



CHEM F111 : General Chemistry

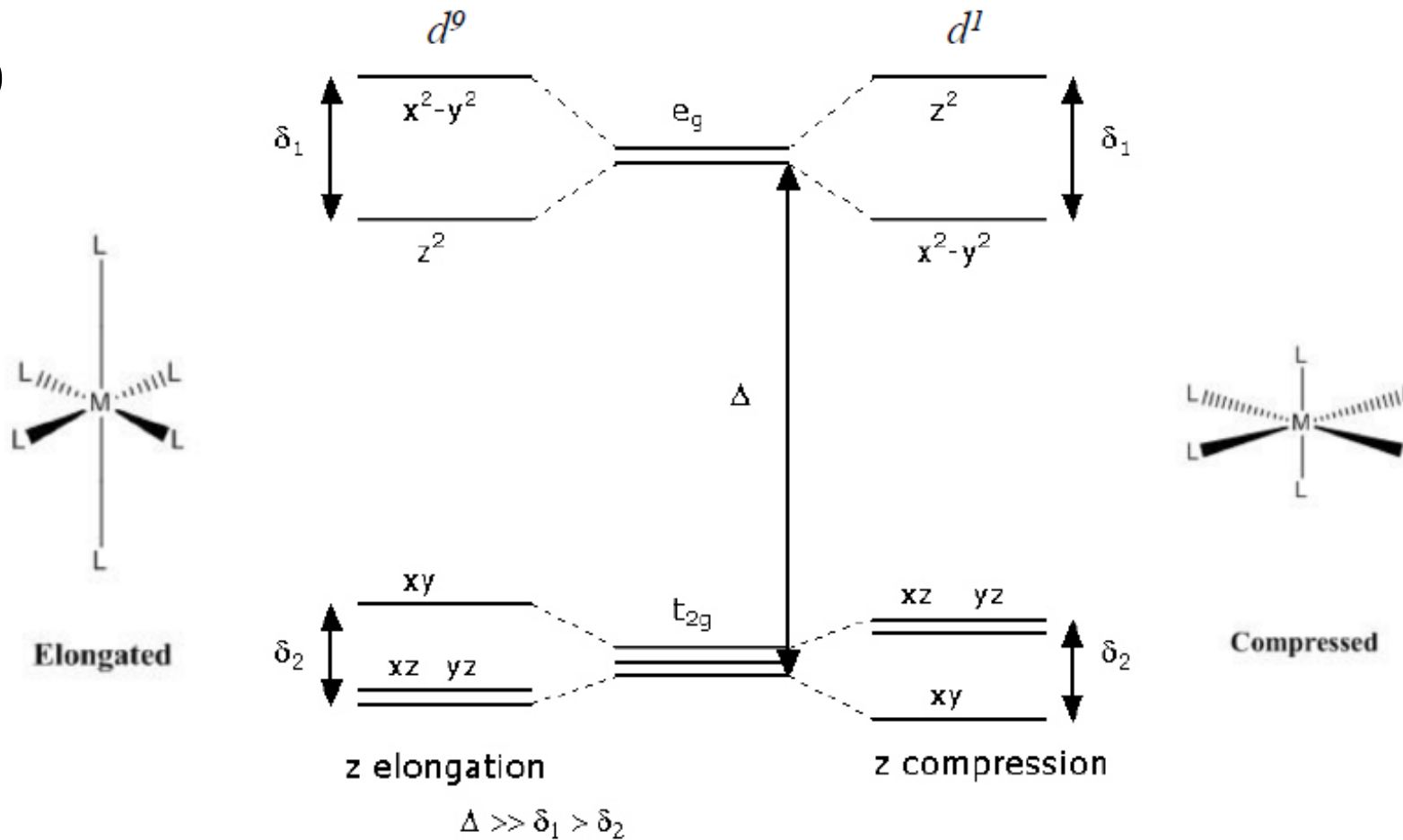
Semester II: AY 2017-18

Lecture-26, 23-03-2018

Students are hereby instructed to submit the mid-sem answer sheet immediately (not later than Monday, 26-03-2018, 17.30 hrs) to the tutorial instructor.

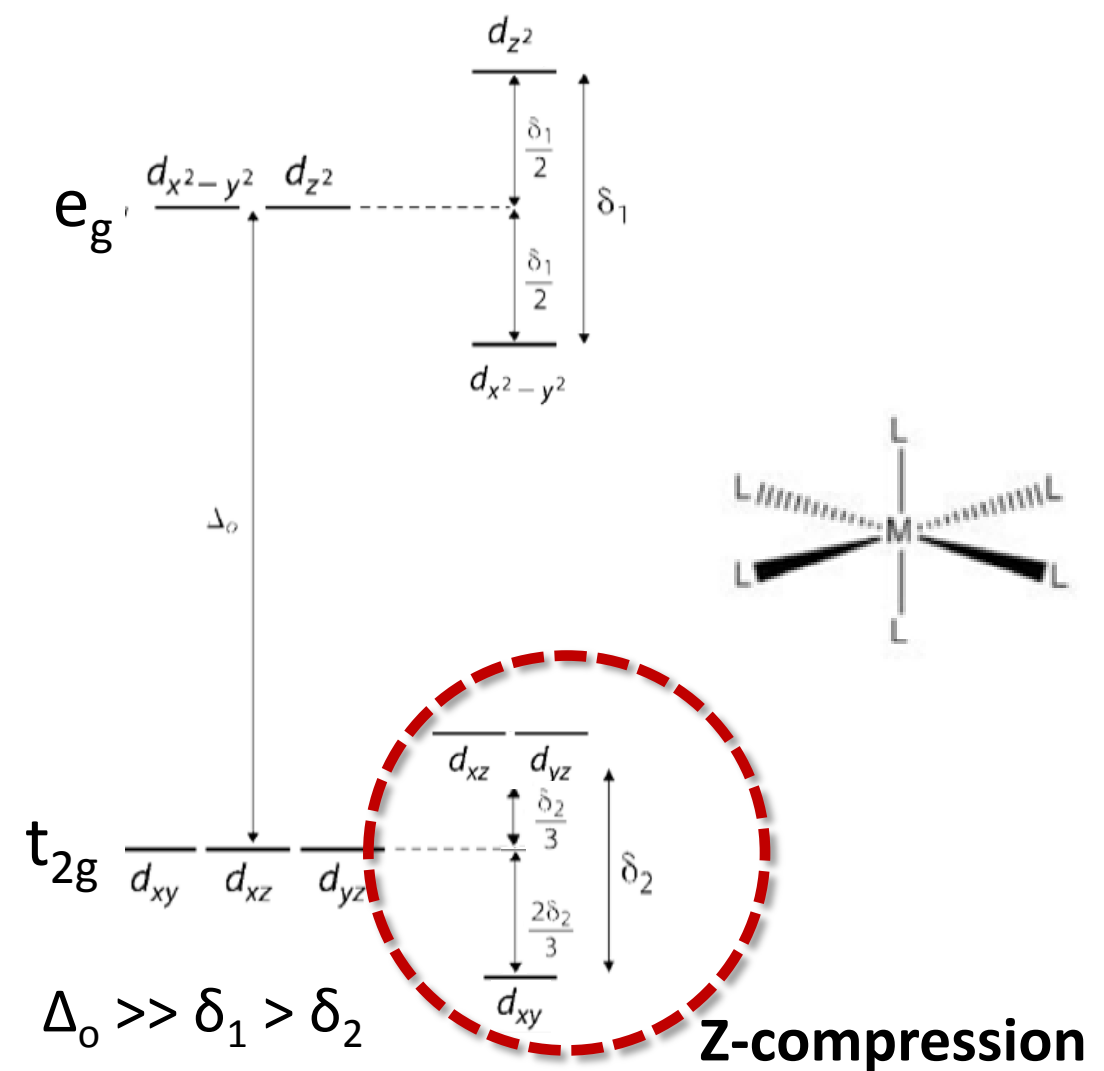
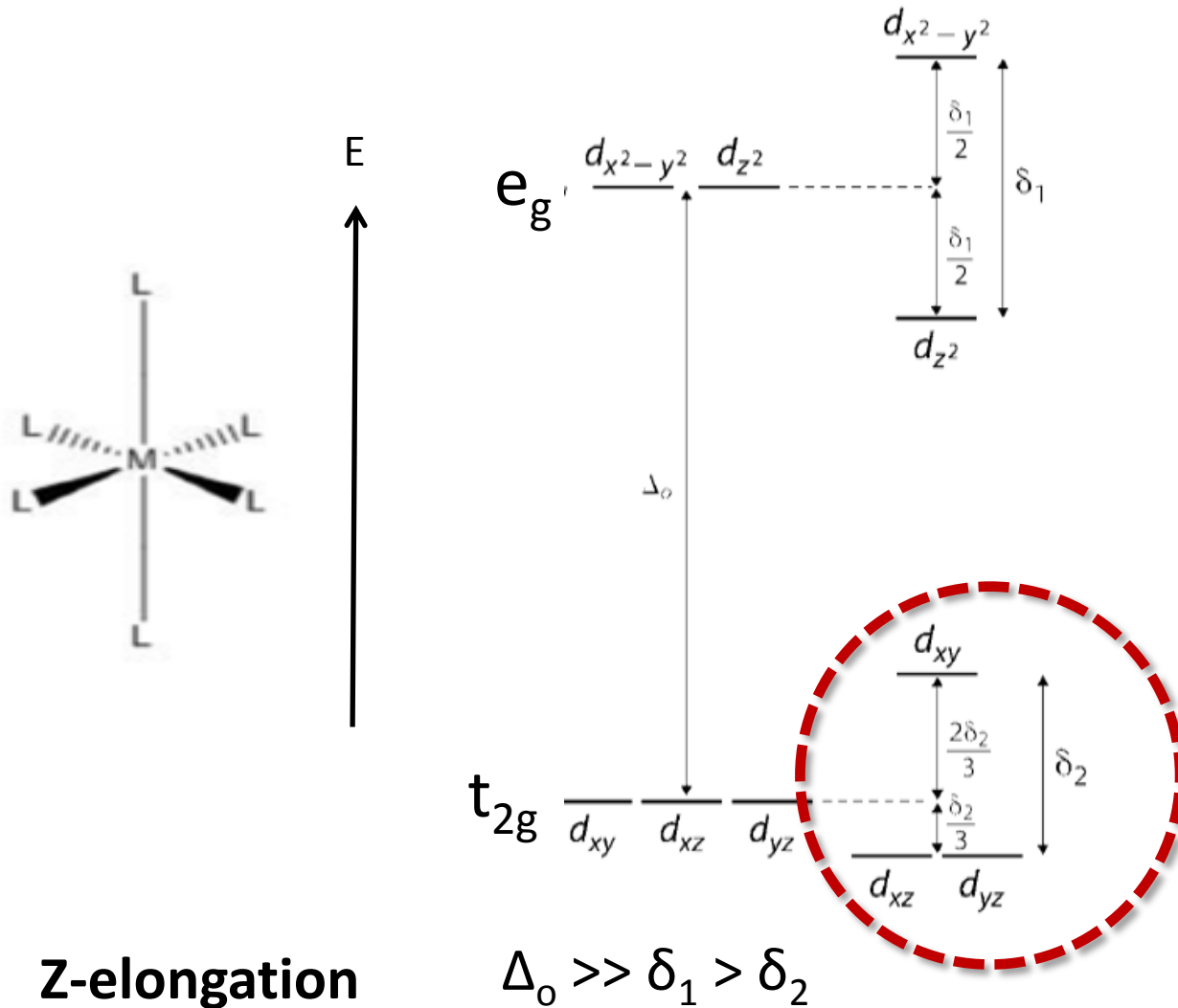
Summary of lecture 25

d^1 vs. d^9



Distortions are more pronounced if the degeneracy occurs in an e_g orbital

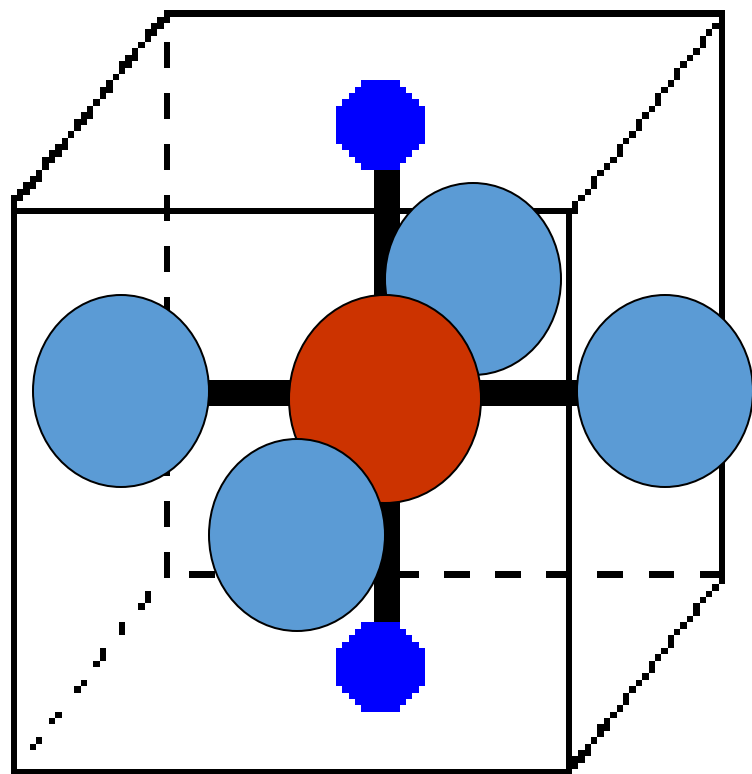
Summary of lecture 25



Summary of lecture 25

Natural distortion due to different kinds of bondings: No Jahn-Teller Distortion

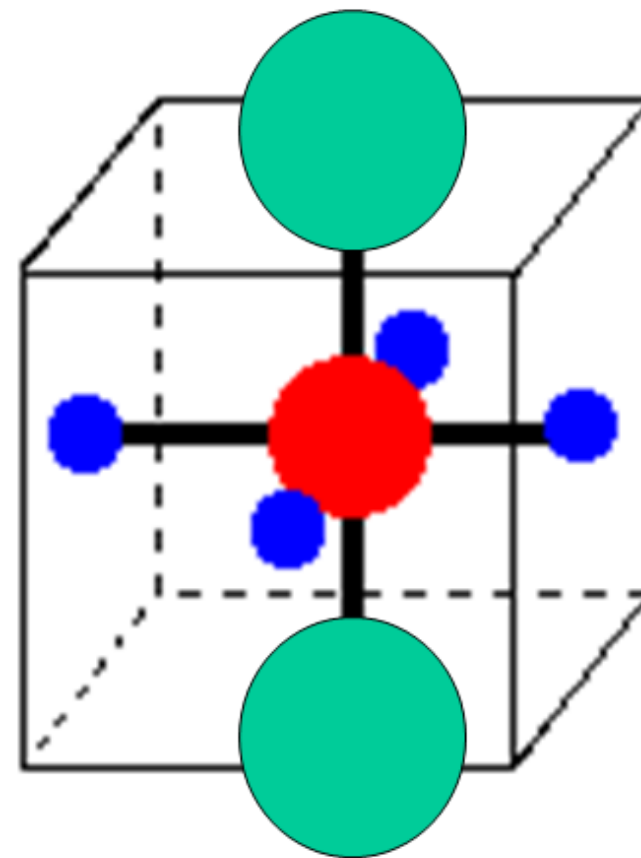
Example: $[\text{MnF}_2\text{Cl}_4]^{4-}$



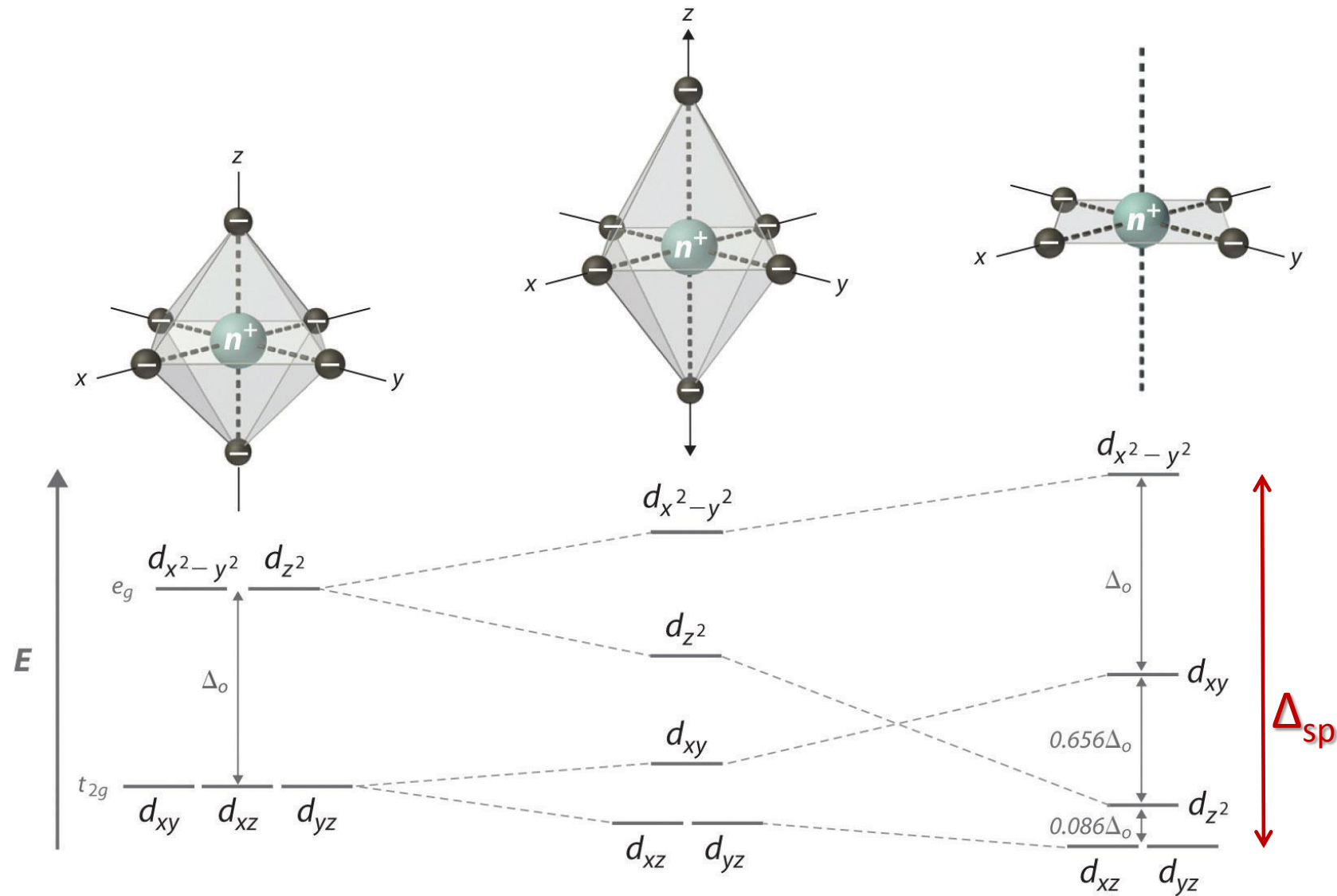
Compression
along z -axis

Elongation
along z -axis

Example: $[\text{MnF}_4\text{Cl}_2]^{4-}$

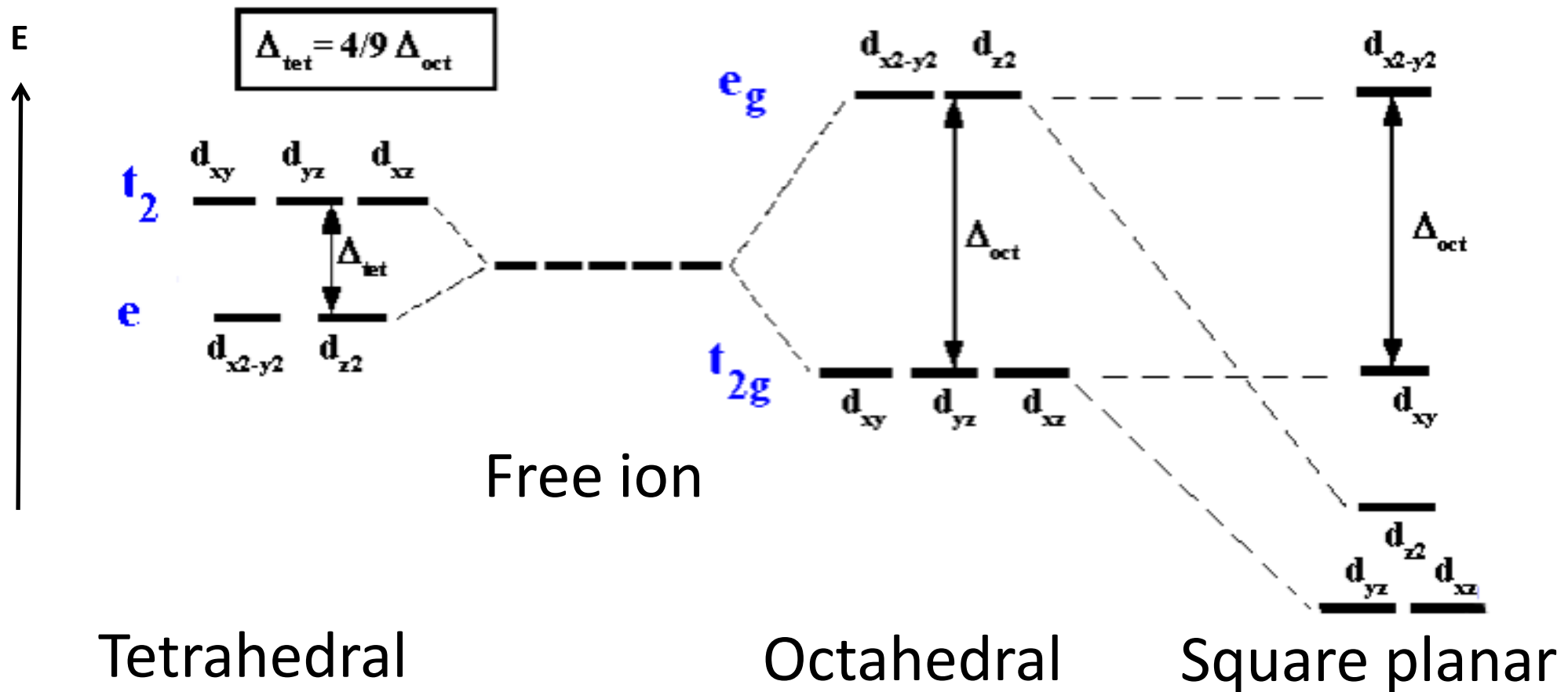


Summary of lecture 25



Oh vs. square planar geometry

Energy levels of the d-orbitals in common stereochemistries



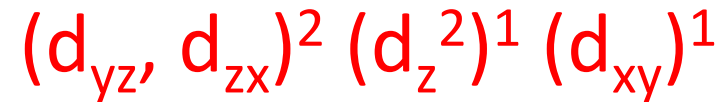
Square planar system: example



d^4

Cr^{2+}

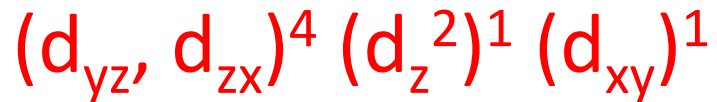
4 unpaired electrons



d^6

Fe^{2+}

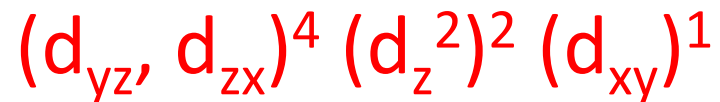
2 unpaired electrons



d^7

Co^{2+}

1 unpaired electron

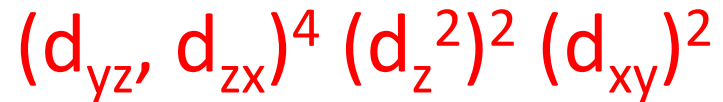


Square planar system: example



d^8

0 unpaired electrons



Ni^{2+} , Rh^+ , Ir^+

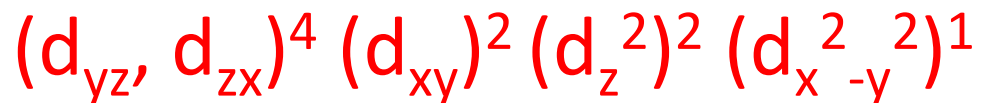
Strong ligands

Au^{+3} , Pt^{2+} , Pd^{2+}

Strong or weak ligands.

d^9 Cu^{2+}

1 unpaired electron



Example: d^8 system



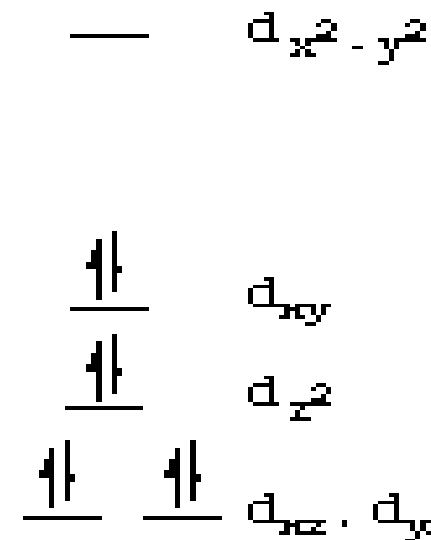
$\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2(\text{H}_2\text{O})_2$ - diamagnetic

$\text{Ni}^{+2} \rightarrow d^8 + \text{dia} \rightarrow \text{Square Planar}$

$[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; water is only lattice component.

d_z^2 is occupied and $d_{x^2-y^2}$ is vacant;

Ligands approach Only in x, -x, y, -y directions



Square planar d^8 complexes
are diamagnetic

Example: d^8 system

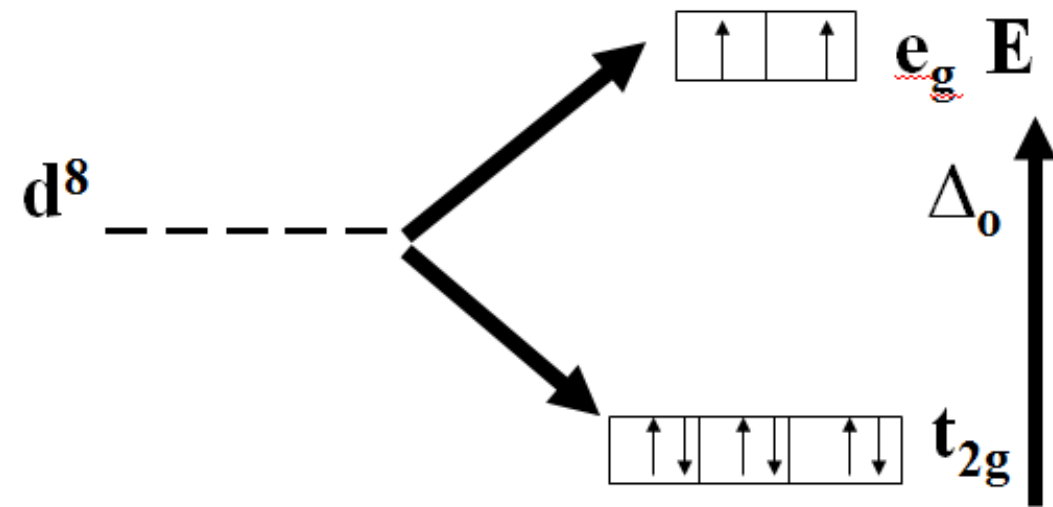


$\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2(\text{H}_2\text{O})_2$ - paramagnetic $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$

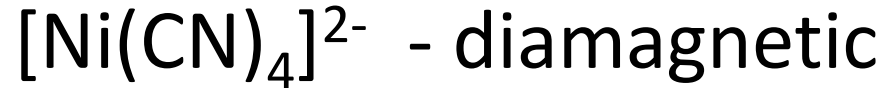
Here also $\text{Ni}^{+2} \rightarrow d^8$ but para \rightarrow Octahedral

d^8 configuration in a
strong/weak field is
 $t_{2g}^6 e_g^2$

Symmetric distribution



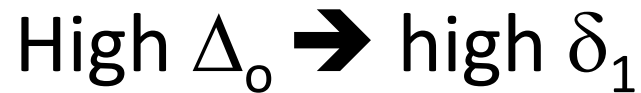
Example: d⁸ system



Here Nickel is in oxidation state +2;



Here this is entirely due to CN^- being a strong ligand.



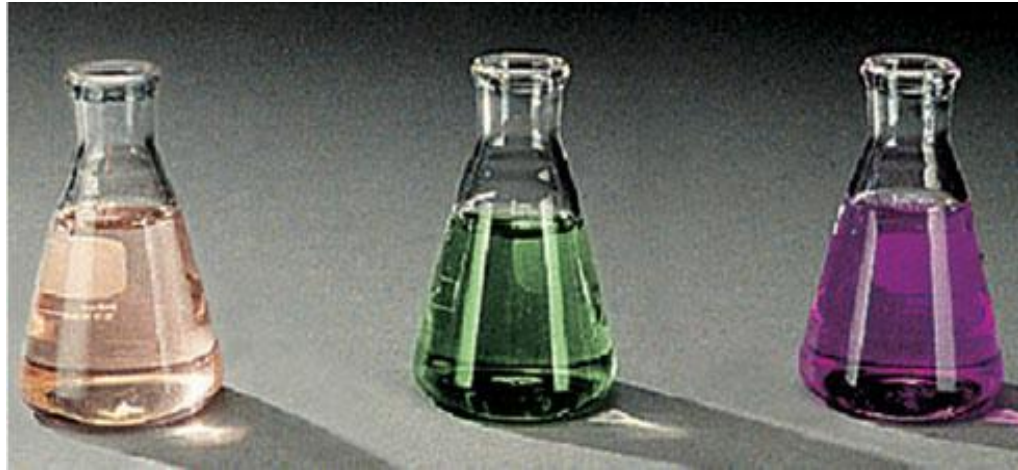
Here $\text{Ni}^0 \rightarrow d^{10}$ (No 4s electrons)
Therefore it has to be diamagnetic
as there is no unpaired electron in
the metal orbitals.

Are Jahn-Teller distortions possible in tetrahedral environments? Do you think such distortions are likely to occur? Justify your answer.

Jahn-Teller distortions are possible **whenever there is a partially filled degenerate set of energy levels**. This can of course occur here if either the e or t_2 levels are only partially filled. However, since **neither set of orbitals is oriented directly towards the ligands**, the relative amount of **stabilization gained is smaller** than when the e_g set is partially occupied in an octahedron so such distortions are much less likely to occur in a tetrahedral environment

Electronic spectra of octahedral complexes

Transition metal complexes

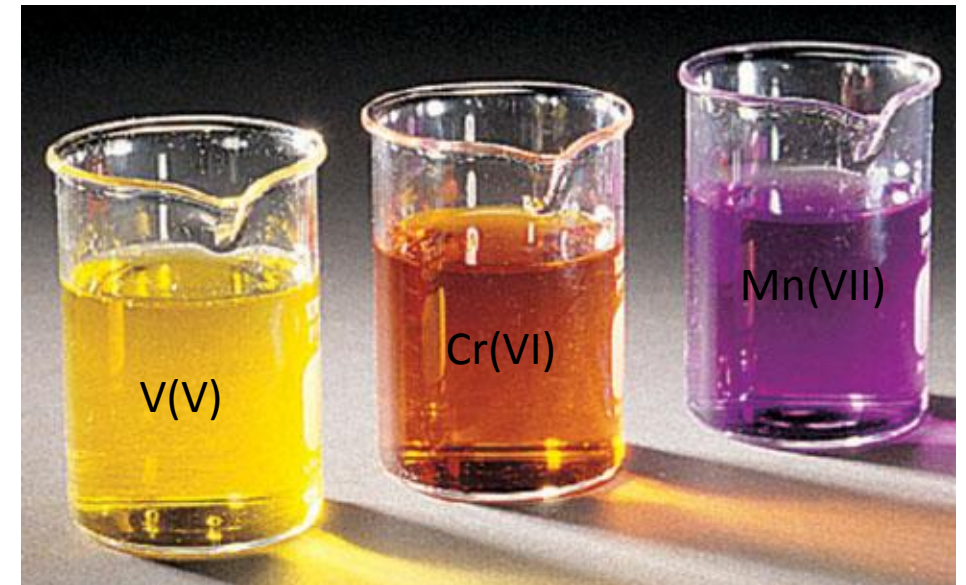
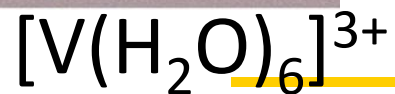
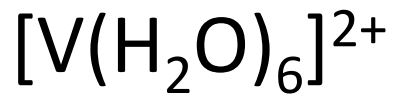


Mn(II)

Mn(VI)

Mn(VII)

One of the most characteristic chemical properties of these elements is the occurrence of *multiple oxidation states*.



V(V)

Cr(VI)

Mn(VII)

Electronic spectroscopy of Oh com.



Spectra arise because electrons may be promoted from one energy level to another

The spectrum of a colored solution may be measured quite easily using a spectrophotometer

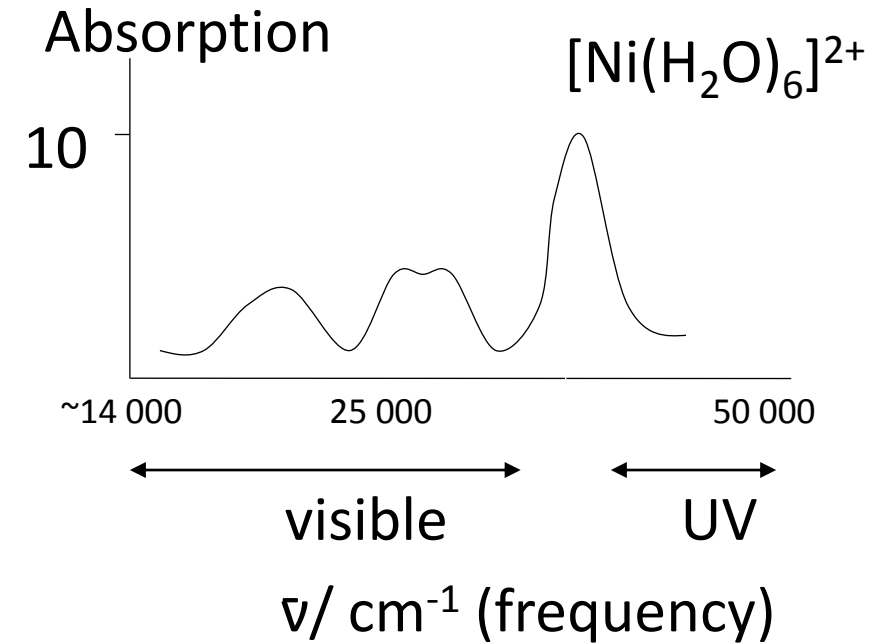
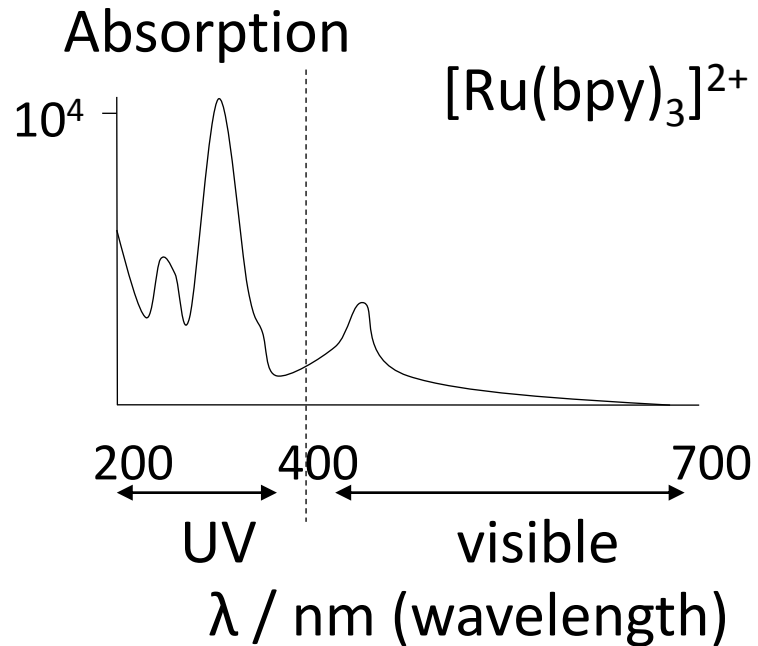
$$\log(I_0/I) = A$$

$$A = \epsilon \cdot c \cdot l$$

Electronic spectroscopy of Oh com.



Absorption of radiation leading to electronic transitions within a molecule or complex



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

Electronic spectroscopy of Oh com.



Absorption maxima in a visible spectrum have **three important characteristics**

1. **number** (how many)

This depends on the electron configuration of the metal centre

2. **position** (what wavelength/energy)

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

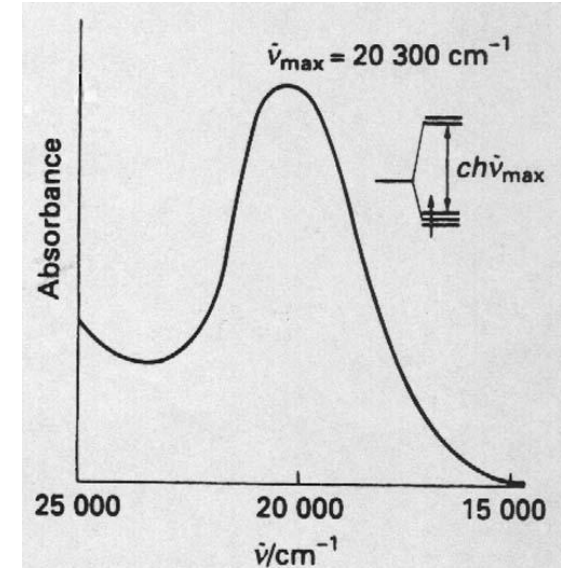
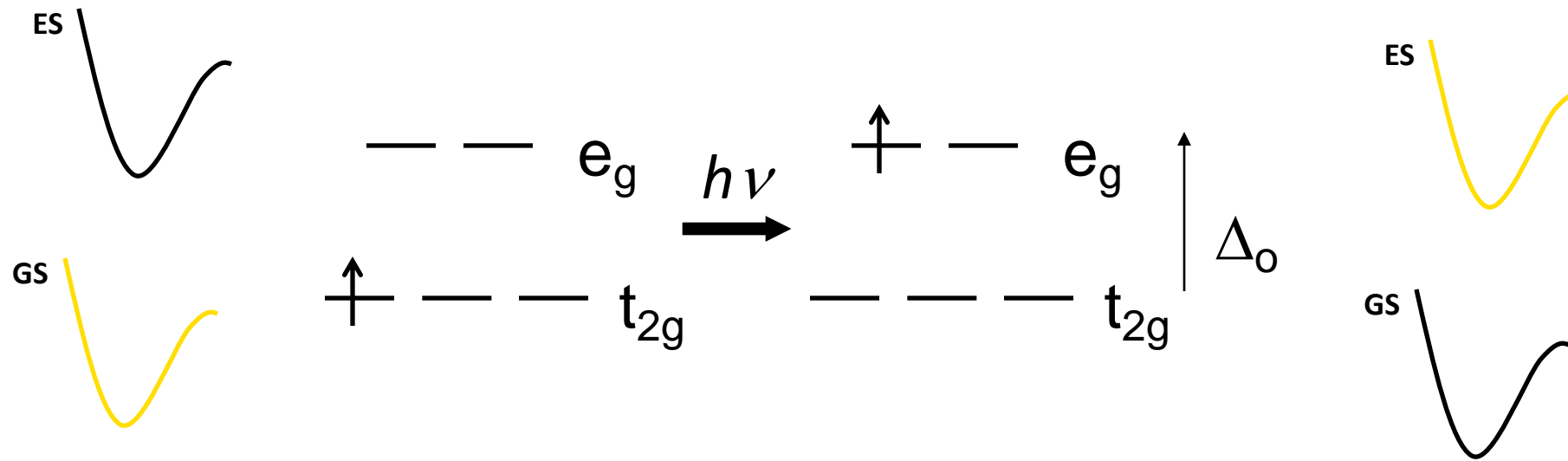
3. **intensity**

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

Electronic spectroscopy of Oh com.



The energy of the absorption by $[\text{Ti}(\text{OH}_2)_6]^{3+}$ is the ligand-field splitting, Δ_o



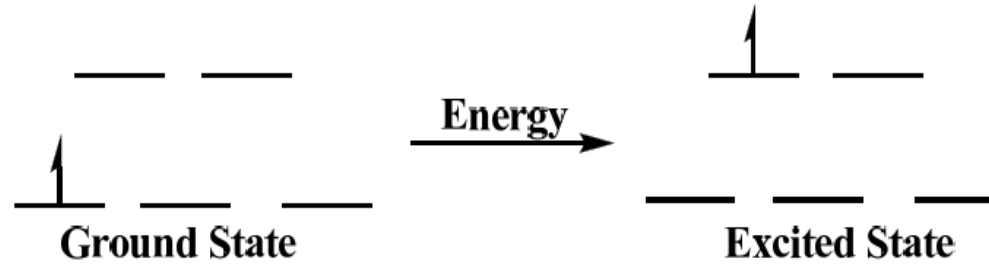
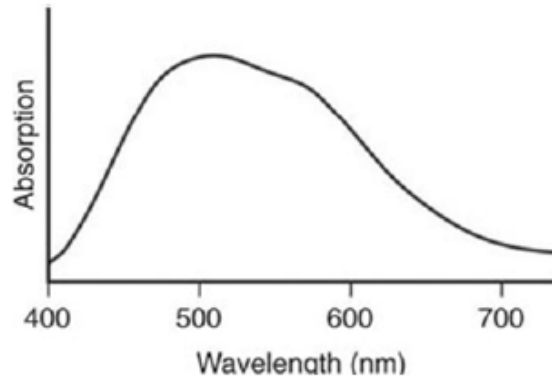
complex in electronic
ground state (GS)

→ d-d transition →

complex in electronic
excited state (ES)

$[\text{Ti}(\text{OH}_2)_6]^{3+} \lambda_{\text{max}} = 510 \text{ nm}$ Δ_o is 243 kJ mol^{-1} or $20\,300 \text{ cm}^{-1}$
($3d^1$ system)

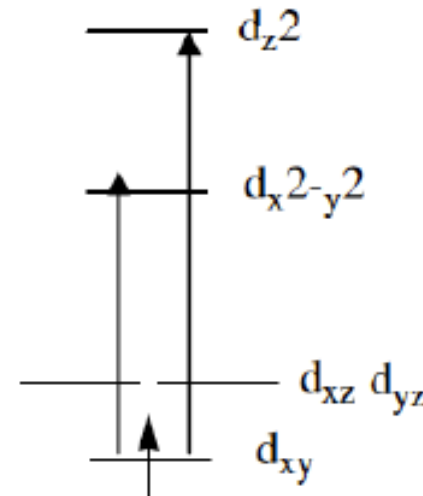
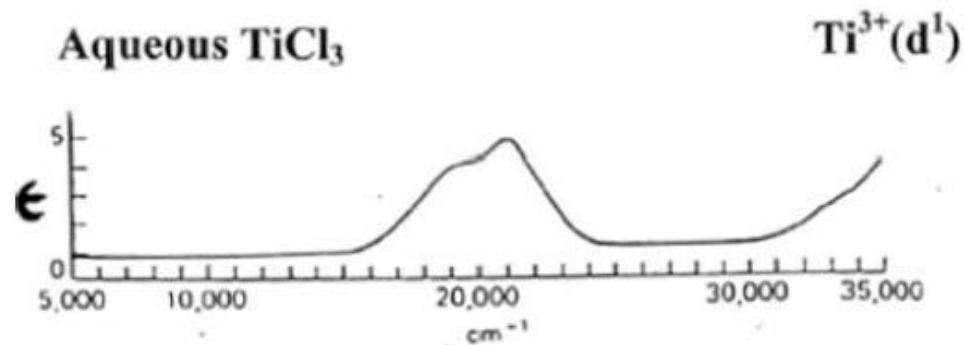
Color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex



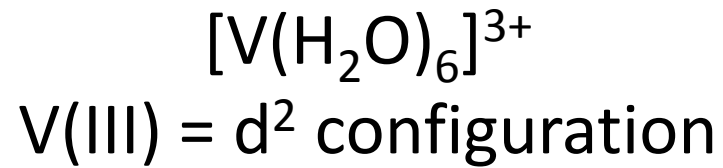
Absorption at 520 nm gives the complex its purple color



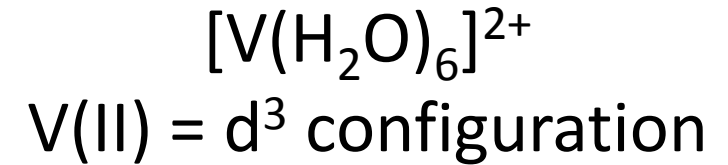
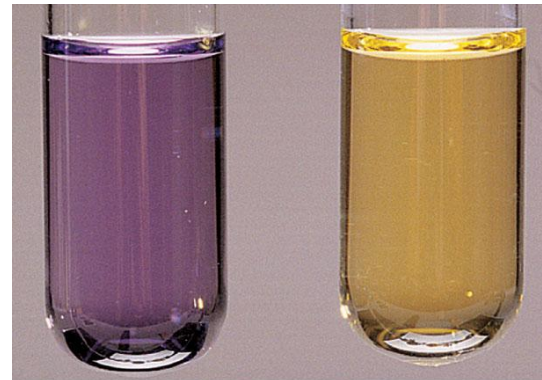
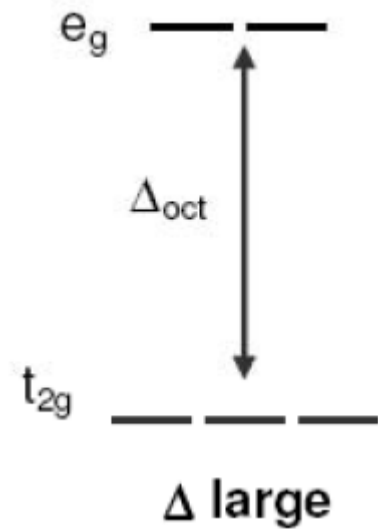
A more resolved absorption spectrum of the complex has a shoulder



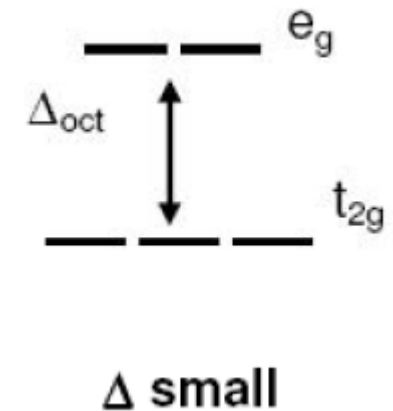
Color and CFT



Violet light absorbed
complex appears yellow



Yellow light absorbed
complex appears violet



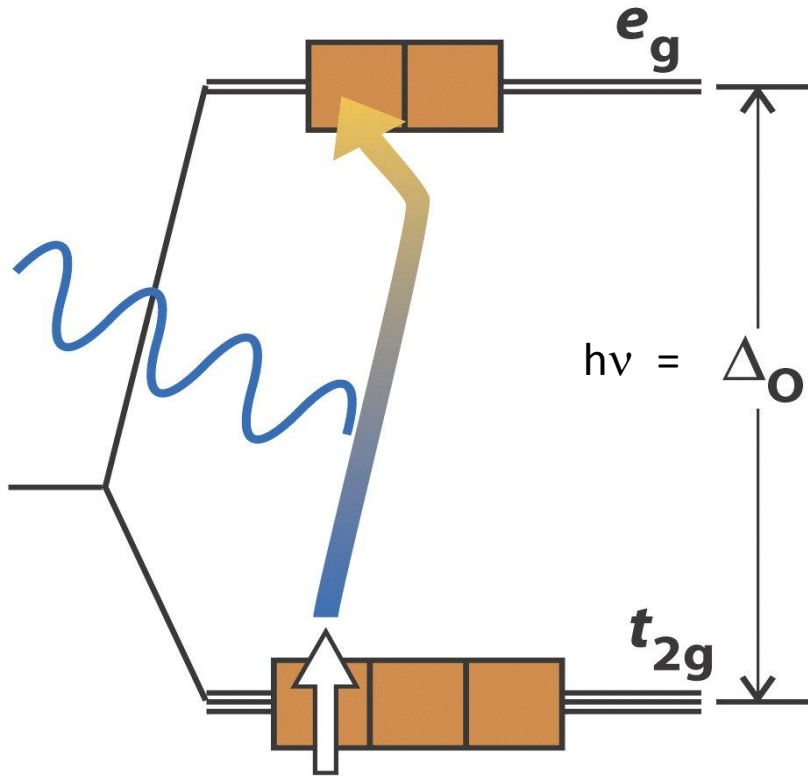
Why different colors??



The color of the aqueous solution is due to the transition of electrons from one d level to another d level.....**why not only one color??**
different colors are seen for different compounds because,

- ✓ The d orbitals are at different energy levels and hence there are many transition
- ✓ The splitting of d orbitals in different environments
- ✓ The splitting depends upon the geometry of the complex, the nature of the ligands, and the oxidation state of the central metal atom

Electronic spectroscopy of Oh com.



The energy gap between the e_g and t_{2g} orbitals, Δ_o , (the crystal field splitting) equals the energy of a photon:

$$\Delta_o = h\nu = \Delta E$$

As Δ_o varies, $h\nu$ will also vary and the color of the compound will change

Absorption of a photon causes a jump from a t_{2g} to an e_g orbital

Electronic spectroscopy of Oh com.



- ❖ Laporte 'orbital' selection rule: Transitions which involve a change in the subsidiary quantum number $\Delta l = \pm 1$ are “Laporte allowed” and therefore have a high absorbance.
- ❖ Thus, for Ca, $s^2 = s^1p^1$, l changes by +1 and ϵ is very high. In contrast d-d transitions are “Laporte forbidden” and ϵ is less. Transition metal ion forms a complex and surrounded by ligands, *mixing of d and p orbitals*.
- ❖ Spin selection rule: During transitions between energy levels, an electron does not change its spin, i.e., $\Delta S = 0$ (why Mn^{2+} high spin complexes are off white or pale flesh colored?)

Ground state term symbol

Ground terms
for d^1 - d^{10}
configurations

Configuration	Example	Ground term	m_l	M_L	S
			2 1 0 -1 -2		
d^1	Ti ³⁺	2D	↑	2	$\frac{1}{2}$
d^2	V ³⁺	3F	↑ ↑	3	1
d^3	Cr ³⁺	4F	↑ ↑ ↑	3	$\frac{1}{2}$
d^4	Cr ²⁺	5D	↑ ↑ ↑ ↑	2	2
d^5	Mn ²⁺	6S	↑ ↑ ↑ ↑ ↑	0	$2\frac{1}{2}$
d^6	Fe ²⁺	5D	↑↓ ↑ ↑ ↑ ↑	2	2
d^7	Co ²⁺	4F	↑↓ ↑↓ ↑ ↑ ↑	3	$\frac{1}{2}$
d^8	Ni ²⁺	3F	↑↓ ↑↓ ↑↓ ↑ ↑	3	1
d^9	Cu ²⁺	2D	↑↓ ↑↓ ↑↓ ↑↓ ↑	2	$\frac{1}{2}$

Discussed topics.....

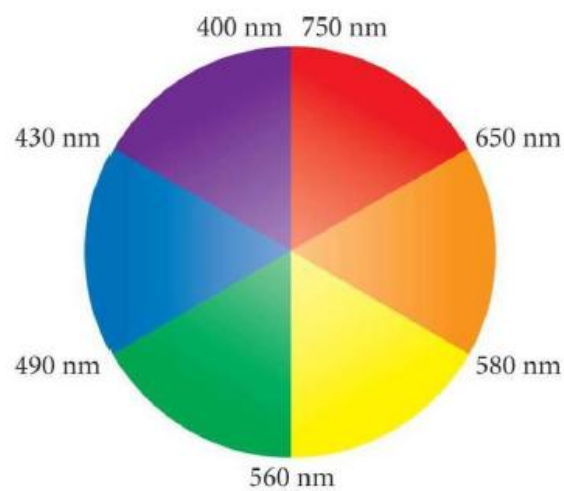


- ✓ Octahedral vs. square planar geometry
- ✓ Electron distribution in square planar system
- ✓ Example of square planar system
- ✓ Electronic spectra of octahedral complex
- ✓ Different colors in octahedral complexes

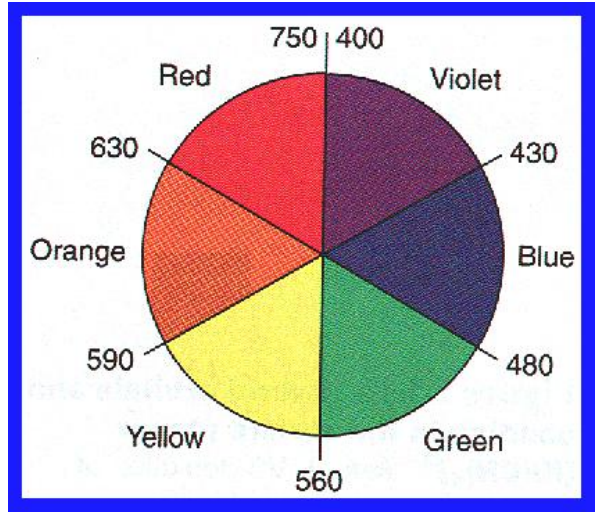
Color of Transition metal comp. (supporting slide)



Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520



absorbed
color



observed
color