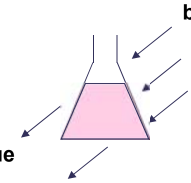
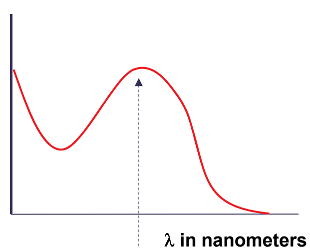
Electronic Spectroscopy
of
Transition Metal Complexes

Absorption of Light

$[Ti(OH_2)_6]^{3+}$ = d^1 ion, octahedra

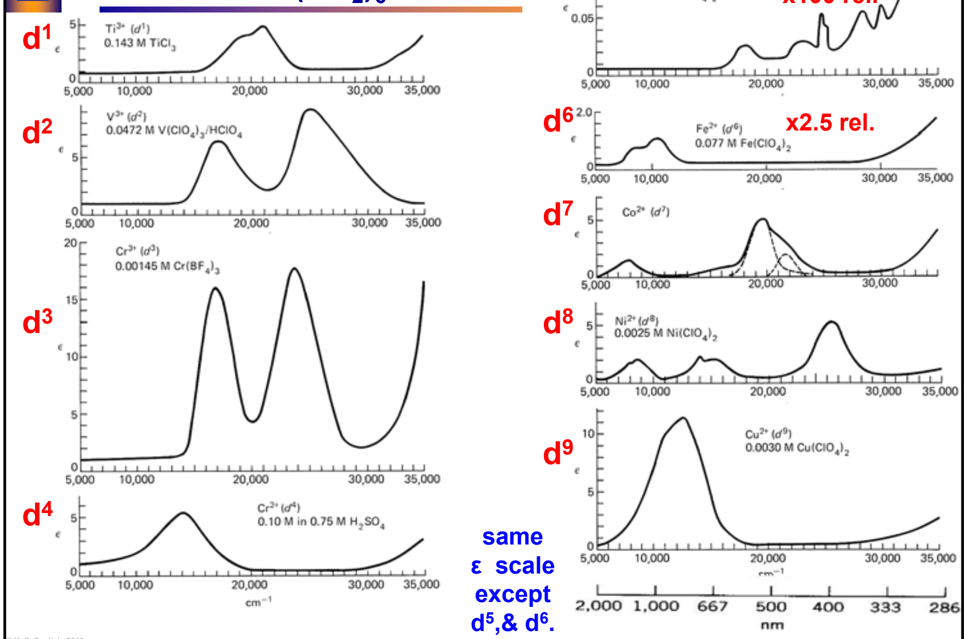




λ_{max} = 510 nm

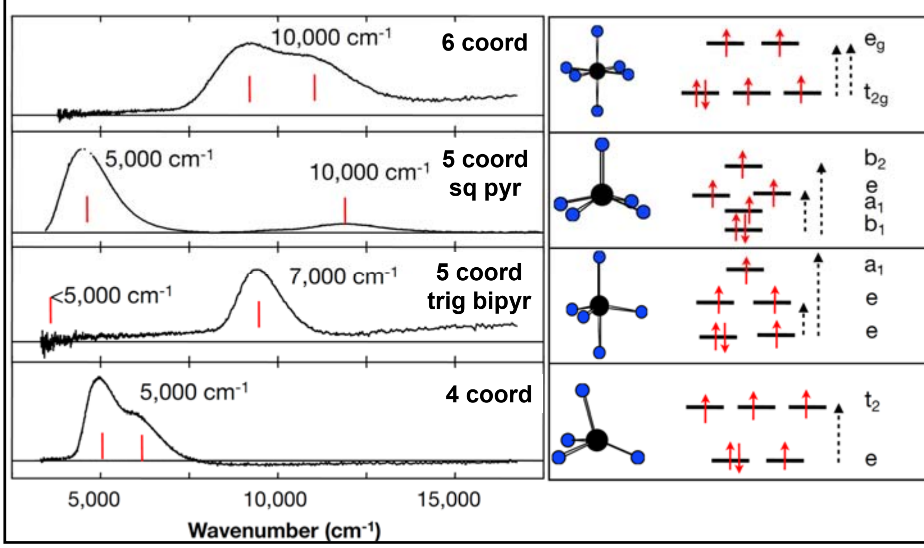
This complex appears light purple because it absorbs green light.

d-d Transitions: $d^1 - d^9$ of $M(OH_2)_6^{n+}$



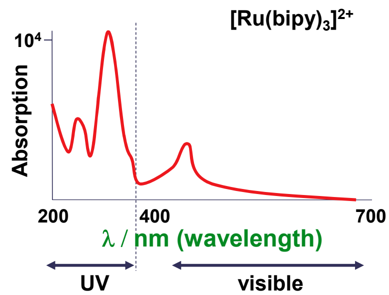
d-d Transitions vs. Coord. Geometry

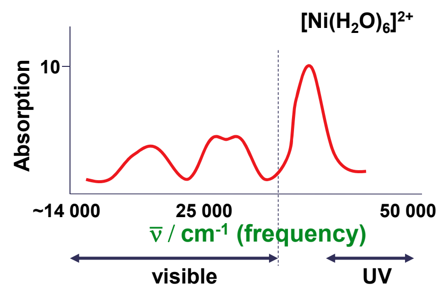
High Spin Fe^{II}, d^6



What is electronic spectroscopy?

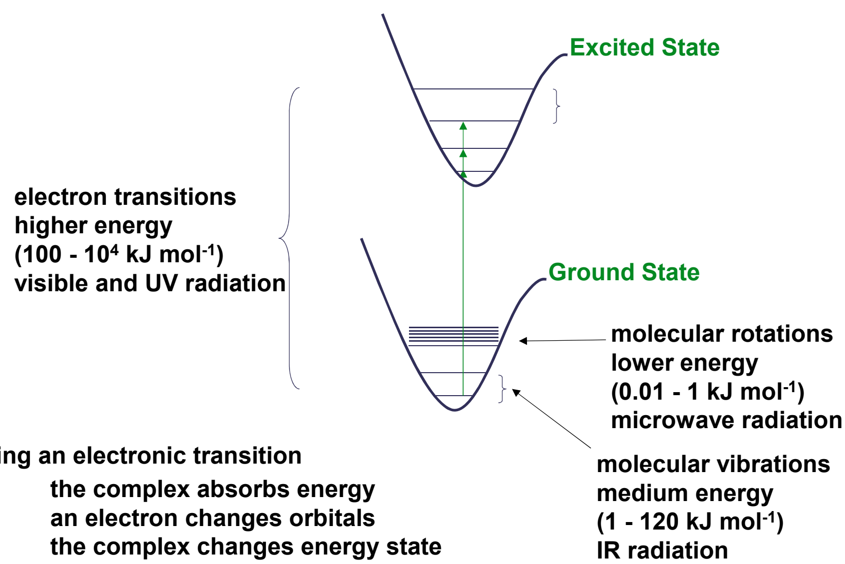
Absorption of radiation leading to electronic transitions within a metal complex.





UV	=	higher energy transitions:	between ligand orbitals
visible	=	lower energy transitions:	between d-orbitals of transition metals or between metal and ligand orbitals

Energy of Transitions



During an electronic transition
- the complex absorbs energy
- an electron changes orbitals
- the complex changes energy state
- the structure changes slightly

Characteristics of Absorption Spectra

1. ***Number of peaks***

   This depends on the electron configuration of the metal center.

2. ***Energy: what wavelength or frequency***

   Depends on the ligand field splitting parameter, Δ_{oct} or Δ_{tet}, and on the degree of inter-electron repulsion.

3. ***Intensity***

   This depends on the "allowedness" of the transitions, which is described by two "selection rules."

***Measurement* of Absorption Spectra: Beer's Law**

$$A = \varepsilon(l)(C)$$

ε is the extinction coefficient, measure of absorption cross-section
l, is semi-obvious - the pathlength of the light
C, also semi-obvious - the concentration of the sample

Extinction Coefficients

ε is the extinction coefficient, i.e., cross-section for photons has units: usually in M^{-1} cm^{-1}

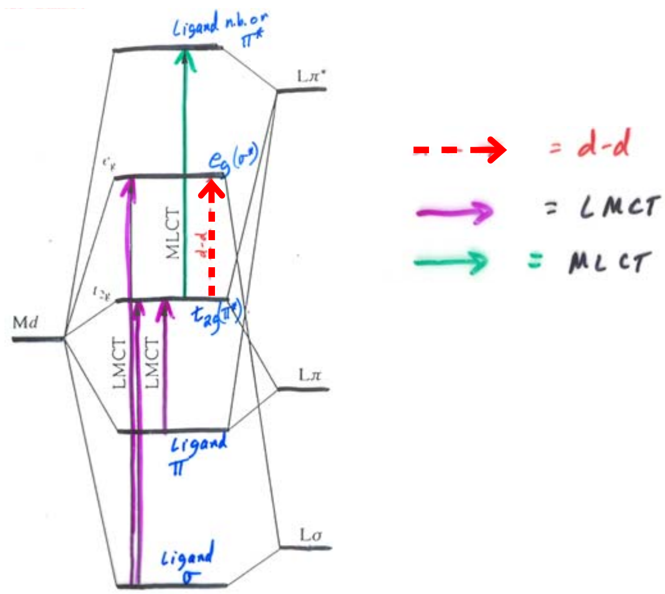
Large ε: allowed Transition

Small ε: partiallly allowed (spin or symmetry forbidden)

Very small ε: "forbidden" (both spin and symmetry forbidden)

ε >1000	**Charge transfer: spin and symmetry allowed**
1000 – 10	**Spin Allowed– d-d transitions in non-O_h (tetrahedral…)**
10 – 1	**Spin allowed, symmetry forbidden: O_h**
<1	**Spin Forbidden, Symmetry Forbidden**

d-d and Charge Transfer Transitions



Types of Electronic Transitions in TM Complexes

d-d:
usually in the visible region
relatively weak, $\varepsilon \sim 1 - 100$ if spin allowed
< 0.1 if spin forbidden
energy varies with Δ_o (or Δ_t)

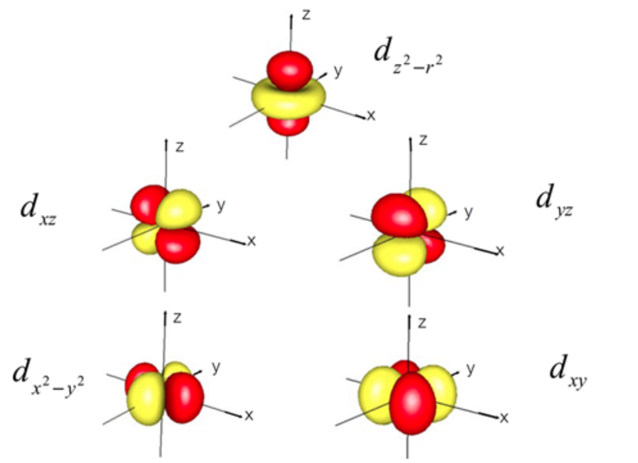
LMCT:
Ligand to Metal Charge Transfer
σ_L or $\pi_L \xrightarrow{h\upsilon} d^*$
very intense, generally in UV or near UV

MLCT:
Metal to Ligand Charge Transfer
$d^* \xrightarrow{h\upsilon} \pi_L$
very intense ($\varepsilon \sim 100 - 10{,}000$)
needs π-acceptor Ligand (CO, CN^-, …

LL:
Ligand to Ligand
$\pi_L \xrightarrow{h\upsilon} \pi_L^*$
very intense ($\varepsilon \sim 100 - 10{,}000$)

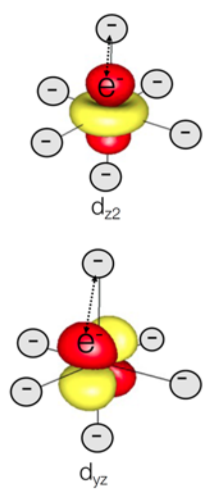
Rydberg:
localized MO $\xrightarrow{h\upsilon}$ high energy,
highly delocalized, deep UV

Ligand Field Splitting of d-orbitals



Know these by heart!

Ligand Field Splitting of d-orbitals



The Negatively Charged Ligands Produce an Electric Field+Potential

⇩

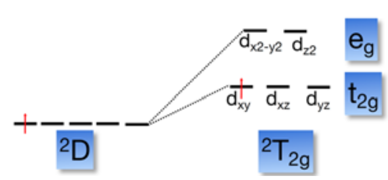
The Field Interacts with the d-Electrons on the Metal (Repulsion)

⇩

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



d Orbitals in a Ligand Field

- There are 5 d-orbitals; they have different shapes (and you'd better know them!).
- When you put ligands around the metal ion, the ligands are Lewis bases, they donate an electron pair towards the metal.
- That RAISES THE ENERGY OF THE d-ORBITALS!
- The d-orbitals are anti-bonding or at best non-bonding.
- The stability of the bonding comes from the ligand orbitals being stabilized by delocalization onto the metal ion (by mixing into the d-orbitals).
- The d-orbitals aren't all the same in how much they feel the ligand lone pairs.

d Orbitals in a Octahedral Ligand Field

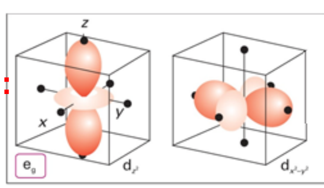
Let's consider d-orbitals in an octahedral complex:
i.e., an octahedral "Ligand Field".

The 6 ligands are put on the x, y, z axes (black dots below)

Two d-orbitals are pointing right at the ligands (anti-bonding).

Three d-orbitals are pointing in-between ligands (nonbonding).

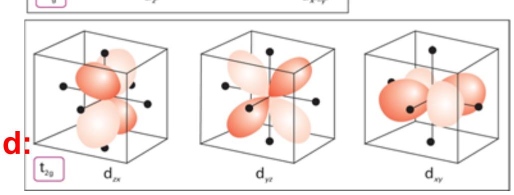
Antibonding d:



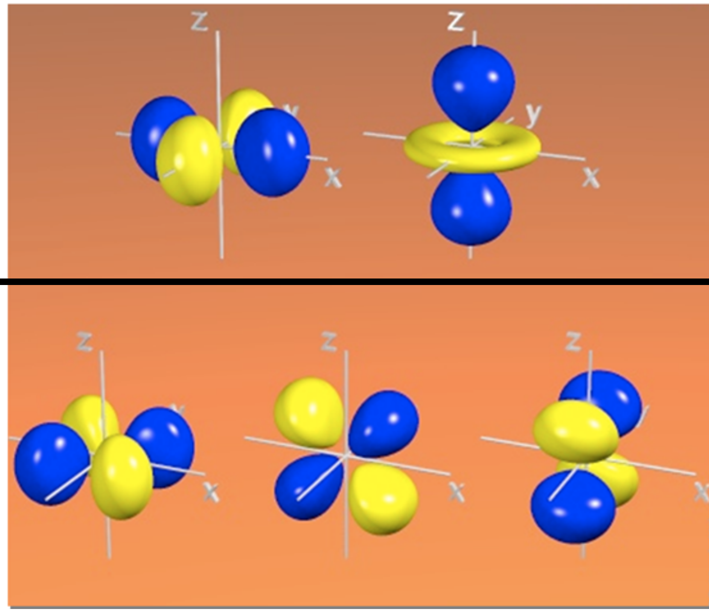
How do we know e_g or t_{2g}?

Character table!

Nonbonding d:



Two Kinds of d Orbitals in Octahedral Field



e_g — Pointed at Ligands.

t_{2g} — Pointed between Ligands.

d orbitals in O_h

d orbitals: z^2, x^2-y^2, xy, xz, yz

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$\boxed{x^2+y^2+z^2}$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Note: There are only 5 d-orbitals,
but there are 6 quadratics!

No d-orbital is ever $x^2 + y^2 + z^2$

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

d Orbitals in a Tetrahedral Ligand Field

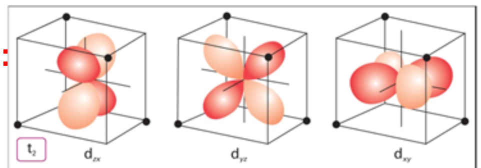
Let's now consider d-orbitals in a tetrahedral complex:
i.e., an tetrahedral "Ligand Field".

The 4 ligands are put on corners of cube (black dots below)

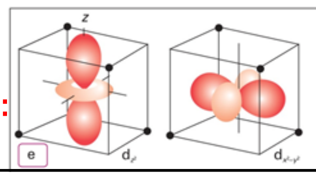
Three d-orbitals are pointing right at the ligands (anti-bonding).

Two d-orbitals are pointing in-between ligands (nonbonding).

Antibonding d:



Nonbonding d:



How do we know t_2 or e?

Character table!

d Orbitals in T_d

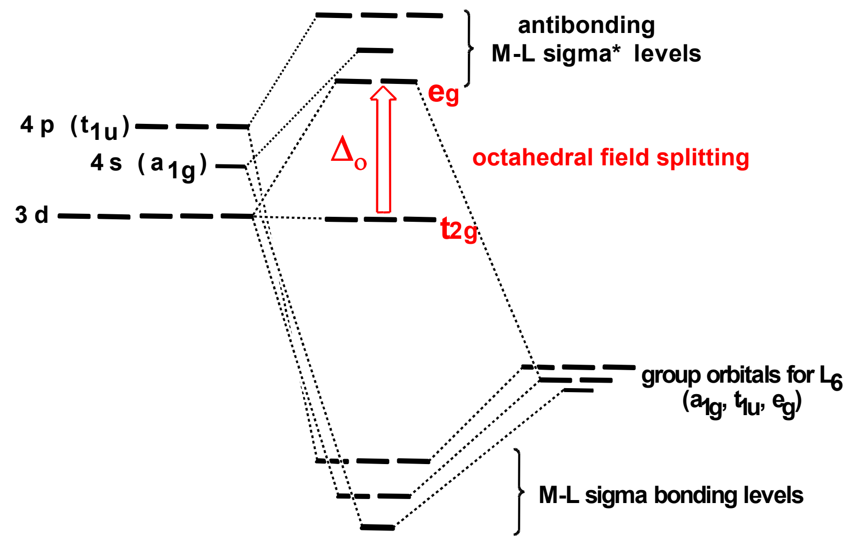
d orbitals: z^2, x^2-y^2, xy, xz, yz

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

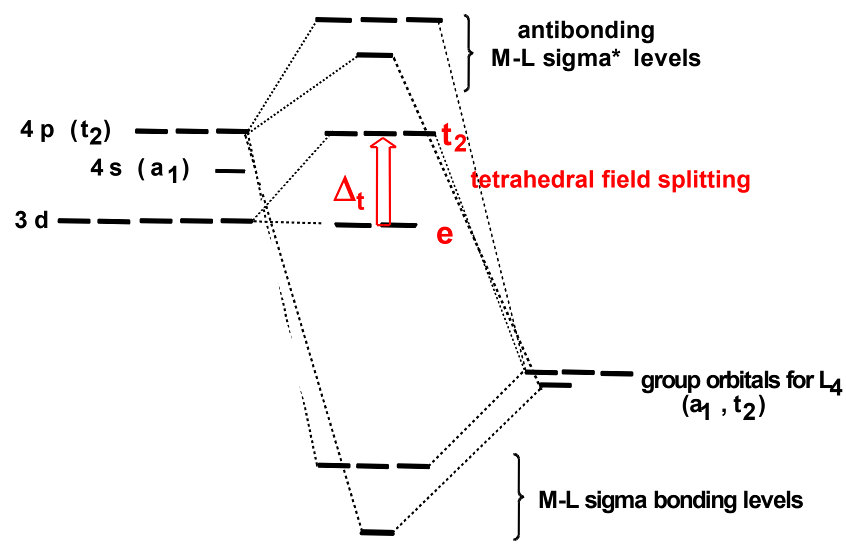
Why no subscript "g"?

No d-orbital is ever $x^2 + y^2 + z^2$
$2z^2$-x^2-y^2 : dz^2

The Octahedral *Ligand* Field M.O.s



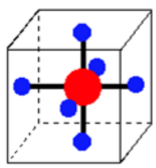
The Tetrahedral *Ligand* Field M.O.s

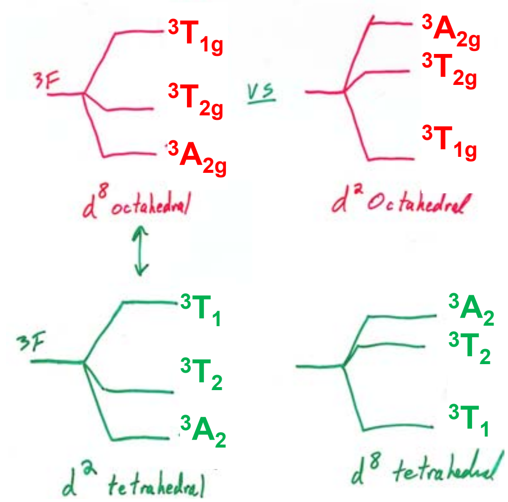


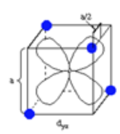
The Tetrahedral *Ligand* Field M.O.s

$\Delta_{tet} \sim 4/9\ \Delta_{oct} = 4/9\ \Delta_o$

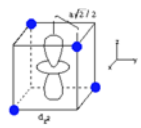
smaller splitting, therefore usually high spin.







The d_{yz} orbital in tetrahedral coordination. Electrons in this orbital can approach within a distance of a/2 to ligand electrons.

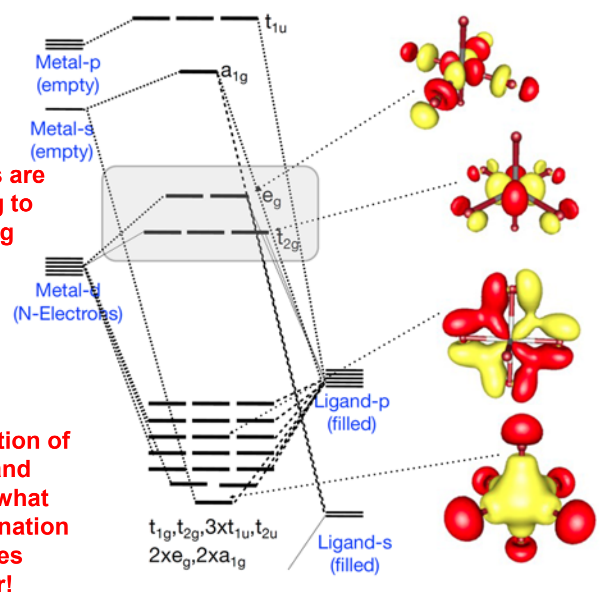


The d_{z^2} orbital in tetrahedral coordination: electrons in d_{z^2} are further from the ligands than electrons in d_{yz}.

"Real" MOs of Coordination Complexes

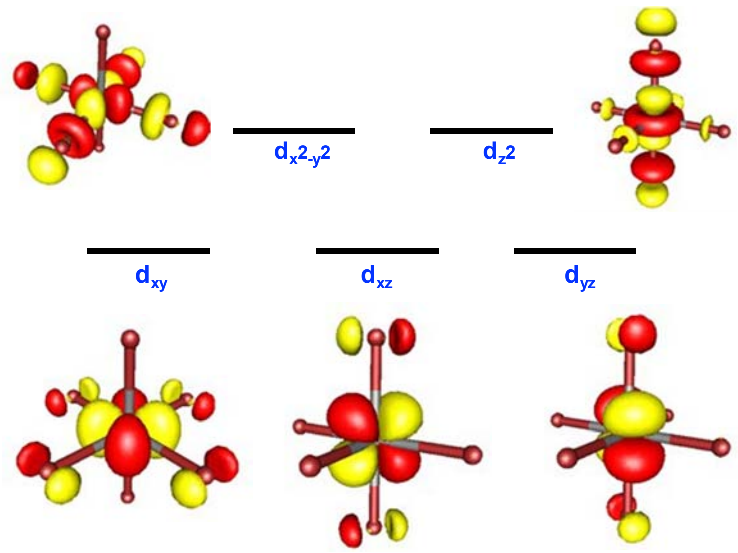
The d orbitals are non-bonding to antibonding

The stabilization of these ligand orbitals is what holds coordination complexes together!



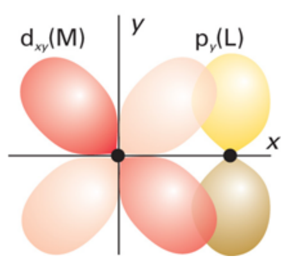
"Real" MOs of Coordination Complexes

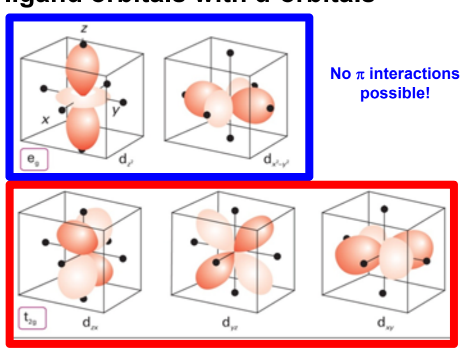
$[FeCl_6]^{3-}$



π Metal-Ligand Overlap

There is a second kind of overlap of ligand orbitals with d-orbitals (in O_h, only for d_{xy}, d_{xz}, d_{yz} ≡ d_π).





Three kinds of Ligands:

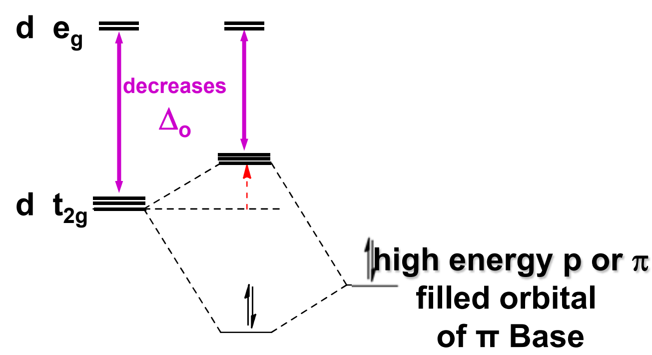
1. Non-π σ-donors (i.e., σ bases)
2. π-donors (i.e., π-bases)
3. π-acceptors (i.e., π-acids)

BOTH are ALSO σ-donors!

π interaction < σ interaction

π interaction = 0 for non-π bonding ligands (e.g. NH_3)

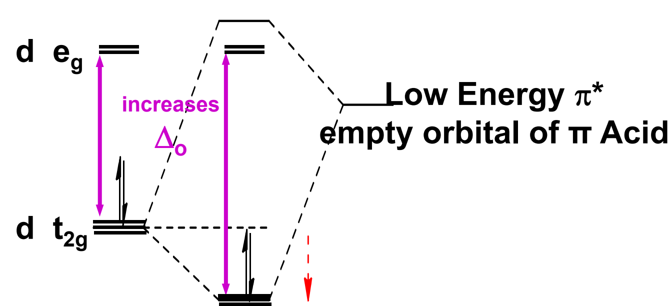
π-donor (π base) Ligands



π Bases are “weak-field” ligands (e.g., I^-, Br^-, Cl^-, S^{2-}, SCN^-).

π Bases **decrease** d-d splitting relative to σ only donors (e.g., NH_3).

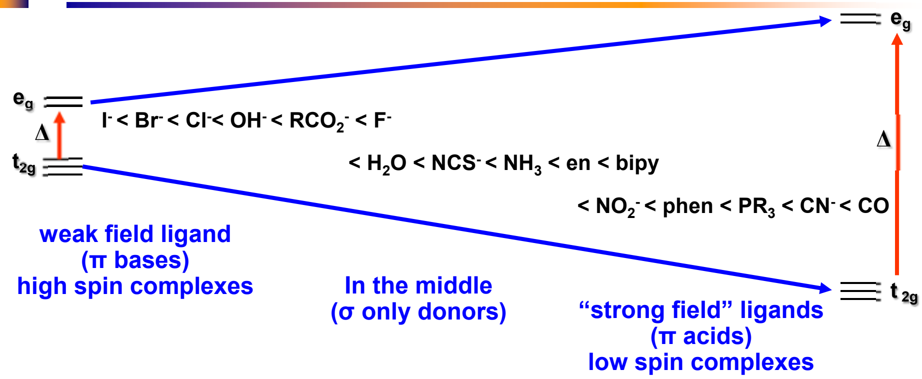
π-acceptor (π acid) Ligands



π Acids “back π-bonding” are “strong-field” ligands
(e.g., CO, PF_3, PR_3, CN^-, i.e., low lying π* orbitals).
“back π-bonding” means e- flow from filled metal d to empty ligand π*.

π Acids **increase** d-d splitting relative to σ only donors (e.g., NH_3).

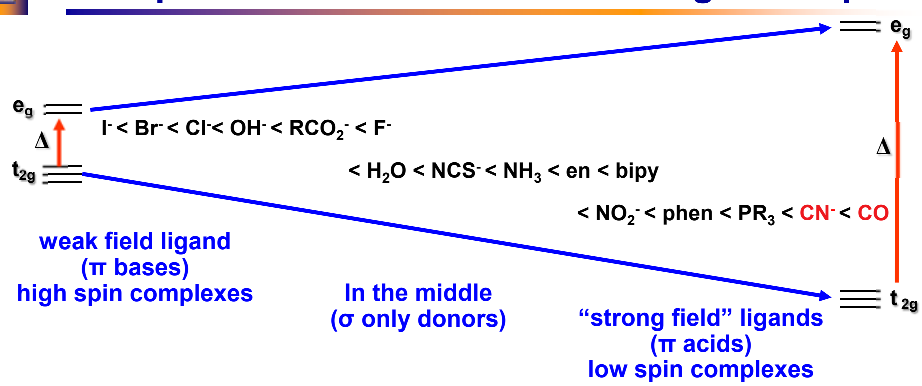
The Spectrochemical Series: "Tuning the Gap"



Octahedral splitting = Δ_o is larger for

- High metal ion charge
- Ligands with strong σ donation
- Ligands with weak π donation
- Ligands with strong π acception
- 2nd & 3rd Row T.M.

The Spectrochemical Series: "Tuning the Gap"



Why does CN^- lead to large splitting (big Δ) ?

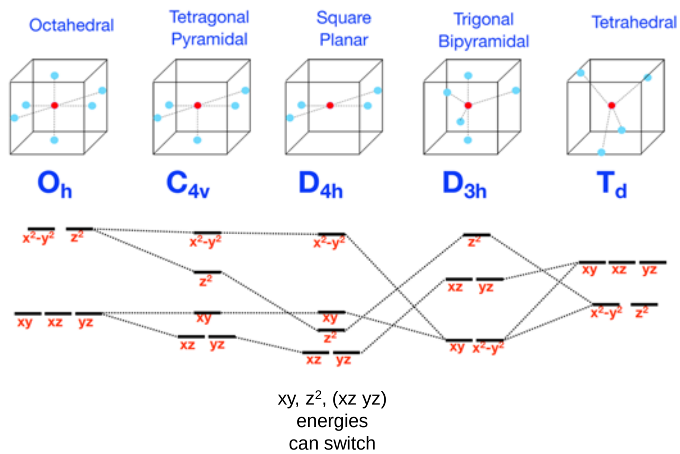
Highly basic: raises energy of e_g levels.

π-bonding: lowers energy of t_{2g} orbitals, π-back bonding.

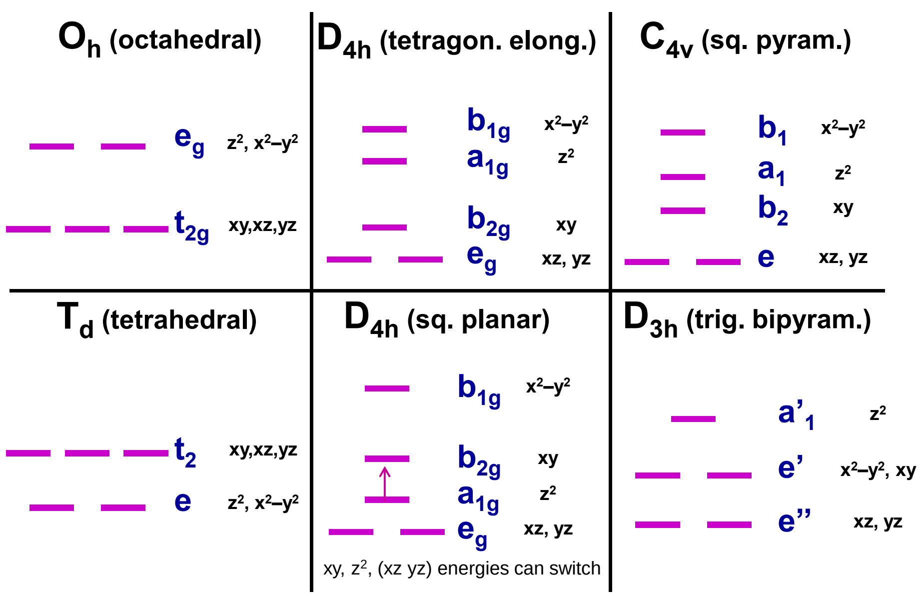
In contrast, consider CO:

little σ basicity (not protonated) – mostly π-back bonding effect (i.e., lowers t_{2g} orbitals a lot)

d Orbital Splittings vs. Ligand Field Symmetry



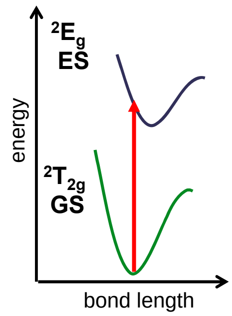
d Orbital Splittings vs. Ligand Field Symmetry

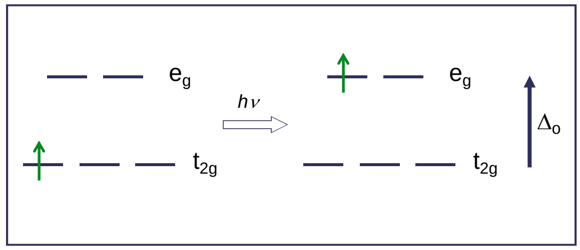


Ligand Field Splitting of d-orbitals, d^1

Analysis of the UV-vis Spectrum of $[Ti(OH_2)_6]^{3+}$: $h\nu \sim \Delta_o$

Simplest case because only one electron





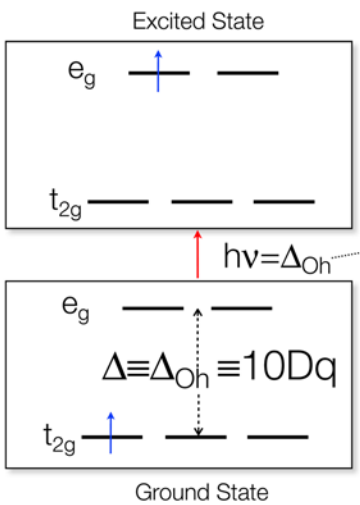
complex in electronic ground state (GS) ⟶ **the "*d-d* transition"** ⟶ **complex in electronic excited state (ES)**

$[Ti(OH_2)_6]^{3+}$ λ_{max} = 510 nm Δ_o is ∴ 243 kJ mol^{-1}

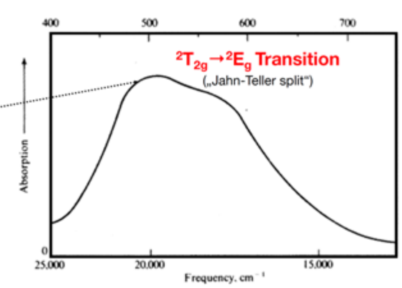
20,300 cm^{-1}

An electron changes orbital, the ion changes energy state, and Ti-O bonds elongate.

Ligand Field Splitting of d-orbitals, d^1



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



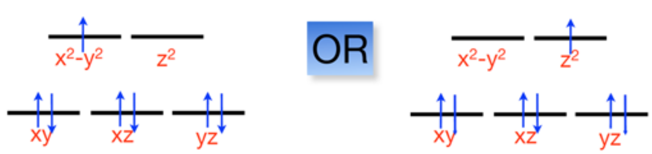
Jahn-Teller Distortions

Jahn-Teller Theorem:
Any system which has a partially-filled degenerate set of orbitals will undergo a distortion to split that degeneracy and lower the electronic energy of the system.

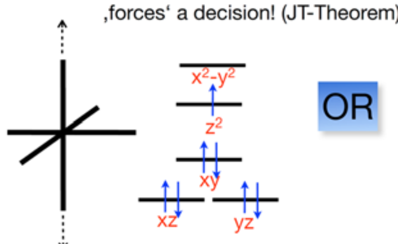
J.-T. NEVER tells you what distortion will be best,
ONLY that there MUST be one that will lower the energy.

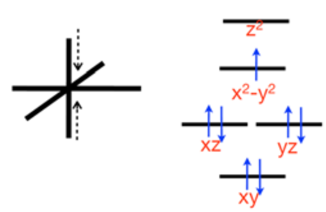
Jahn-Teller Distortions

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



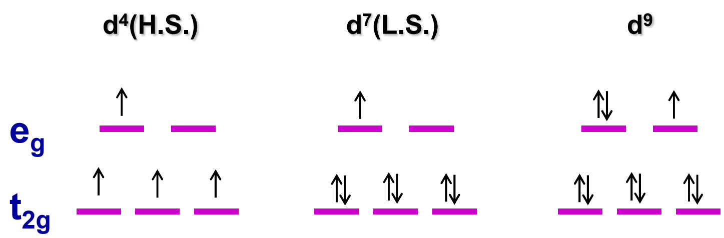
ANSWER: There is **ALWAYS** a nuclear motion that removes the degeneracy and ‚forces' a decision! (JT-Theorem)





Other Cases of Jahn-Teller Distortions

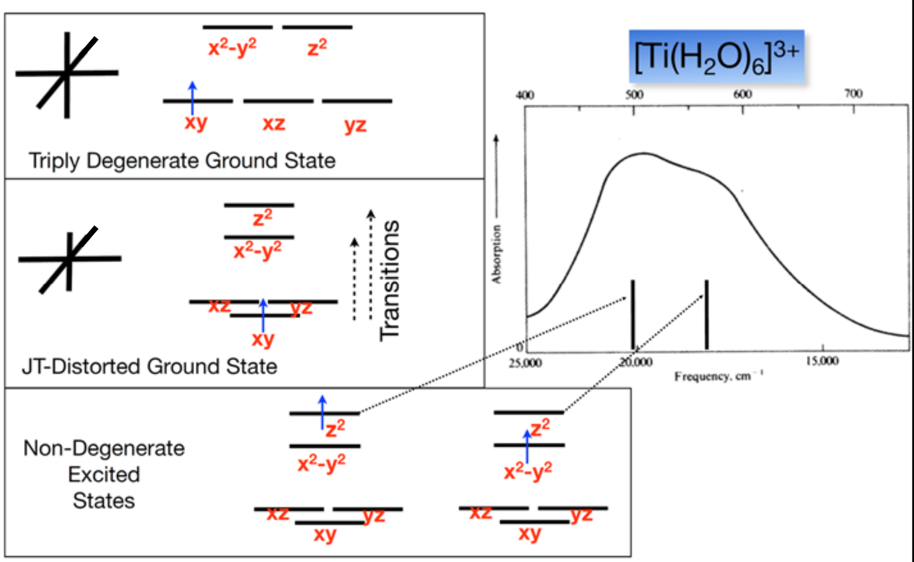
Strongest J-T distortions:



Number of electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn–Teller	w	w		s		w	w		s	
Low-spin Jahn–Teller	w	w		w	w		s		s	

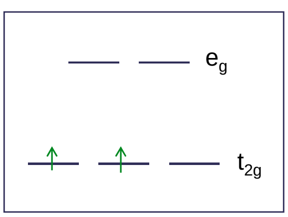
w = weak Jahn–Teller effect expected (t_{2g} orbitals unevenly occupied); s = strong Jahn–Teller effect exp
(e_g orbitals unevenly occupied); No entry = no Jahn–Teller effect expected.

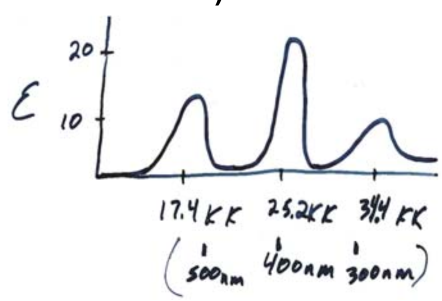
Jahn-Teller Distortion, d^1



Limitations of MO Diagrams

V^{3+} in Al_2O_3 (octahedral O coordination) = d^2 ion

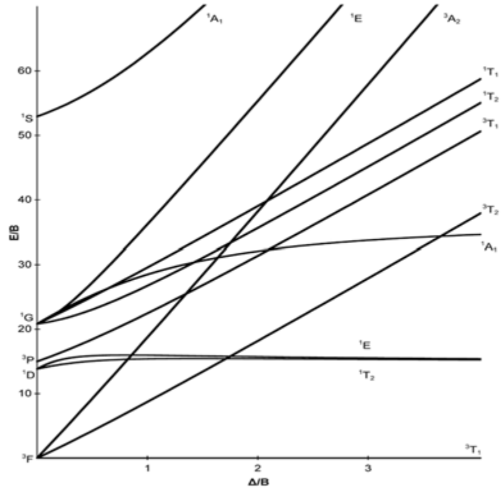




For the d^2 complex we see three bands!
The electronic structure is more complicated than represented by orbital energies alone.

The problem: orbital energy diagrams ignore inter-electron repulsion,
i.e., several states comprise the $(t_{2g})^1(e_g)^1$ configuration,
with different inter-electron repulsion energies.
What are these bands? Are they d-d transitions or …?

Use of Tanabe-Sugano Diagrams, d^2



So, what's B?

i.e., Racah parameter

$\Delta = 10D_q$ = ligand field splitting

Use of Tanabe-Sugano Diagrams, d^2

$10Dq = \Delta$

TABLE 9.17

CRYSTAL FIELD AND NEPHELAUXETIC PARAMETERS FOR d^6 COMPLEXES
(All spin-paired; 10 *Dq*, *B* and *C* in wavenumbers)

Complex	10 *Dq*	*B*	*β*	*C*	*C*/*B*(*γ*)
$Fe(o\text{-}phen)_3^{2+}$	13,110	602	0.68		
$Fe(CN)_6^{4-}$	32,200	490	0.55		
$Fe(CNO)_6^{4-}$	27,000	410	0.46		
$Ru(H_2O)_6^{2+}$	19,800	475	0.76		
$Ruen_3^{2+}$	28,100	420	0.68		
$Rudien_2^{2+}$	28,800	430	0.69		
$Co(CN)_6^{3-}$	32,200	400	0.36		
$Codtp_3$	14,200	400	0.36	1620	4.05
$Co(NH_3)_6^{3+}$	22,870	615	0.56	3090	5.02
$Coen_3^{3+}$	23,160	590	0.53	2900	4.91
$Co(CNO)_6^{3-}$	26,100	450	0.405		
$Co(H_2O)_6^{3+}$	20,760	510	0.46	4260	8.36
$Coox_3^{3-}$	18,020	540	0.49		
$Rh(NH_3)_6^{3-}$	34,000	430	0.60		
$Rh(SCN)_6^{3-}$	~20,300				
$Rh(CN)_6^{3-}$	~45,500				
RhF_6^{3-}	23,300	460	0.64	~1850	4.0
$RhCl_6^{3-}$	20,400	350	0.49		
$RhBr_6^{3-}$	19,000	290	0.40		
$Rhdtp_3$	21,900	210	0.29		
$Ir(NH_3)_6^{3+}$	41,200	470	0.71		
$IrCl_6^{3-}$	25,000	300	0.46		
$Iren_3^{3+}$	~41,400				
$Ir(NH_3)_5H_2O^{3+}$	40,400	550	0.83		
$Irdtp_3$	26,700	160	0.24		
$Irdsep_3$	25,000	135	0.20		
PtF_6^{4-}	33,000	380	0.53		

Use of Tanabe-Sugano Diagrams

B value (Racah parameter) in Tanabe-Sugano Diagrams
decreases as inter-electronic repulsions decrease

decreases for **lower oxidation states,**
2^{nd} and 3^{rd} row metals,
larger d orbitals
greater covalency
more polarizable ligand
more polarizable metal

$\beta = \dfrac{\text{B in complex}}{\text{B in Free Ion}}$

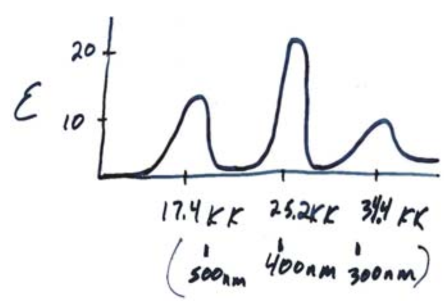
Nephelauxetic Series ("Cloud Expanding"):

F > O > N > Cl > Br > S ~ I > Se

β~ 1 **β~ 0.3**

Use of Tanabe-Sugano Diagrams

V^{3+} in Al_2O_3 (octahedral O coordination) = d^2 ion



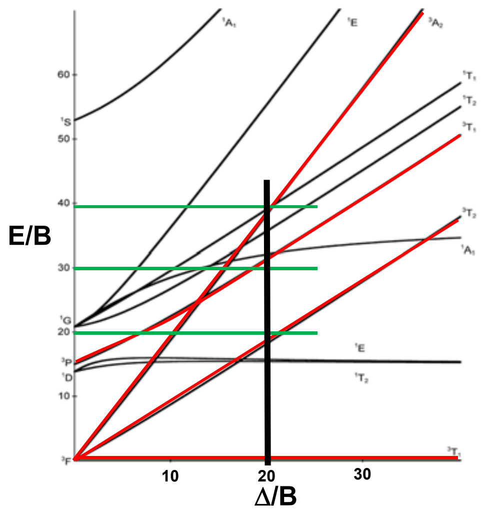
Remember T.-S. diagrams are normalized energies.

For V^{3+}, B = 866 cm^{-1} and C/B = 3.6 cm^{-1} (look up, e.g., previous page)

So, E/B of the 3 bands are 20.1, 29.1, 29.9

Tanabe-Sugano Diagram for d^2 Ions

spin allowed transitions in red



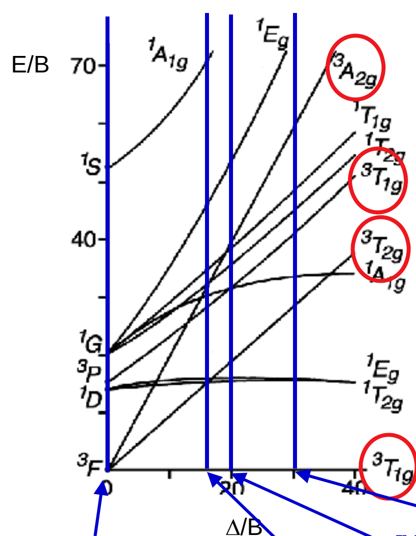
V^{3+} in Al_2O_3

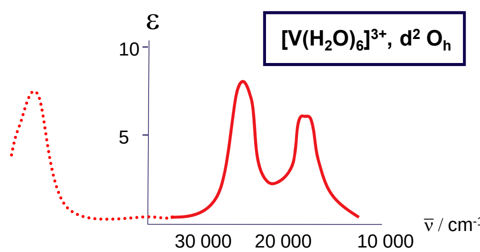
E/B = 39.9
29.1
20.1

So, all three bands are accounted for as spin allowed d-d transitions.

$\Delta = 2\,B = 17000\ cm^{-1}$

Tanabe-Sugano Diagram for d^2 Ions: Spectra





$[V(H_2O)_6]^{3+}$, d^2 O_h

$[V(NH_3)_6]^{3+}$

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

Gaseous V^{3+}
(in principle 4 transitions but only 1 is spin allowed)

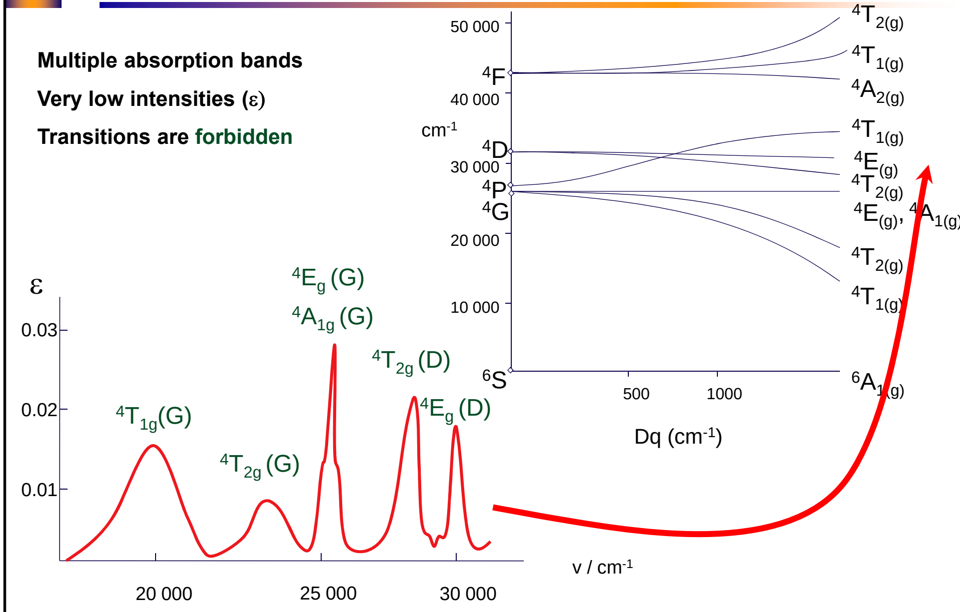
$[V(H_2O)_6]^{3+}$ (in principle, 10 transitions/ excited states, but only 3 are spin allowed)

d^5 Octahedral Case: $[Mn(H_2O)_6]^{2+}$

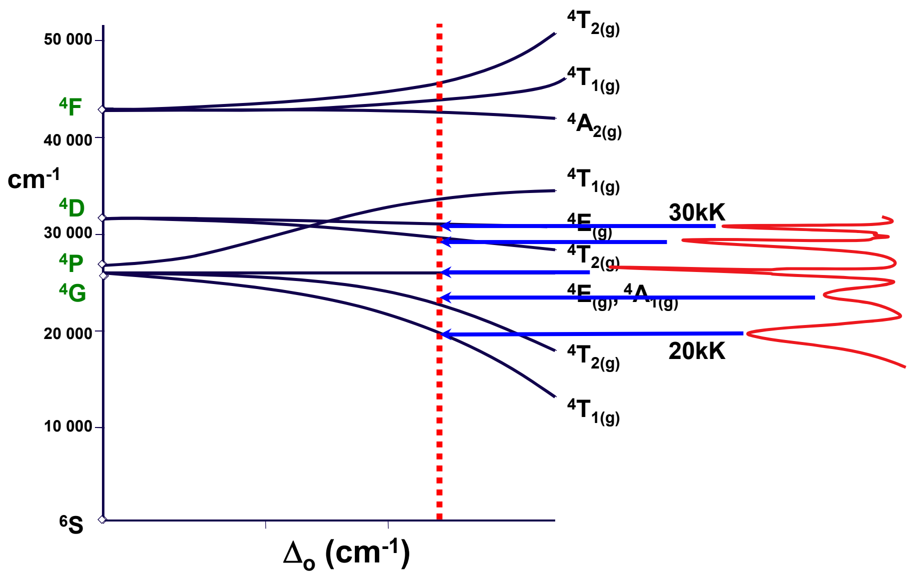
Multiple absorption bands

Very low intensities (ε)

Transitions are forbidden

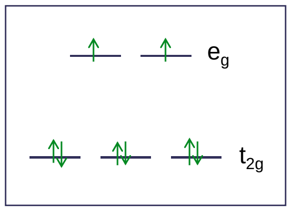


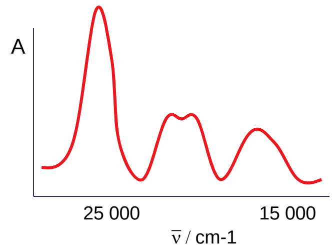
d ^{5} Octahedral Case: $[Mn(H_2O)_6]^{2+}$



d^8 Octahedral Case: $[Ni(H_2O)_6]^{2+}$

$[Ni(OH_2)_6]^{2+}$ = d^8 ion

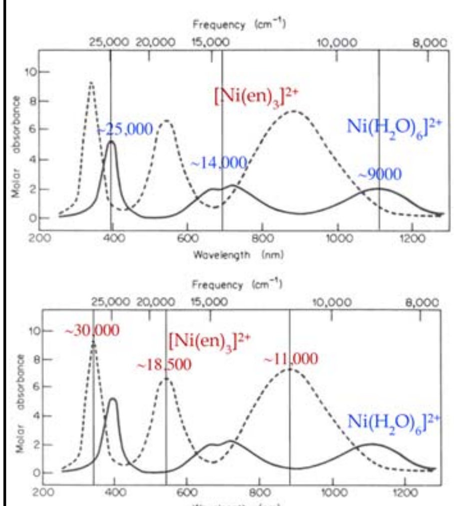


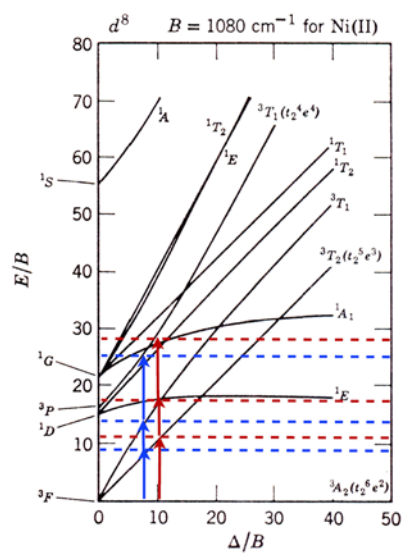


For the *d*^{8} complex we see at least three bands!

The electronic structure is more complicated than represented by orbital energies alone.

d^8 Octahedral Case: $[Ni(H_2O)_6]^{2+}$ vs. $Ni(en)_3^{2+}$





Selection Rules

Selection rules determine the intensity of electronic transitions
(intensity ~ allowedness)

Spin Selection Rule

$$\boxed{\Delta S = 0}$$

There must be no change in spin multiplicity during an electronic transition (for light elements where S is a "good" QN.

Symmetry (a.k.a. Laporte) Selection Rule (essentially dipole change requirement)

$$\boxed{\Delta l = \pm 1}$$

For centrosymmetric systems
there must be a change in parity during an electronic transition: i.e.,

g ⇔ u

Basically, d-d transitions are forbidden for octahedral complexes.

Selection Rules

Spin Selection Rule

There must be no change in spin multiplicity during an electronic transition.

$$\phi_{trip} : \alpha(1)\alpha(2),\quad \beta(1)\beta(2),\quad \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

$$\phi_{sing} : \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

$$\int \phi_{sing}\,\phi_{trip\,\alpha\alpha}\,d\tau = \frac{1}{\sqrt{2}} \int (\alpha(1)\beta(2) - \beta(1)\alpha(2))\,\alpha(1)\alpha(2)\,d\tau_1 d\tau_2$$

$$= \frac{1}{\sqrt{2}}\left(\int \alpha(1)\alpha(1)\,d\tau_1 \int \beta(2)\alpha(2)\,d\tau_2 - \int \beta(1)\alpha(1)\,d\tau_1 \int \alpha(2)\alpha(2)\,d\tau_2\right)$$

$$= 0 - 0 = 0$$

Selection Rules

Orbital Selection Rule

There must be a change in dipole moment during an electronic transition.

$$\int \psi_{el_m}^{*} \, \hat{\mu} \, \psi_{el_\ell} \, d\tau \neq 0$$

i.f.f. $\Gamma(\psi_{el_m}) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\psi_{el_\ell})$

contains the totally symmetric irred. rep. of the molecules pt. group. (A_{1g}).

Selection Rules

Orbital Selection Rule

There must be a change in dipole moment during an electronic transition.

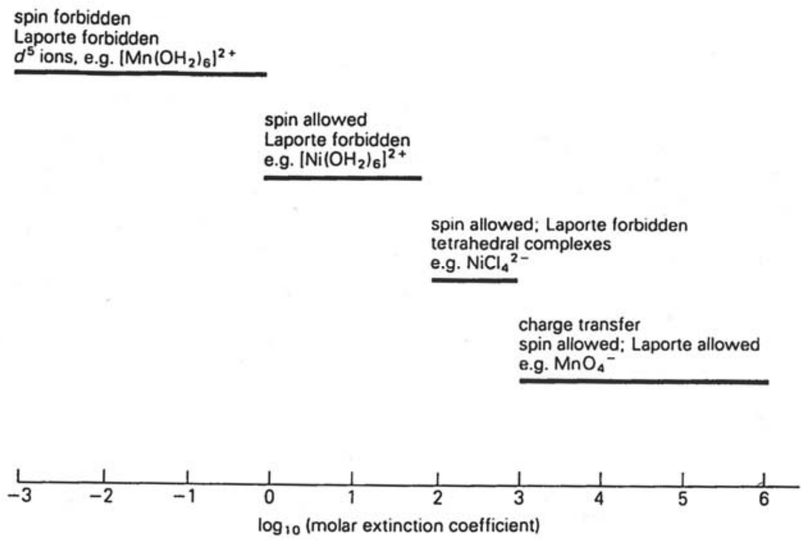
e.g., for d-orbitals, $\Gamma_d = \Gamma_g$ but $\Gamma_\mu = \Gamma_u$ (i.e., x, y, z)

$$\Gamma(\psi_{el_m}) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\psi_{el_\ell}) = \Gamma_g \otimes \Gamma_u \otimes \Gamma_g$$

$$= \Gamma_u \neq A_{1g}$$

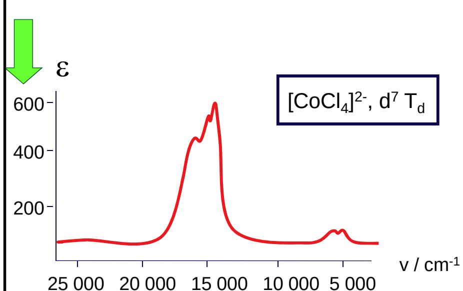
So, d-d transitions are orbitally (“LaPorte”) forbidden!

Selection Rules

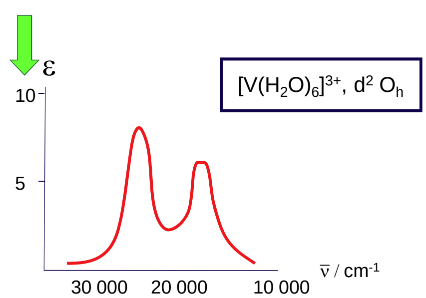


Relaxation of the Laporte Selection Rule. Tetrahedral vs. Octahedral Complexes

No inversion center in T_d, therefore no ungerade vs. gerade!



Spin-allowed;
Laporte-allowed

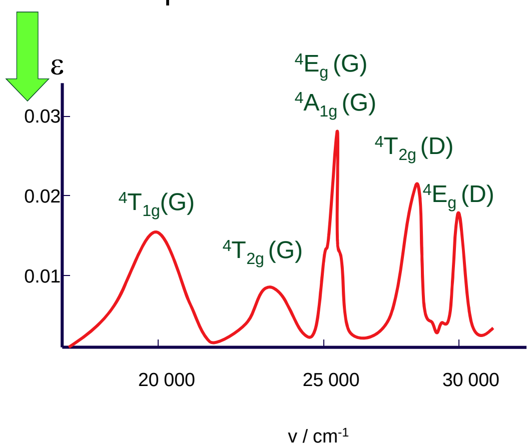


Spin-allowed;
Laporte-forbidden

Forbidden Transitions

h.s. d^5, double-trouble:

- Laporte forbidden
- Spin forbidden



Origin of Forbidden Transition Intensities

1. Spin Forbidden Transitions due to "Spin-Orbit" Coupling

Angular Momentum of "spinning" e^- can couple with Angular Momentum of e^- "moving" in orbital. ≡ Magnetic moment coupling

$\vec{J} = \vec{L} + \vec{S}$ = constant

$\vec{L}$: orbital; $\vec{S}$: spin

For Light Nuclei, Usually $\vec{L}_{GS} = \vec{L}_{XS}$ and $\vec{S}_{GS} = \vec{S}_{XS}$

Some Mixing does occur (L & S are not "good Q.N.")

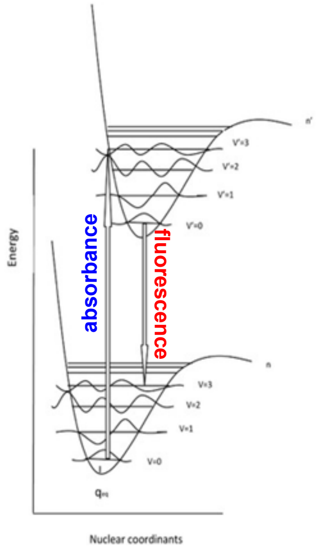
$$^1\psi + {}^3\psi \xrightarrow{S.O.C.} [a\,{}^1\psi + b\,{}^3\psi],\ [b\,{}^1\psi + a\,{}^3\psi]$$

$a >> b$

∴ $^1\psi_{mixed} \rightarrow {}^3\psi_{mixed}$ not without overlap in spin space

Origin of Forbidden Transition Intensities

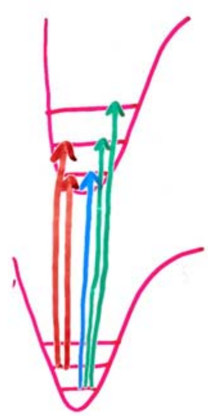
Consider electronic transitions:



It's not just about
the electronic state:
we must also consider
the vibrational sub-states!

Origin of Forbidden Transition Intensities

Vibronic Coupling:



↑ = 0-0 transition
no change in vibrational motion
(i.e. nuclear wave function

↑ = vibronic transitions
from G.S. vib. mode to
electronic + vibrational excited
state
(Intensities follow Franck-Condon Principle)

↑ = hot bands due to
vibrationally hot electronic
G.S. molecules (weak)

Vibronic Transitions

consider

$$M^{x}_{\ell m} = \int \psi_m^* \hat{\mu}_x \psi_\ell \, d\tau$$

Franck-Condon Principle says $\hat{\mu}_x$ operates only on e^- coordinates

Assume $\psi = \psi_{vib} \; \psi_{electronic} \; \psi_{spin}$

$$M^{x}_{\ell m} = \underbrace{\int \psi^*_{vib_m} \psi_{vib_\ell} \, d\tau_{nuc}}_{\text{Franck Condon Factor}} \; \underbrace{\int \psi_{el_m} \hat{\mu}_x \psi_{el_\ell} \, d\tau_{el}}_{\text{orbital Selection rules}} \; \underbrace{\int \psi^*_{sp_m} \psi_{sp_\ell}}_{\text{Spin Selection Rules}}$$

"Lo Porte"

Vibronic Transitions: Franck-Condon Factor

$\hat{\mu}$ is function of e^- positions only.

i.e. nuclear motion (vibrations) are slow relative to electronic transitions.

$\Rightarrow$ internuclear distances remain fixed during electronic transition

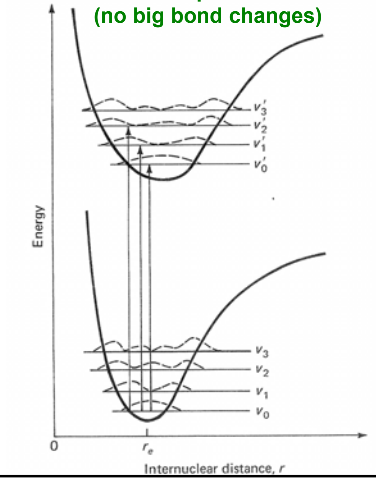
$\Rightarrow$ "Vertical" Transitions

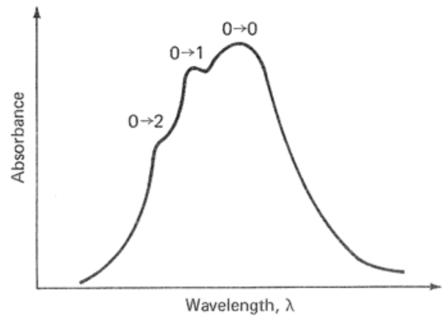
$\Rightarrow$ Franck-Condon Barriers if Overlap bad.

Vibronic Transitions: Franck-Condon Factor

Franck-Condon Principle: nuclear much slower than electron motion.
Corollary: electronic transitions are "vertical" (i.e., nucleus can't move).
Consequence: overlap between GS vibration and XS vibration matters.

Non-displaced XS
(no big bond changes)





Vibronic Transitions: Franck-Condon Factor

Franck-Condon Principle: nuclear much slower than electron motion.
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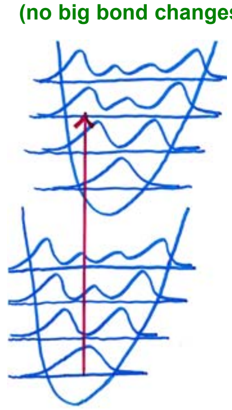
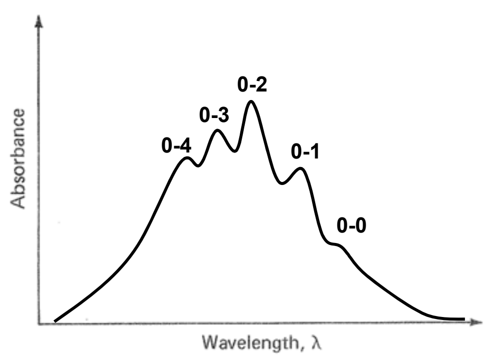
Displaced XS
(no big bond changes)





Vibronic Coupling Selection Rules

$$f \propto \left| \int \psi^*_{el_{XS}} \, \psi^*_{vib_{XS}} \, \hat{M} \, \psi_{el_{GS}} \, \psi_{vib_{GS}} \, d\tau \right|^2$$

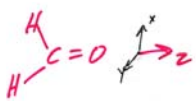
So, does this integral (in red) $\neq 0$?

$\Gamma^{el}_{XS} \times \Gamma^{vib}_{XS} \times \hat{M} \times \Gamma^{el}_{GS} \times \Gamma^{vib}_{GS}$ contain A_{1g} ?

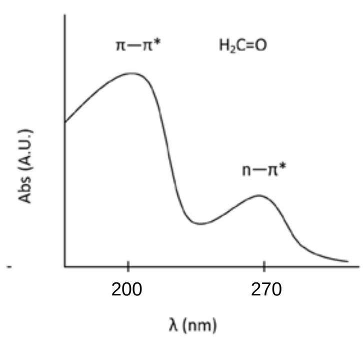
Γ_x
Γ_y
Γ_z

A_{1g} for non-hot bands

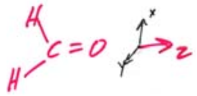
Electronic Transitions: Formaldehyde



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y



Electronic Transitions: Formaldehyde



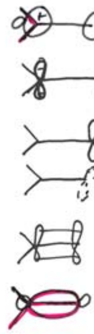
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

$\Gamma_\mu = B_1 + B_2 + A_1$
x y z

Consider the C=O orbitals
i.e., the frontier orbitals:

Energy

σ^* — a_1 $p_z^C - p_z^O$
π^* — b_1 $p_y^C - p_y^O$
n_b ⥮ b_2 p_x^O
n_a ⥮ a_1 p_y
π ⥮ b_1 $p_x^C + p_x^O$
σ ⥮ a_1 $p_z + p_z$



consider only 2p on O & C

1p, 2s, core C, H-C orbitals are lower in energy.

Electronic Transitions: Formaldehyde

a_1 σ^* —
b_1 π^* —
b_2 n_b ⥮
a_1 n_a ⥮
b_1 π ⥮
a_1 σ ⥮

$n \to \pi^*$ $n \to \sigma^*$ $\pi \to \pi^*$ $\sigma \to \sigma^*$ ....

G.S. : $b_2 \otimes b_2$
$= A_1$

$n \to \pi^*$

$b_1 \otimes b_2 = A_2$

$\Rightarrow A_1 \xrightarrow{n \to \pi^*} A_2$
G.S. E.S

$\Gamma_x = B_1$
$\Gamma_y = B_2$
$\Gamma_z = A_1$

is $n \to \pi^*$ Sym. Allowed?

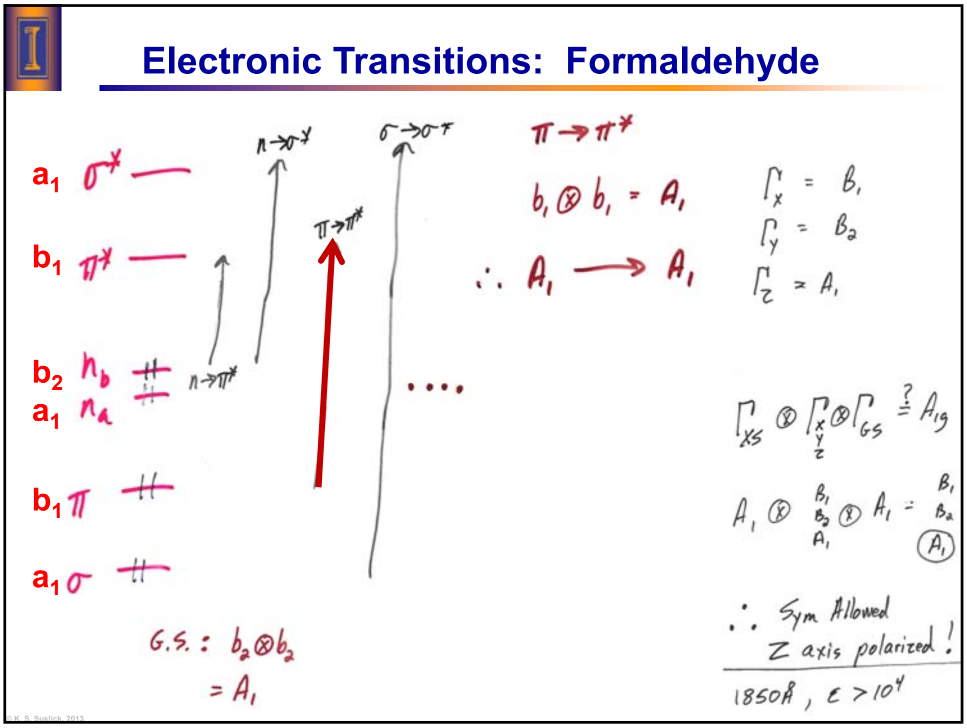
$\Gamma_{A_2} \otimes \Gamma_{x,y,z} \otimes \Gamma_{A_1} = A_2 \otimes \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix} \otimes A_1$

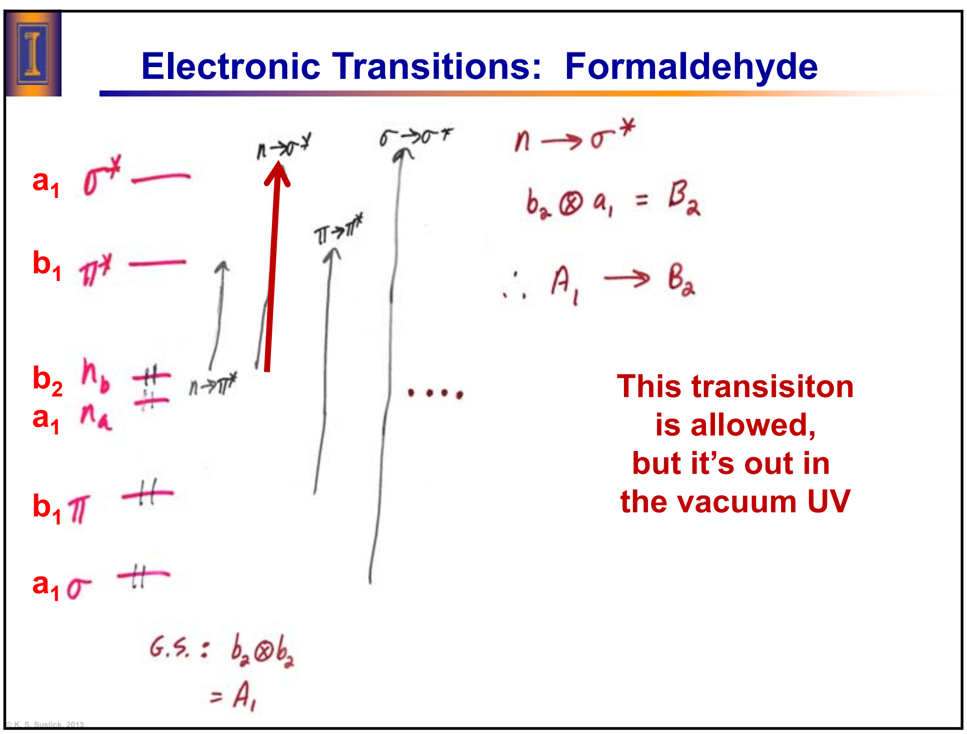
$= B_2 \oplus B_1 \oplus A_2$

no A_1

∴ Sym Forbidden

λ_{max} at 2700Å, $\varepsilon = 100$


Electronic Transitions: Formaldehyde
a_1 σ^*
b_1 π^*
b_2 n_b
a_1 n_a
b_1 π
a_1 σ
$n \to \sigma^*$
$\sigma \to \sigma^*$
$\pi \to \pi^*$
$n \to \pi^*$
$\pi \to \pi^*$
$b_1 \otimes b_1 = A_1$
$\therefore A_1 \longrightarrow A_1$
$\Gamma_x = B_1$
$\Gamma_y = B_2$
$\Gamma_z = A_1$
$\Gamma_{XS} \otimes \Gamma_{x,y,z} \otimes \Gamma_{GS} \overset{?}{=} A_{1g}$
$A_1 \otimes \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix} \otimes A_1 = \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix}$
$\therefore$ Sym Allowed
Z axis polarized!
1850Å, $\epsilon > 10^4$
G.S.: $b_2 \otimes b_2 = A_1$


Electronic Transitions: Formaldehyde
a_1 σ^*
b_1 π^*
b_2 n_b
a_1 n_a
b_1 π
a_1 σ
$n \to \sigma^*$
$\sigma \to \sigma^*$
$\pi \to \pi^*$
$n \to \pi^*$
$n \longrightarrow \sigma^*$
$b_2 \otimes a_1 = B_2$
$\therefore A_1 \longrightarrow B_2$
This transisiton
is allowed,
but it's out in
the vacuum UV
G.S.: $b_2 \otimes b_2 = A_1$

Vibronic Transitions: H_2CO

In summary, 2 transitions observed:

(but where did the forbidden transition get ε =100?!)

2700 Å	1850 Å
$\varepsilon = 100$	$\varepsilon > 10^4$
$n_b \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
${}^1A_1 \rightarrow {}^1A_2$	${}^1A_1 \rightarrow {}^1A_1$
forbidden	allowed

6 Vibrational Normal Modes exist: $3a_1 + b_1 + 2b_2$

So, let's consider the effect of vibronic coupling on the forbidden ${}^1A_2 \rightarrow {}^1A_1$

$$\Gamma_{vib}^{XS} \times \Gamma_{el}^{XS} \times M \times \Gamma_{el}^{GS} \times \Gamma_{vib}^{GS}$$

$$\begin{matrix} 3a_1 \\ b_1 \\ b_2 \end{matrix} \times A_2 \times \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix} \times A_1 \times \begin{matrix} 3a_1 \\ b_1 \\ 2b_2 \end{matrix}$$

Vibronic Transitions: H_2CO

$$\Gamma_{vib}^{XS} \otimes \Gamma_{el}^{XS} \otimes M \otimes \Gamma_{el}^{XS} \otimes \Gamma_{vib}^{GS}$$

$$\begin{matrix} 3a_1 \\ \boxed{b_1} \\ \boxed{b_2} \end{matrix} \times \boxed{A_2} \times \begin{matrix} x\ \boxed{B_1} \\ y\ \boxed{B_2} \\ z\ A_1 \end{matrix} \times \boxed{A_1} \times \begin{matrix} \boxed{3a_1} \\ \cancel{b_1} \\ \cancel{2b_2} \end{matrix} = A_1(y)$$

= A_1 (z)

XXX

XXX

∴ Allowed in y-polarization

and in x-polarization but Not z.

Hot Bands (not populated at RT)

Vibronic Transitions: $Co(NH_3)_6^{3+}$ O_h

Givens: 1. $^1A_{1g}$ G.S. (d^6 S = 0)

2. Two electronic XSs, $^1T_{1g}$ and $^1T_{2g}$

3. Co-N vibrations (15): a_{1g}, e_g, $\boxed{2\ t_{1u}}$, t_{2g}, $\boxed{t_{2u}}$

4. $\Gamma_\mu = T_{1u}$

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1		
E_g	2	–1	0	0	2	2	0	–1	2	0		$(2z^2-x^2-y^2, \sqrt{3}(x^2-y^2))$
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1		
E_u	2	–1	0	0	2	–2	0	1	–2	0		
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1		

Is $^1A_{1g} \rightarrow {}^1T_{1g}$ allowed?

$$T_{1g} \otimes \overset{\mu}{T_{1u}} \otimes A_{1g} = A_{1u} + E_u + \boxed{T_{1u}} + \boxed{T_{2u}} \quad \text{i.e., NO } A_{1g}\,!$$

Vibronic coupling with vibrations t_{1u} and t_{2u} so some intensity expected (ε ~ 50).

Vibronic Transitions: $Co(NH_3)_6^{3+}$ O_h

Givens: 1. $^1A_{1g}$ G.S. (d^6 S = 0)

2. Two electronic XSs, $^1T_{1g}$ and $^1T_{2g}$

3. Co-N vibrations (15): a_{1g}, e_g, $\boxed{2\ t_{1u}}$, t_{2g}, $\boxed{t_{2u}}$

4. $\Gamma_\mu = T_{1u}$

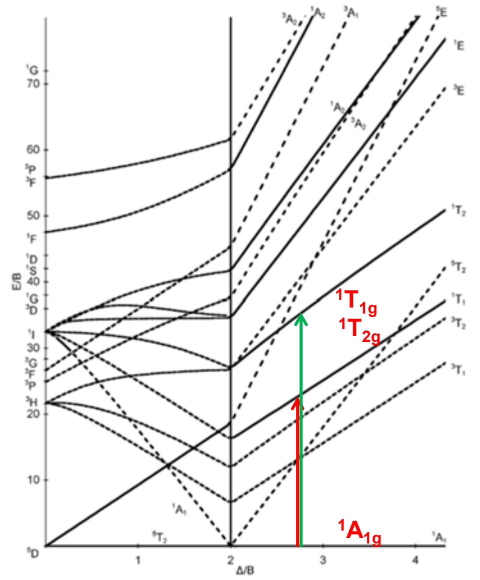
O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1		
E_g	2	–1	0	0	2	2	0	–1	2	0		$(2z^2-x^2-y^2, \sqrt{3}(x^2-y^2))$
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1		
E_u	2	–1	0	0	2	–2	0	1	–2	0		
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1		

Is $^1A_{1g} \rightarrow {}^1T_{2g}$ allowed?

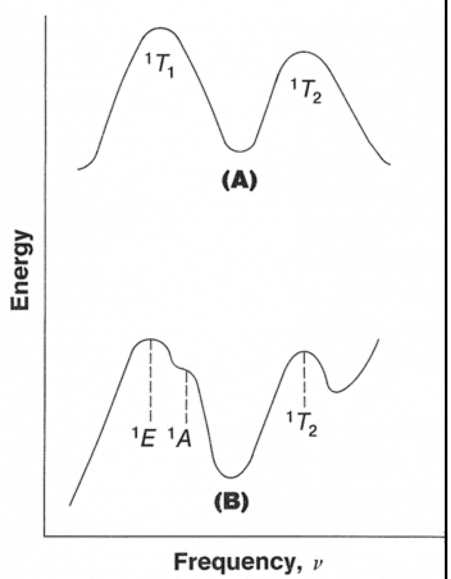
$$T_{2g} \otimes \overset{\mu}{T_{1u}} \otimes A_{1g} = A_{2u} + E_u + \boxed{T_{1u}} + \boxed{T_{2u}} \quad \text{i.e., NO } A_{1g}\,!$$

Vibronic coupling with vibrations t_{1u} and t_{2u} so again, some intensity expected (ε ~ 50).

Vibronic Transitions: $Co(NH_3)_6^{3+}$



(A) $Co(NH_3)_6^{3+}$ and (B) $Co(NH_3)_5Cl^{2+}$.



Other Intensity Stealing Mechanisms

1. "d-p" Mixing

e.g. $Co X_4^{-2}$, tetrahedral, A_2 G.S.

2 absorbances:	20,000 cm^{-1}	6,000 cm^{-1}
Both d→d	ε = 600	ε = 50
	$A_2 \rightarrow T_1$	$A_2 \rightarrow T_2$

In T_d, $\Gamma_{xy,yz,xz} = T_2 = \Gamma_{p_x,p_y,p_z}$

$\Gamma_{x^2-y^2,z^2} = E$

$T_1 \times T_2 \times A_2 = \boxed{A_1} + E + T_1 + T_2$

∴ $A_2 \rightarrow T_1$ allowed, even though it's a d-d transition

Note: T_d has no $\underline{\underline{i}}$. "d-p" mixed

$T_2 \times T_2 \times A_2 = A_2 + E + T_1 + T_2$

∴ $A_2 \rightarrow T_2$ not allowed

No d-p mixing

∴ No allowedness

Other Intensity Stealing Mechanisms

2. Magnetic Dipole of Rad. Field

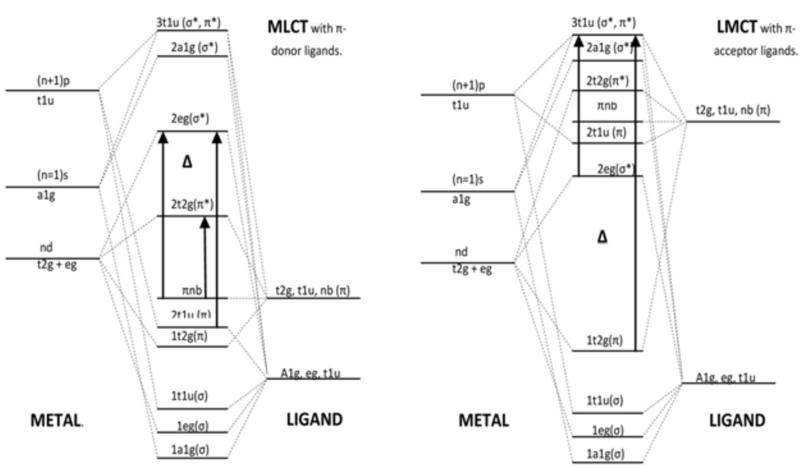
$\varepsilon < 1$ $\hat{M}_{mag} = R_x, R_y, R_z$

(rotates e^- density)

3. Quadrupole Coupling

$\varepsilon < 10^{-2}$ $\hat{M}_{Quad} = xy, xz, yz, z^2, x^2+y^2$

Charge-Transfer (CT) Transitions



Charge Transfer Transitions

d^0 and d^{10} ions have no d-d transitions, BUT often still colored.

Why?	Zn^{2+}	d^{10} ion		colorless
	TiF_4	d^0 ion		white
	$TiCl_4$	d^0 ion		white
	$TiBr_4$	d^0 ion		orange
	TiI_4	d^0 ion		dark brown
	$[MnO_4]^-$	Mn(VII)	d^0 ion	intensely purple
	$[Cr_2O_7]^-$	Cr(VI)	d^0 ion	bright orange
	$[Cu(MeCN)_4]^+$	Cu(I)	d^{10} ion	colorless
	$[Cu(phen)_2]^+$	Cu(I)	d^{10} ion	dark orange

These colors come from excitation of electrons from M-centered orbitals to Ligand-centered orbitals (or the reverse). MLCT and LMCT.

Selection rules for Charge-Transfer (CT) Bands

CT transitions are spin-allowed and symmetry-allowed

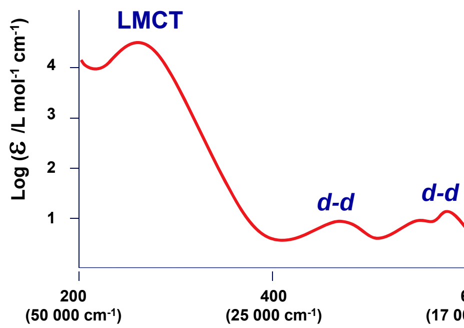
Transitions occur from a singlet G.S. to a singlet E.S.: $\Delta S = 0$

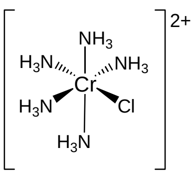
Transitions occur between metal based orbitals with *d*-character and ligand based orbitals with *p*-character: $\Delta l = \pm 1$

allowed CT transitions can therefore be much more intense than *d-d* transitions.

LMCT Transitions

$[Cr(NH_3)_5Cl]^{2+}$, Cr(III), d^3

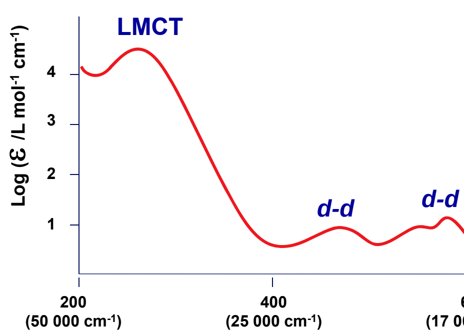


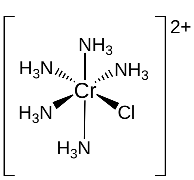


CT bands can dominate the spectrum!

LMCT Transitions

$[Cr(NH_3)_5Cl]^{2+}$, Cr(III), d^3

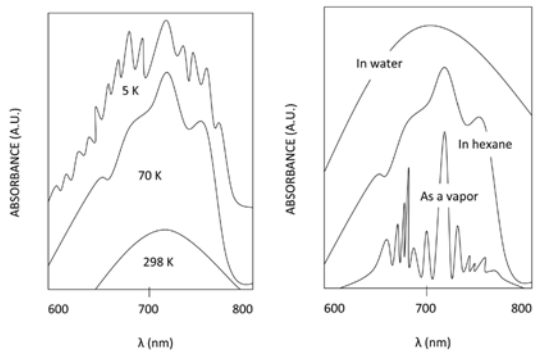




Identifying charge transfer transitions:

- Intensity
- Vibronic fine structure
- Solvatochromism - variation in absorption wavelength with solvent
- Computational modeling

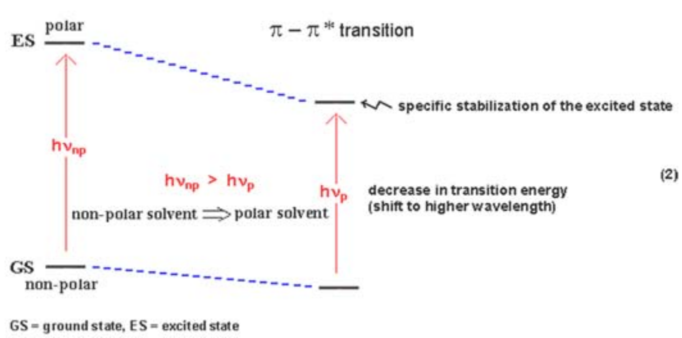
LMCT Transitions



Identifying charge transfer transitions:

- **Intensity**
- **Vibronic fine structure (best at low temp and non-interactive environment)**
- **Solvatochromism - variation in absorption wavelength with solvent**
- **Computational modeling**

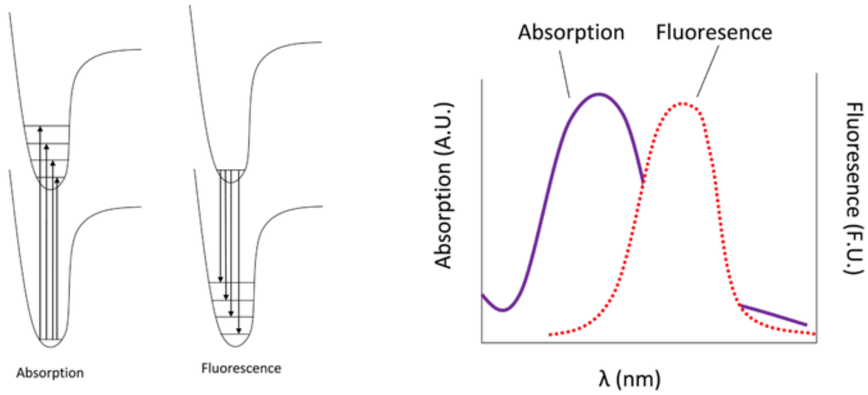
LMCT Transitions



Identifying charge transfer transitions:

- **Intensity**
- **Vibronic fine structure (best at low temp and non-interactive environment)**
- **Solvatochromism - variation in absorption wavelength with solvent**
- **Computational modeling**

Fluorescence vs. Absorbance



**Vibrational relaxation (i.e., dropping to ν=0)
is generally faster than fluorescence
of diamagnetic light element compounds,
but often no fluorescence from TM complexes.**