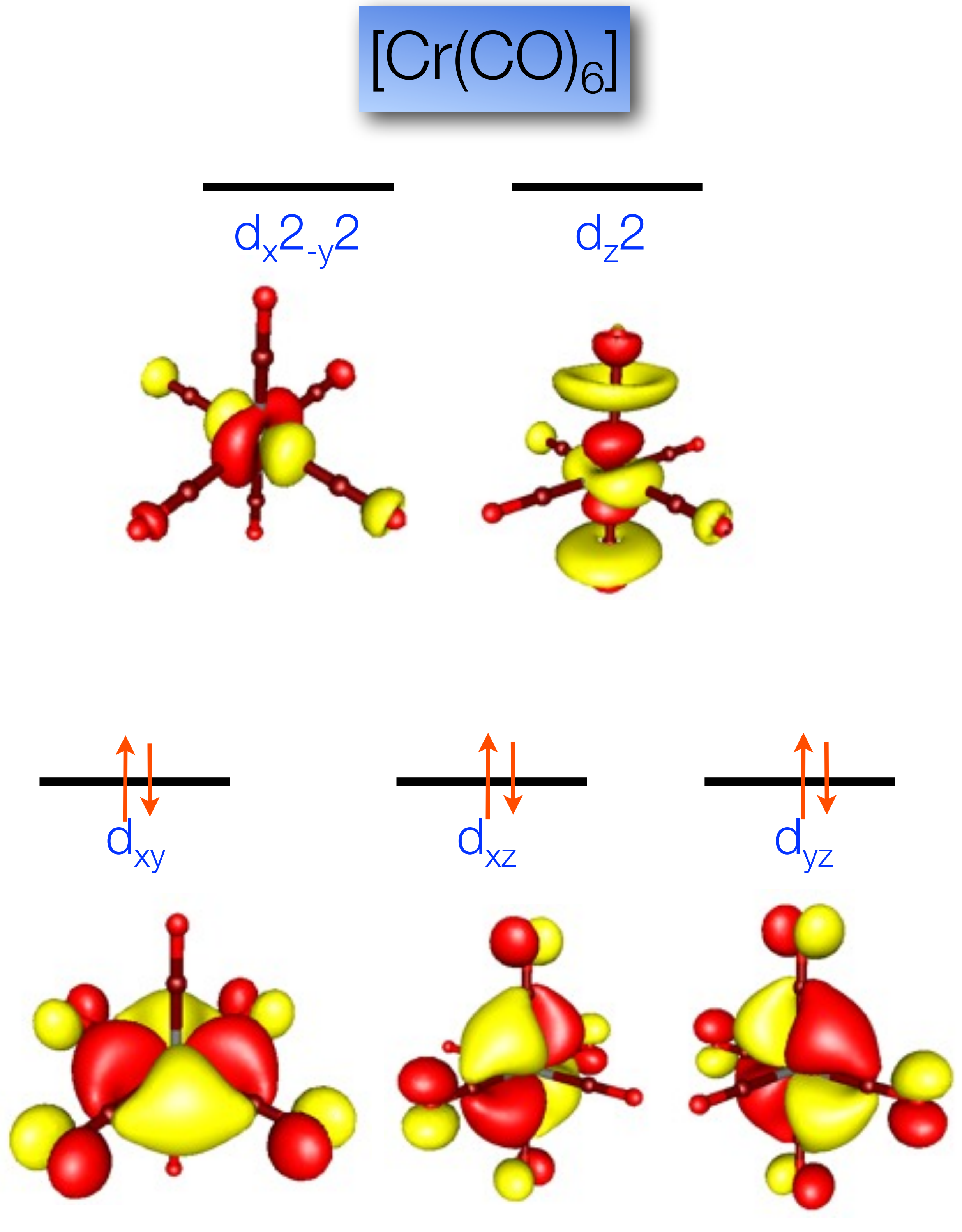
Magnetic Coupling Expected

1. Theory Accounts for Experimental Facts
2. Can Make Semi-Quantitative Estimate of the Ligand Character in the SOMO

π-Bonding and π-Backbonding



$[FeCl_6]^{3-}$



$[Cr(CO)_6]$

Interpretation of the Spectrochemical Series

$I^- < S^{2-} < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO \sim NO < NO^+$

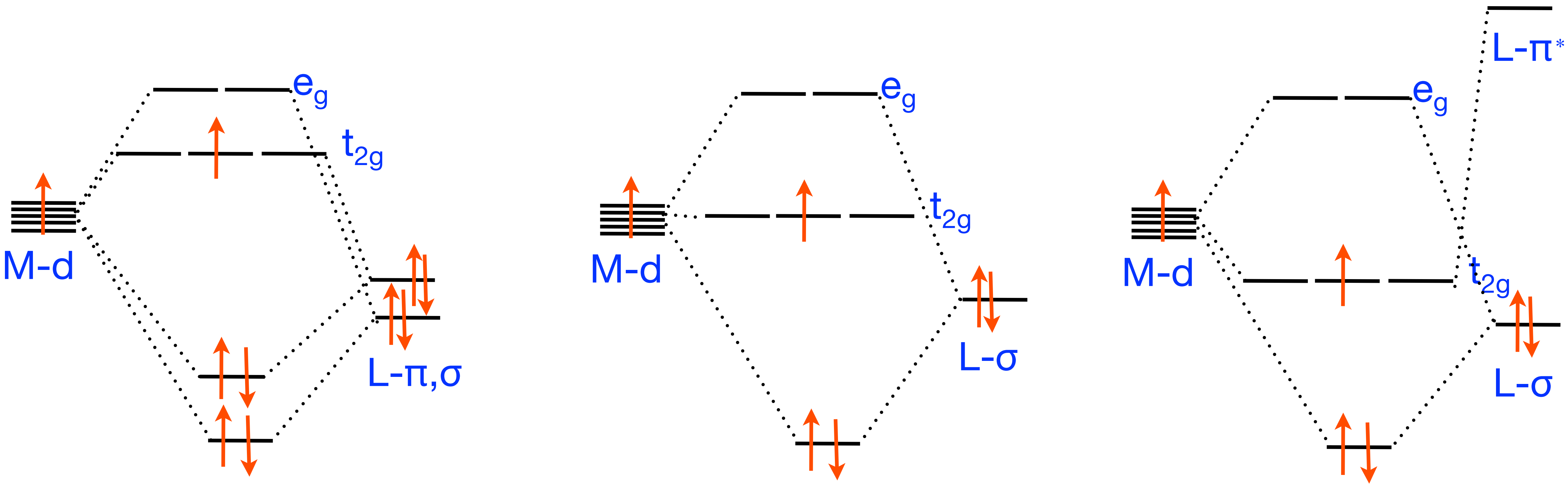
Δ SMALL

Δ LARGE

π-DONOR

π-‘NEUTRAL‘

π-ACCEPTOR



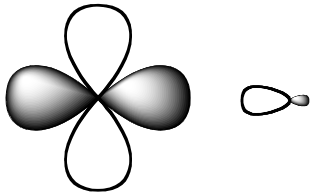
Covalency, Oxidation States and MO Theory

What is Covalency?

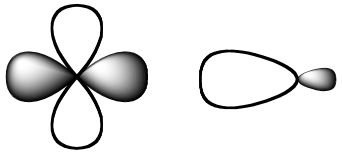
- **Covalency refers to the ability of metal and ligand to share electrons** („soft“ concept with no rigorous definition)
- Operationally, covalency can be defined in MO theory from the mixing coefficients of metal- and ligand orbitals

$$\psi_i \cong \alpha_i \left|M_i\right\rangle - \sqrt{1-\alpha_i^2}\left|L_i\right\rangle$$ (overlap neglected)

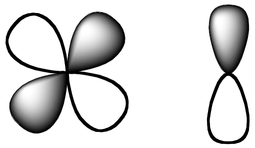
- The value $1-\alpha^2$ can be referred to as „the covalency“ of the specific metal ligand bond. It is the probability of finding the electron that occupies ψ_i at the ligand
  - *The maximal covalency is 0.5, e.g. complete electron sharing*
  - *The covalency might be different in* σ*- and π-bonds (e.g. it is anisotropic)*
  - *In* σ*-donor and π-donor bonds these are antibonding. The bonding counterparts are occupied and lower in energy*
  - *In π-acceptor bonds these orbitals are bonding. The antibonding counterparts are higher in energy and unoccupied*



Typical Ionic bond; hard ligands
Werner type complexes
$\alpha^2=0.8-0.9$



Typical covalent bond
Organometallics; soft ligands
$\alpha^2=0.5-0.8$

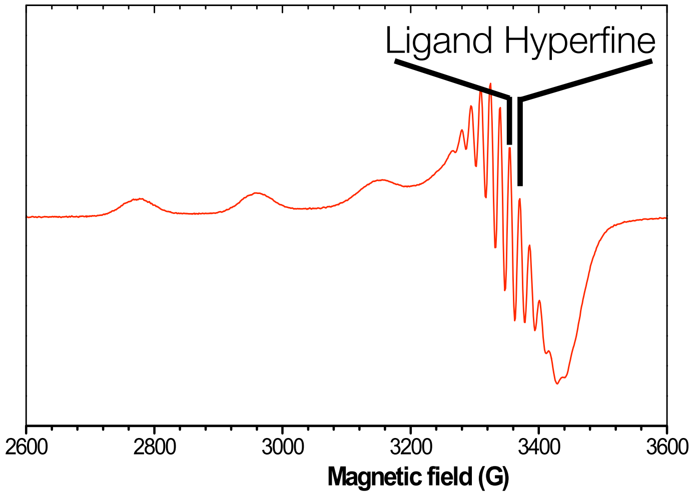


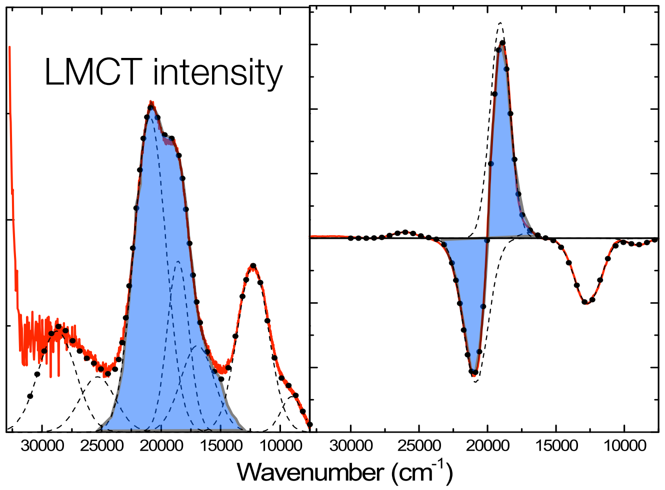
Typical π-backbond
Heterocyclic aromatic ligands ; CO, NO^+...
$\alpha^2=0.7-0.95$

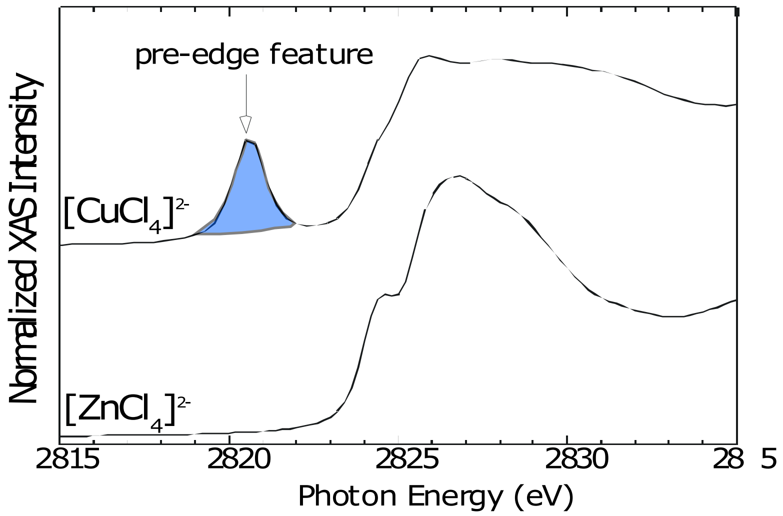
„Measurements“ of Covalency?

★ Can covalency be measured?

- ➡ Rigorously speaking: **NO**! Orbitals are not observables!
- ➡ On a practical level: (more or less) **YES**. Covalency can be correlated with a number of spectroscopic properties
    - **EPR metal- and ligand hyperfine couplings**
    - **Ligand K-edge intensities**
    - **Ligand-to-metal charge transfer intensities**
- ➡ As all of this is „semi-qualitiative“ you can not expect numbers that come out of such an analysis to agree perfectly well. If they do this means that you have probably been good at fudging!







ALL proportional to $1-\alpha^2$

Covalency and Molecular Properties

Metal-Ligand Covalency Affects Many Chemical Properties!

1. The **stability** of a complex increases with metal-ligand covalency
2. Covalency reflects charge-donation. The larger the charge donation the more negative the **redox potential**
3. Covalency may affect ‚**electron transfer pathways**‘
4. Covalency taken to the extreme might mean that ligands are activated for **radical chemistry**
5. ...

Assignment of Oxidation States

- ★ We can take the analysis of covalency one step further in order to „recover“ the concept of an oxidation state from our calculations.
- ★ This is even more approximate since it must be based on a subjective criterion
- ★ Proposed procedure:
  - Analyze the **occupied orbitals** of the compound and determine the orbital covalencies
  - Orbitals that are centered more than, say, **70-80%** on the metal are counted as pure **metal orbitals**
  - **Count the number of electrons in such metal based orbitals**. This gives you the **d^N configuration**
  - The **local spin state** on the metal follows from the singly occupied metal-based orbitals
  - *This fails, if there are some orbitals that are heavily shared with the ligands (metal character < 70%). In this case the oxidation state is ambiguous. Typically, experimens are ambiguous as well in these cases*.

➡ **BUT: Make sure that your calculated electronic structure makes sense by correlating with spectroscopy! Spectroscopy is the experimental way to study electronic structure!**

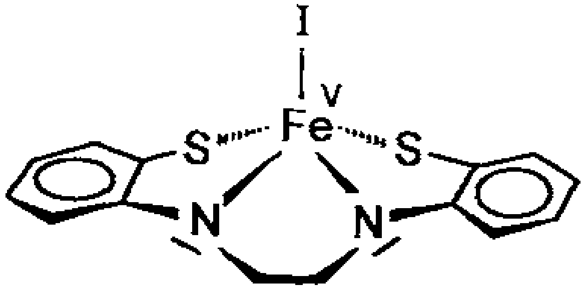
Physical versus Formal Oxidation States

The **formal oxidation state** of a metal ion in a complex is the d^N configuration that arises upon dissociating all ligands in their closed shell „standard“ states taking into account the total charge of the complex

The **physical oxidation state** of a metal ion in a complex is the d^N configuration that arises from an analysis of its electronic structure by means of spectroscopic measurements and molecular orbital calculations

Chaudhuri, P.; Verani, C.N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.,* **2001**, 123, 2213 *„The Art of Establishing Physical Oxidation States in Transition-Metal Complexes Containing Radical Ligands* **“.** However, The concept goes back to CK Jörgensen

- ★ The two often coincide but may well be different! In the example before, the formal oxidation state is Ni(IV) but the physical oxidation state is Ni(II)



2

This complex has first been described by its formal oxidation state of Fe(V) but has a physical oxidation of Fe(III)

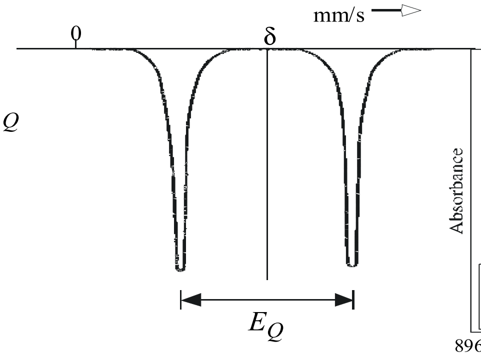
Chlopek, C. *et al. Chem. Eur. J.* **2007**, 13, 8390

Absorption Spectroscopy and Bonding

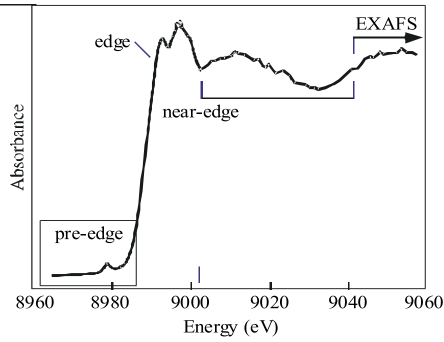
Energy Scale of Spectroscopy

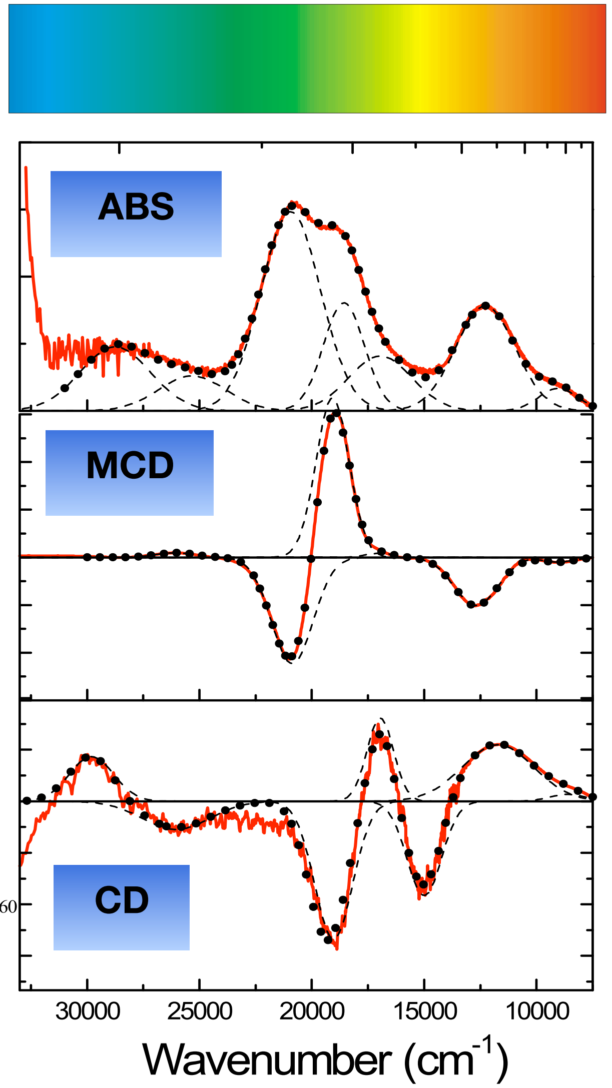
	Gamma	X-Ray	UV/vis	Infrared	Microwave	Radiowave
eV	14000	8000 2000	4 - 1	0.1-0.01	10^{-4} -10^{-5}	10^{-6} -10^{-7}

Möss-bauer

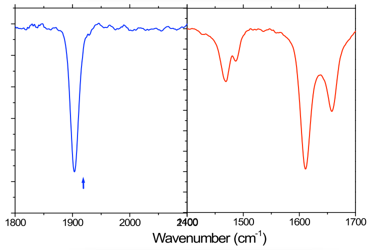


XAS EXAFS

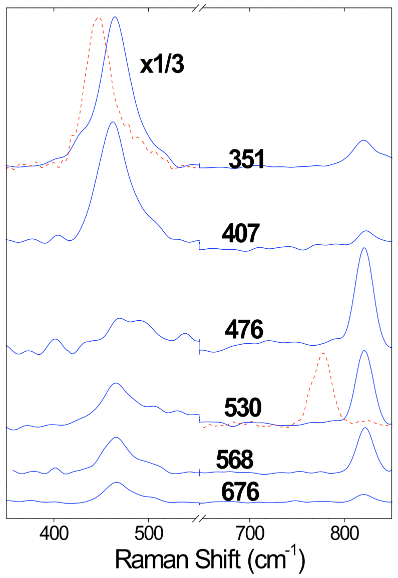




IR

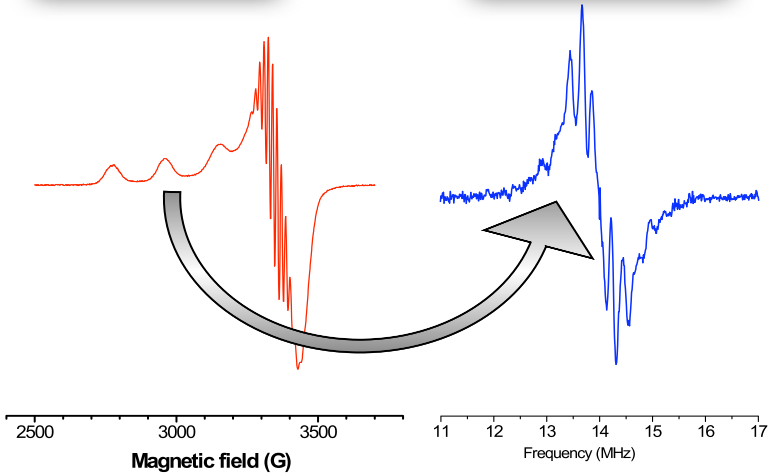


Raman



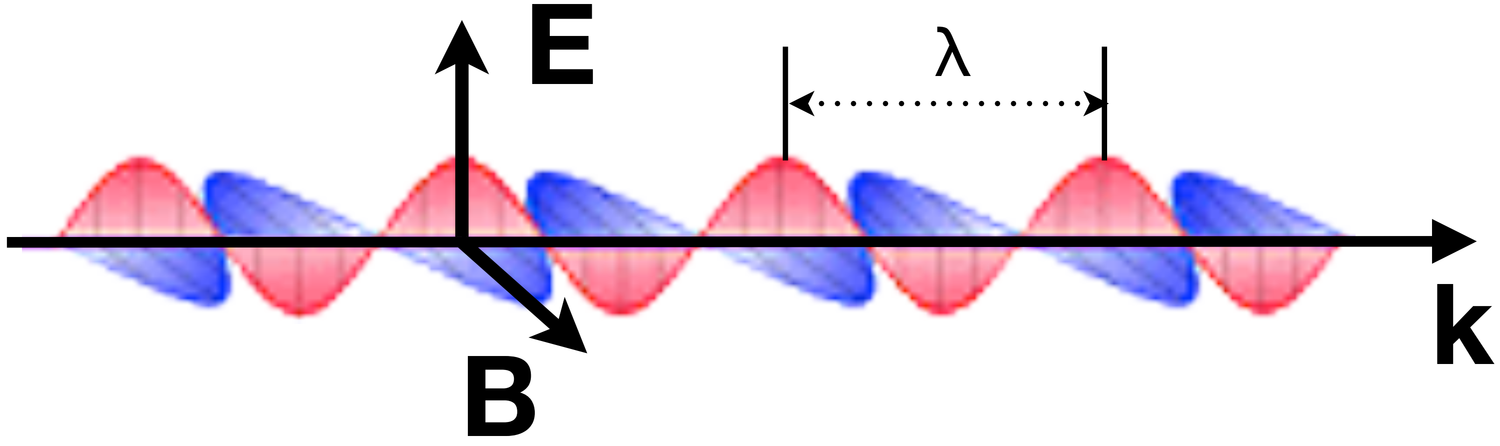
EPR

ENDOR



NMR

Anatomy of a Light Wave



- Wavelength: λ
- Frequency: $\omega=2\pi c/\lambda$
- Electric Field: **E**
- Magnetic Field: **B**
- Propagation Direction: **e**
- Wave vector **k** ($|k|= 2\pi/\lambda$)
- Momentum: $\mathbf{p}=h/2\pi\mathbf{k}$
- Angular Momentum: $\pm h/2\pi$

- Linear Polarization $\frac{1}{\sqrt{2}}\left(\left|\mathbf{k}+\right\rangle+\left|\mathbf{k}-\right\rangle\right)$

- Circular Polarization (RCP, LCP) $\left|\mathbf{k}+\right\rangle \;\; or \;\; \left|\mathbf{k}-\right\rangle$

Light Matter Interaction

From Physics: $\left\langle \Psi_{initial} \mid \hat{H}_1 \mid \Psi_{final} \right\rangle = \frac{e}{2m_e c} A_0 \left\langle \Psi_{initial} \mid \sum_j \left(\vec{e}\vec{p}_j \right) e^{i\vec{k}\vec{r}_j} + ie^{i\vec{k}\vec{r}_j} \hat{s}_i \left[\vec{k} \times \vec{e} \right] \mid \Psi_{final} \right\rangle$

$$= Electric - Dipole + Electric - Quadrupole + Magnetic\,Dipole$$

$$+ \ldots$$

Cross-Section $\sigma(E) = 2\pi \frac{\omega}{I} \left| \left\langle \Psi_{initial} \mid \hat{H}_1 \mid \Psi_{final} \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$

Oscillator Strength $f_{osc} = \frac{m_e c}{2\pi^2 e_2 \hbar} \int \sigma(E)\, dE$

I= intensity of the light beam
c= speed of light
e= elementary charge
m_e= electron mass
r_i=position of electron i
l_i=angular momentum of electron i
s_i= spin angular momentum of electron i

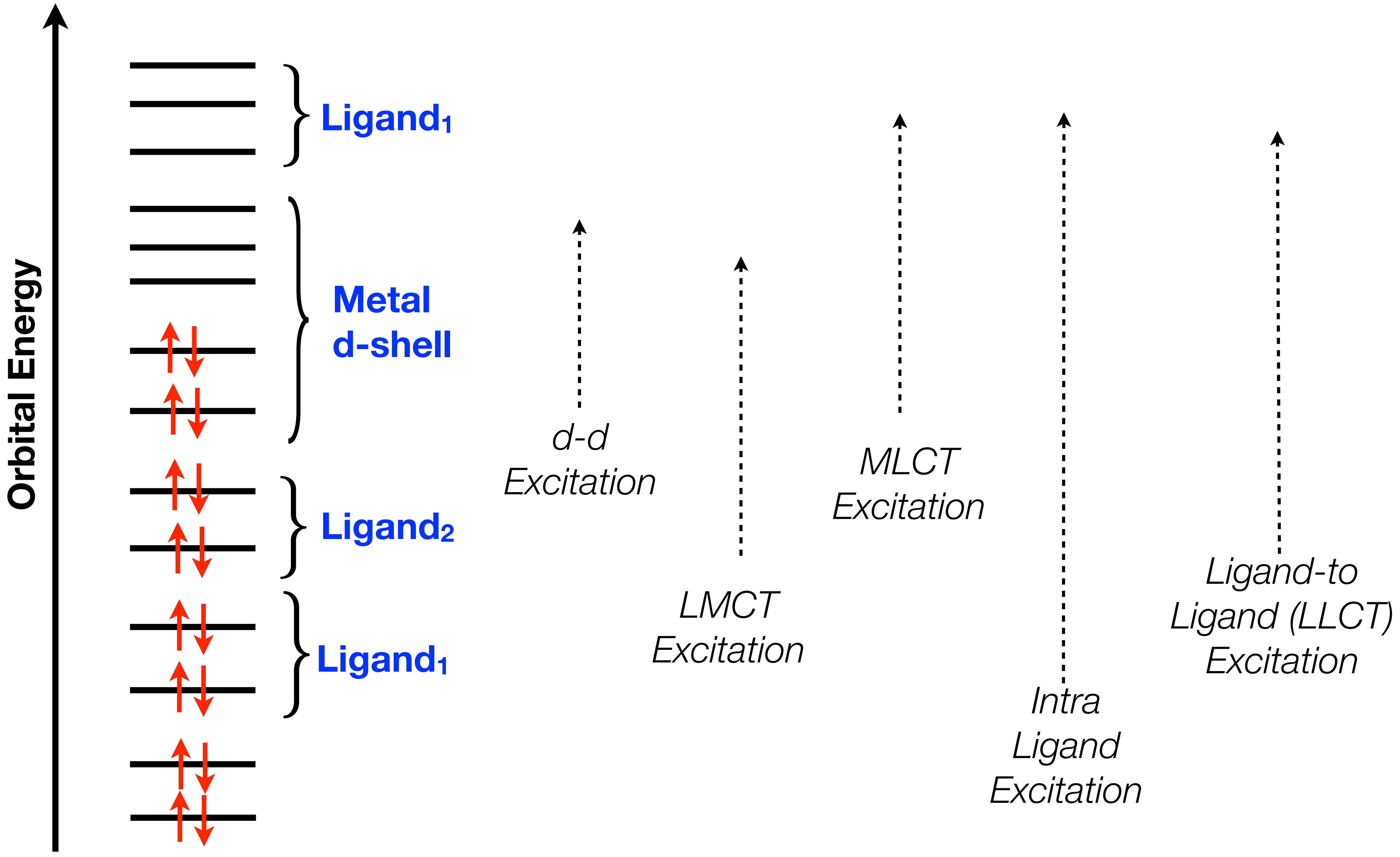
In atomic units for a randomly oriented sample

Electric Dipole $\vec{\mu}_{ED,a} = \sum_A Z_A \vec{R}_{A,a} - \sum_i \vec{r}_{i,a}$ $f_{ED} = \frac{2}{3}(E_f - E_i) \sum_{a=x,y,z} \left| \left\langle \Psi_i \mid \vec{\mu}_{ED,a} \mid \Psi_f \right\rangle \right|^2$

Electric Quadrupole $\vec{\mu}_{EQ,ab} = \sum_i (\vec{r}_{i,a} \vec{r}_{i,b} - \frac{1}{3} r_i^2 \delta_{ab})$ $f_{EQ} = \frac{1}{20} \alpha^2 (E_f - E_i)^3 \sum_{ab=x,y,z} \left| \left\langle \Psi_i \mid \vec{\mu}_{EQ,ab} \mid \Psi_f \right\rangle \right|^2$

Magnetic Dipole $\vec{\mu}_{MD,a} = \frac{1}{2} \sum_i (\vec{l}_i + 2\vec{s}_i)_a$ $f_{MD} = \frac{2}{3} \alpha^2 (E_f - E_i) \sum_{a=x,y,z} \left| \left\langle \Psi_i \mid \vec{\mu}_{MD,a} \mid \Psi_f \right\rangle \right|^2$

Types of Transitions in Transition Metal Complexes



Orbital Energy

Ligand$_1$

Metal d-shell

Ligand$_2$

Ligand$_1$

d-d Excitation

LMCT Excitation

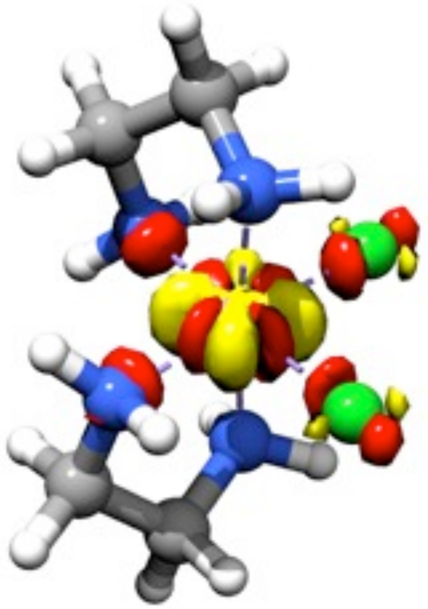
MLCT Excitation

Intra Ligand Excitation

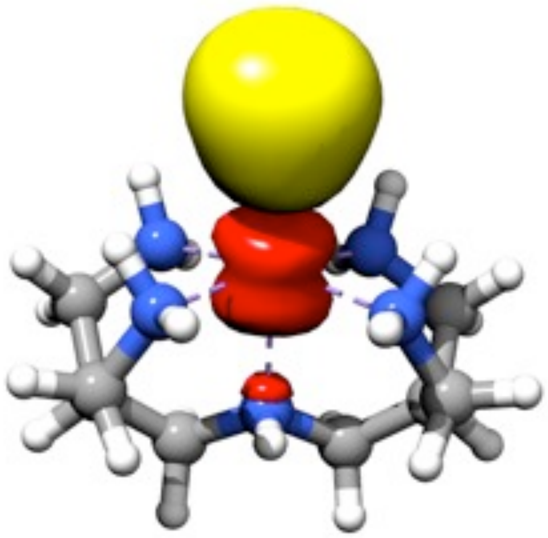
Ligand-to Ligand (LLCT) Excitation

Electronic Difference Densities

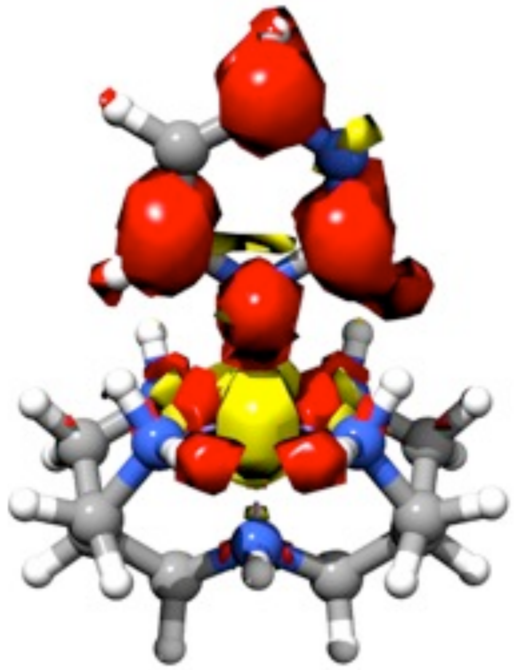
d-d Transition



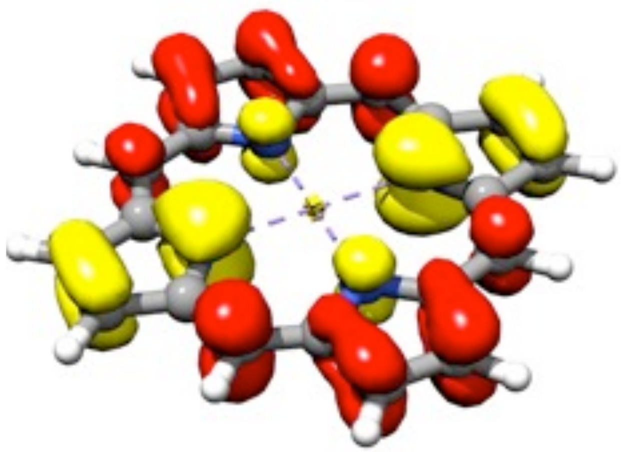
LMCT Transition



MLCT Transition



$\pi \rightarrow \pi^*$ Transition



Red = Electron Gain　*Yellow= Electron Loss*

Spectroscopic Selection Rules

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

$$\left|\left\langle \Psi_{initial} \mid \vec{\mu} \mid \Psi_{final} \right\rangle\right|^{2}$$

- ★ **Spin-Selection rule:**
  - ➡ **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
- ★ **Spatial-Selection rule:**
  - ➡ **The direct product of Ψ_i, Ψ_f, and μ 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

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

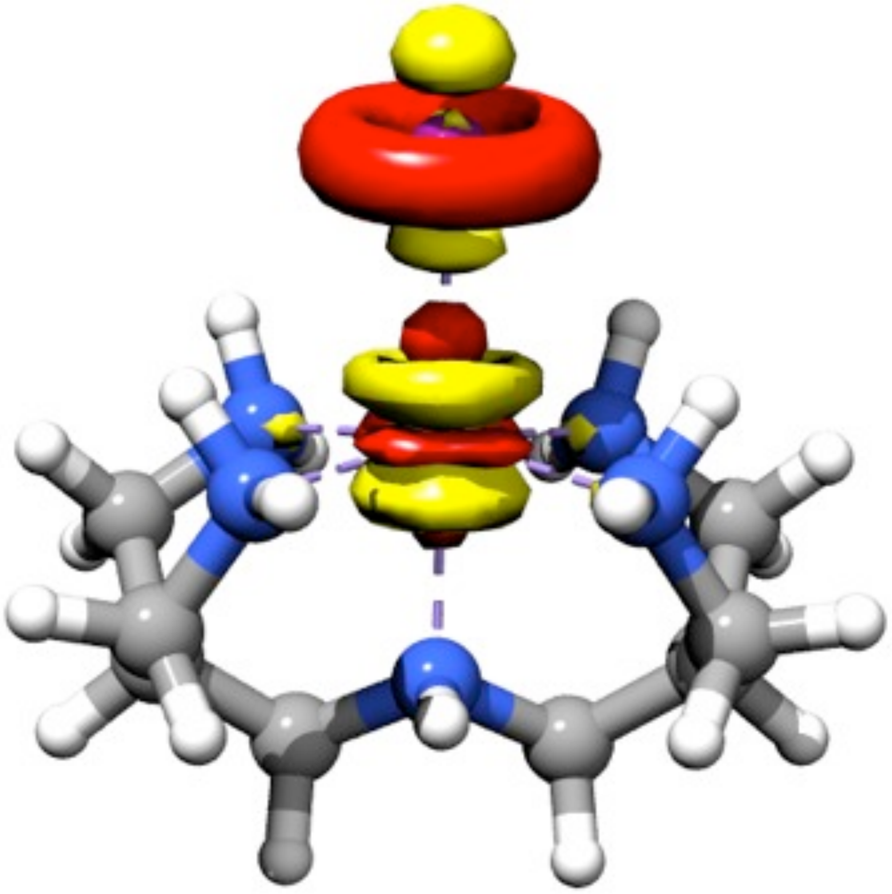
Magnetic Dipole: Transforms as R_x,R_y, R_z

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

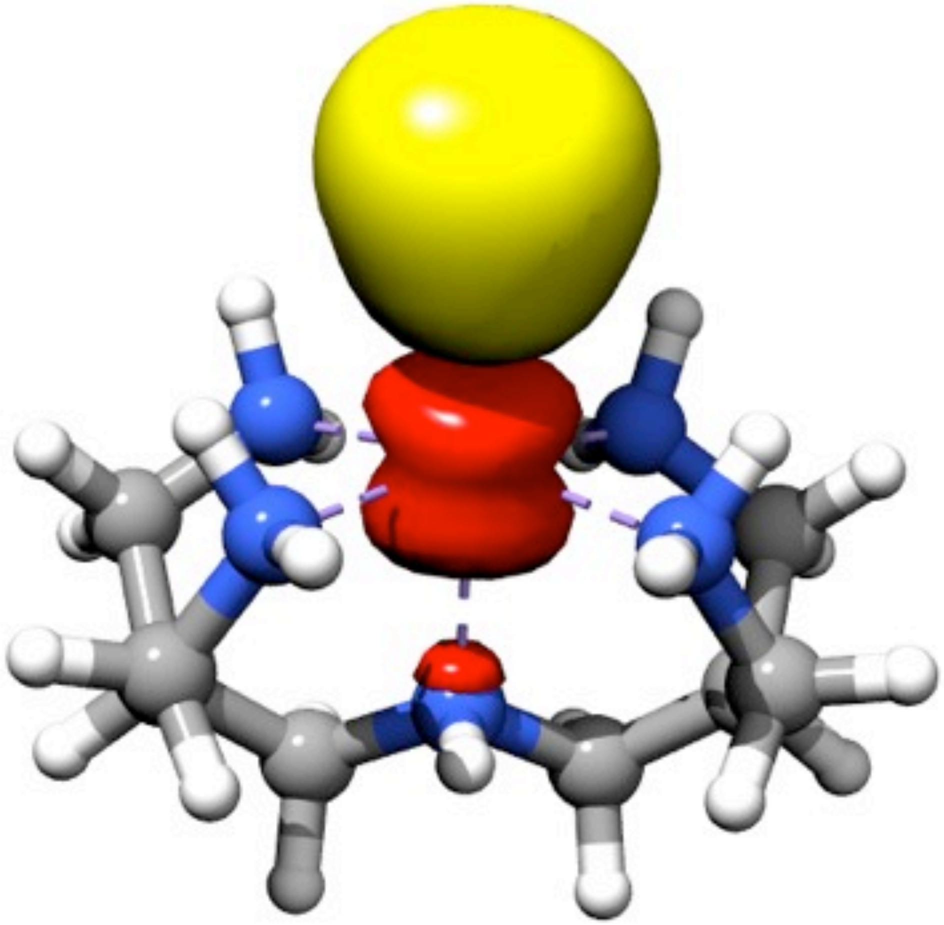
$\}$ If there is a center of inversion only g→g or u→u transitions are allowed

Transition Density versus Difference Densities

Transition Density



Difference Density

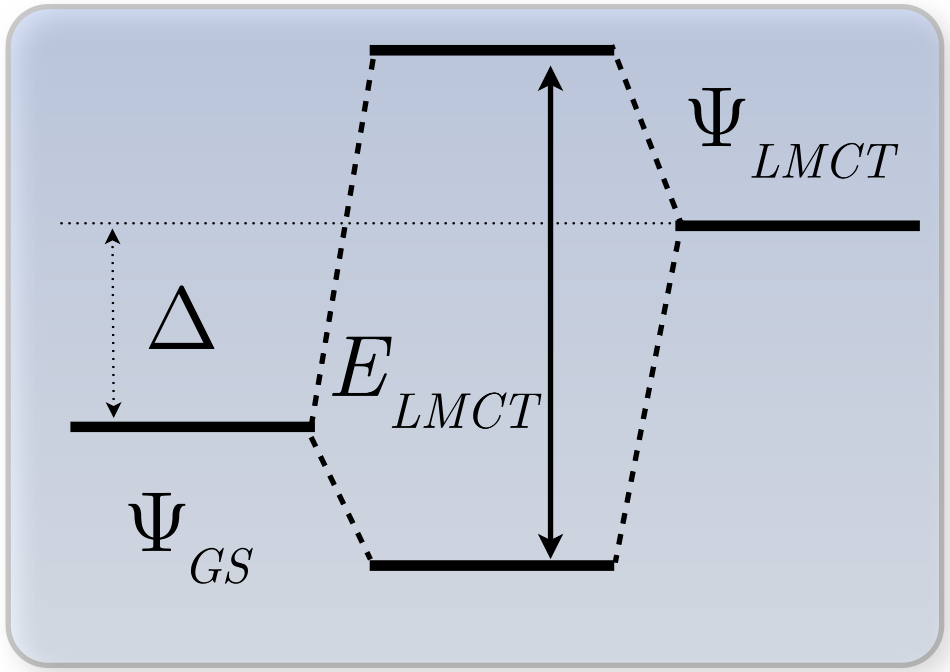


Ligand-to-Metal Charge Transfer Spectra

$\Psi_{GS} = \left|\psi_L \bar{\psi}_L \psi_M\right|$ $\Psi_{LMCT} = \left|\psi_L \bar{\psi}_M \psi_M\right|$

Energy Difference $\Delta = I_L - A_M$

Interaction $\beta = F_{LM} \propto S_{LM}$



Transition Energies:

- ★ Low if ligand is easy to ionize
- ★ Low if metal is strongly oxidizing (high oxidation state)
- ★ Increases for large ML overlap
- ★ Overlap increases for highly polarizable (soft) ligands

Transition Intensities:

- ★ High for large covalent binding (beta=large, Delta=small)
- ★ Maximal for equal mixing (Delta=0)
- ★ Transitions are always most intense for bonding to antibonding excitations (polarized along the M-L bond)

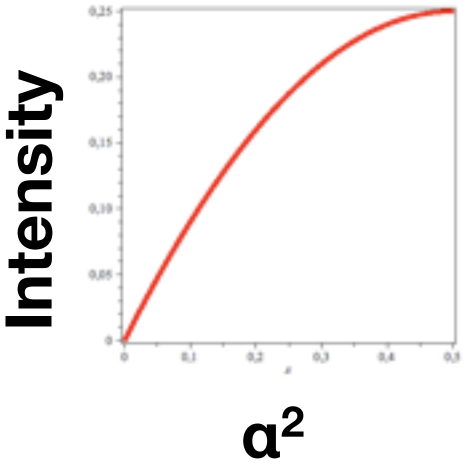
Estimating Covalency

From the little valence bond model, we can obtain the two eigenstates as:

$$\left|\Psi'_{GS}\right\rangle = \alpha\left|\Psi_{GS}\right\rangle + \sqrt{1-\alpha^2}\left|\Psi_{LMCT}\right\rangle \qquad \left|\Psi'_{LMCT}\right\rangle = \sqrt{1-\alpha^2}\left|\Psi_{GS}\right\rangle - \alpha\left|\Psi_{LMCT}\right\rangle$$

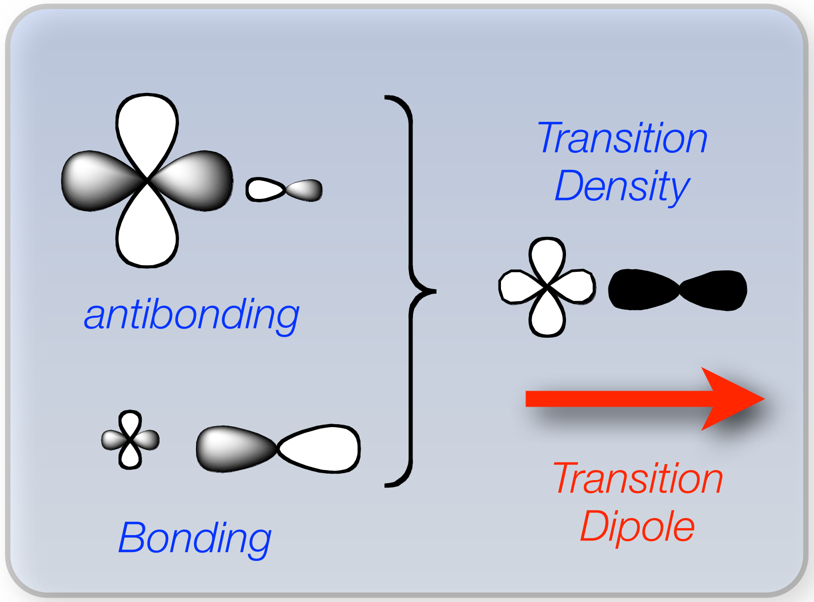
The Transition Energy: $E_{LMCT} = \Delta + 2\frac{\beta^2}{\Delta} - 2\frac{\beta^4}{\Delta^3} + O(\beta^6)$

The Transition Intensity: $\left|\left\langle \Psi'_{GS} \mid \vec{\mu} \mid \Psi'_{LMCT} \right\rangle\right|^2 \equiv D^2_{ML} \approx \alpha^2(1-\alpha^2)R^2_{ML} \approx \frac{\beta^2}{\Delta^2}R^2_{ML}$



This can be turned around to obtain the model parameters from the measurable quantities: ***R*_ML, *D*_ML** and ***E*_LMCT**

$$\beta = \pm D_{ML}\frac{R_{ML}}{R^2_{ML} + 2D^2_{ML}}E_{LMCT} \qquad \Delta = \frac{R^2_{ML}}{R^2_{ML} + 2D^2_{ML}}E_{LMCT}$$



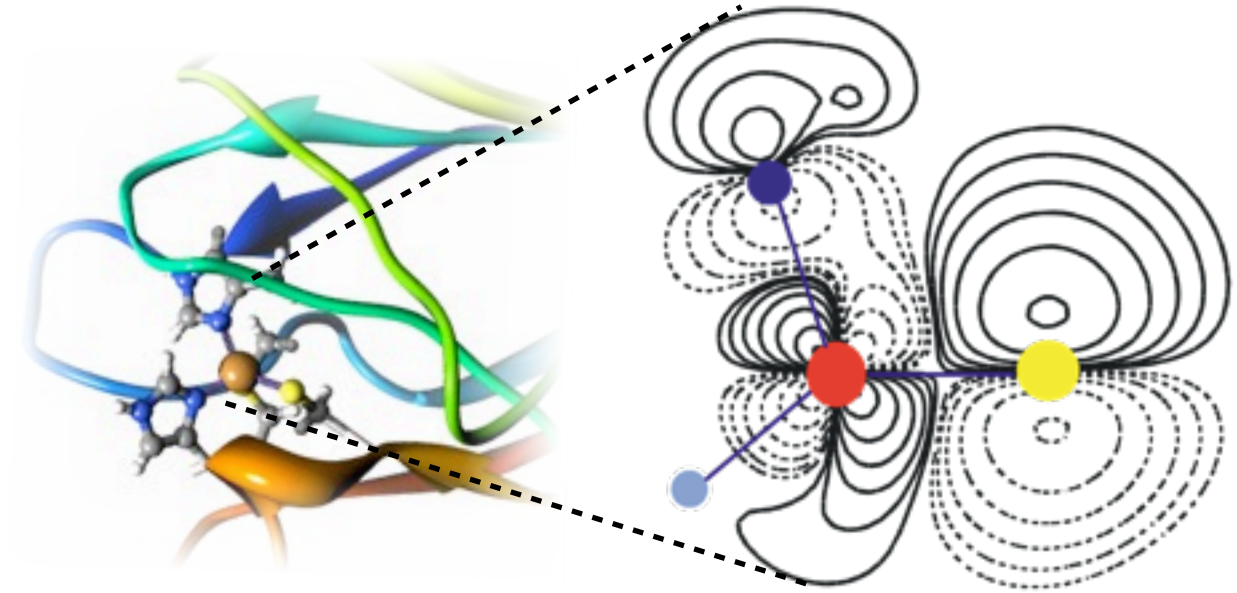
antibonding

Bonding

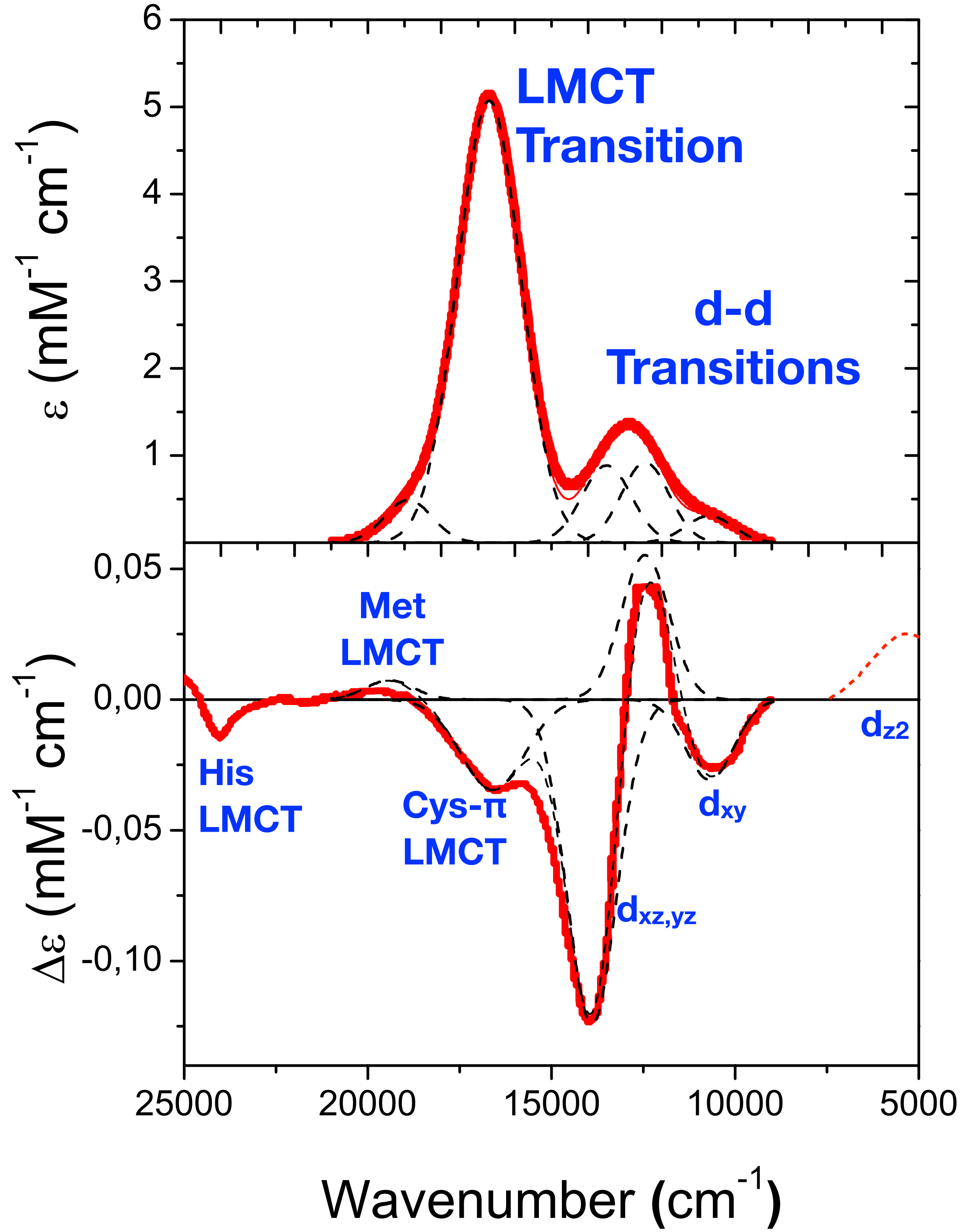
Transition Density

Transition Dipole

LMCT, Covalency and Electron Transfer Pathways



$\mathbf{Cu^{II}(N_{His})_2(^{-}S_{Cys})(S_{Met})}$



Exp.: Gewirth, A.A., Solomon, E.I. *JACS*, **1988**, 110, 3811.

Comparison of LF and MO Theory

LF-Theory

- Looks only at the metal
- Assumes a metal with an „electrostatic **perturbation**“ by pointcharge ligands
- Assumes that the metal orbitals are **pure d-orbitals**
- Can only explain **parts** of the spectroscopic properties
- Is very **simple**
- Is a **MODEL**

MO-Theory

- Looks at the **metal AND the ligands**
- Takes **detailed account** of bonding (σ-versus π–Bonding)
- Acknowledges metal-ligand **orbital mixing**
- Is a basis for the interpretation of **ALL** spectra (and more)
- Is quite **complex**
- Can be made **QUANTITATIVE**

Take Home Messages

1. LF and MO Theories Bring Order to Experimental Results and Define a Language
2. Optical Properties (d-d transitions,CT Transitions)
3. Magnetic Properties (Susceptibility, EPR)
4. Thermodynamic Properties (Stabilities)
5. Kinetic Properties (Ligand Exchange Reactions)
6. Bonding (Covalency, Sigma vs Pi bonding, Backbonding)
7. Defines Parameters (Δ,B) to Semi-Quantitatively Treat these Effects
8. MO Theory can Quantitatively Model Transition Metal Complexes and Active Sites to Predict Properties with good Accuracy

The end