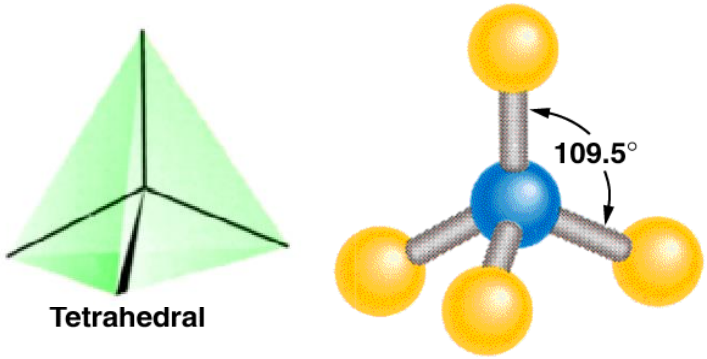
Bonding in Transition Metal compounds
Uv-Vis Spectroscopy

- The total number of points of attachment to the central element is termed the **coordination number** and this can vary from 2 to as many as 16, but is usually 6.

- In simple terms, the coordination number of a complex is influenced by the **relative sizes** of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the **electronic configuration** of the metal ion.

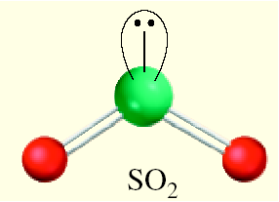
Methane



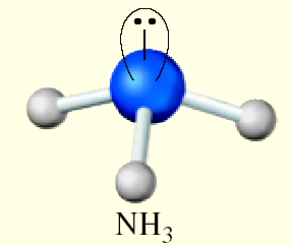
- Based on the radius ratio, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate.

- It is important to recognize that every geometry has a specific coordination number, but every complex wish a specific coordination number will have a choice of several possible geometries (i.e., there is not a one-to-one correspondance between coordination number and geometry).

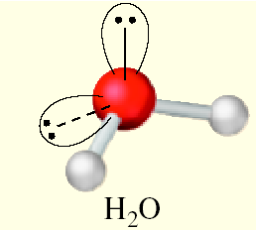
bent



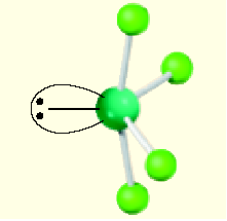
trigonal pyrami



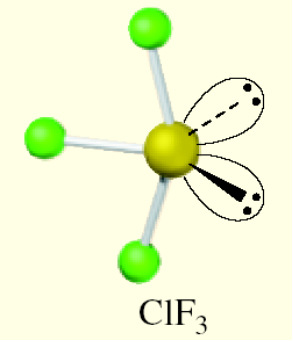
bent



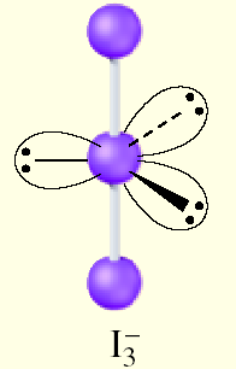
distorted tetrahed



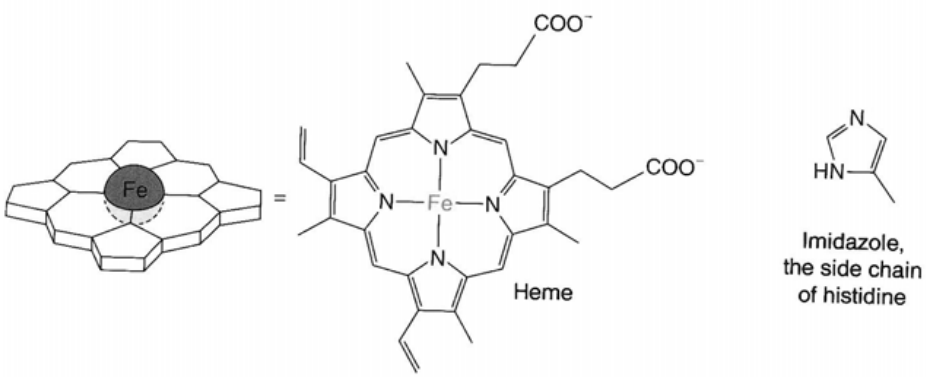
T-shaped



linear



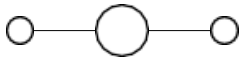
Coordination Geometry



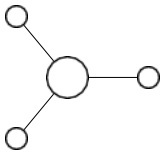
- Metals can dictate the coordination geometry, but usually ligands play a larger role, especially in biological systems.

Standard Coordination Geometries, CN = 2, 3

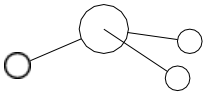
Linear



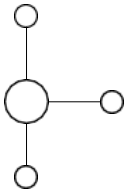
Trigonal



Pyramidal

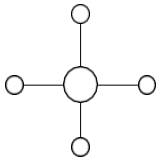


T-Shaped

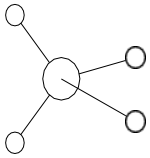


Standard Coordination Geometries, CN = 4

Square planar

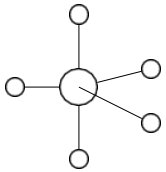


Tetrahedral

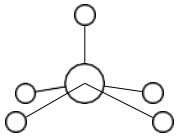


Standard Coordination Geometries, CN = 5, 6

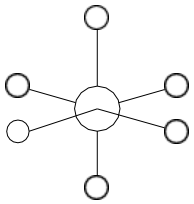
Trigonal bipyramidal



Square pyramidal

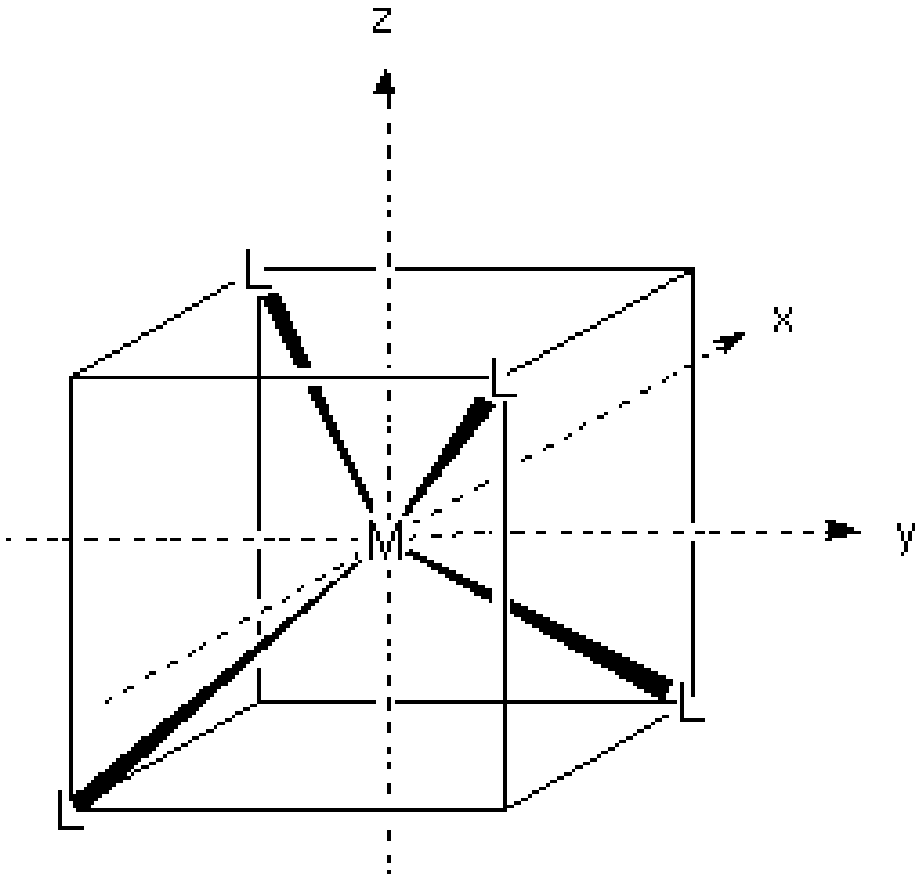


Octahedral



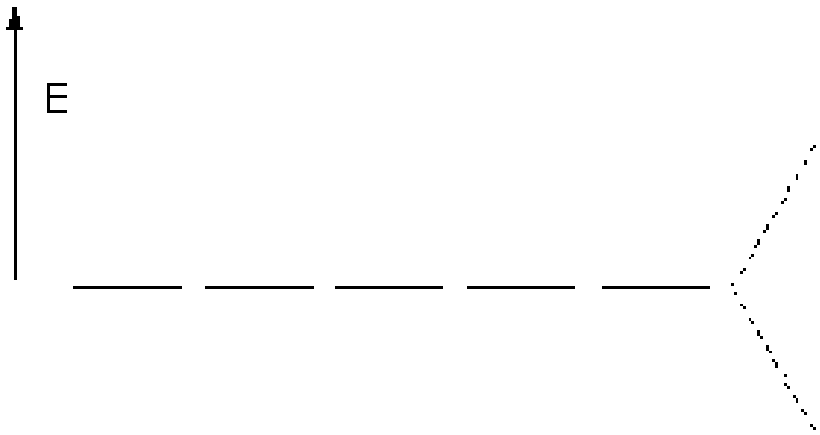
- Which set of d-orbitals comes in closer contact to the ligands (and is therefore de-stabilized) ?

A. d_{xz}, d_{yz} and d_{xy}
B. d_{xz}, d_{yz} and d_{z^2}
C. $d_{x^2-y^2}$ and d_{z^2}
D. $d_{x^2-y^2}$, d_{xz} and d_{xy}
E. d_{xz} and d_{yz}



Energy Level Splitting

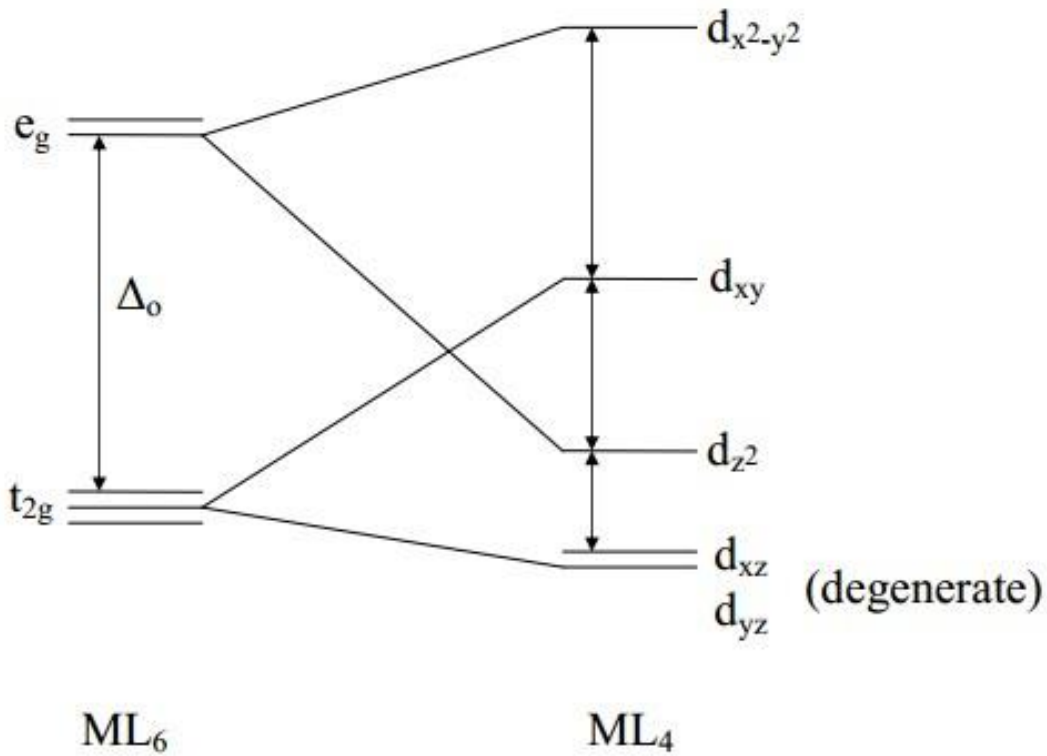
- How do we expect the d-energy levels to split up in a tetrahedral field ?

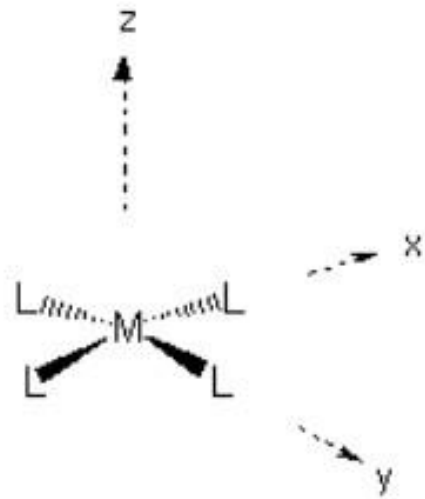


How many d-electrons are OK for tetrahedral ?

Square Planar from Octahedral

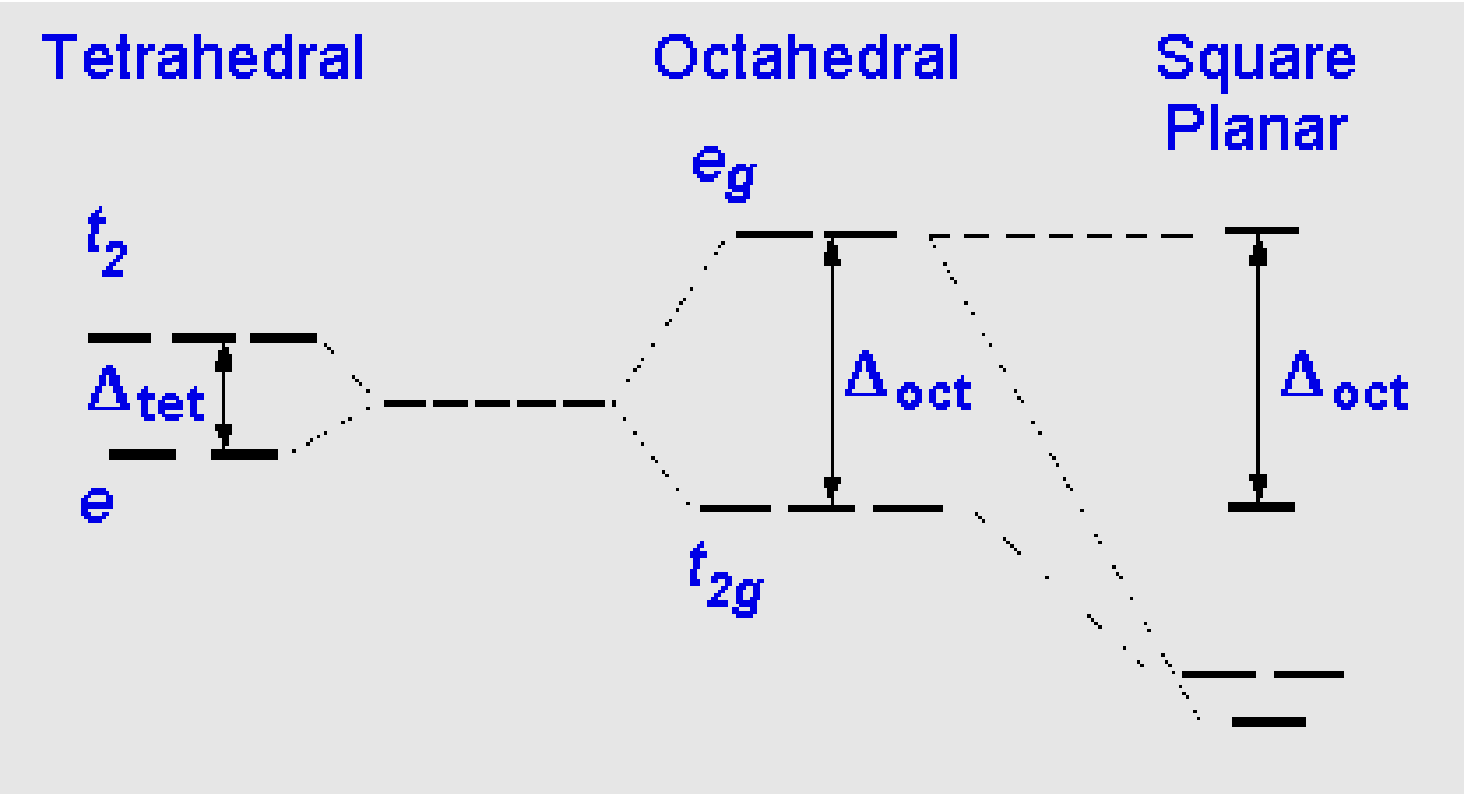
- How would the d-orbitals split from an octahedral complex ?





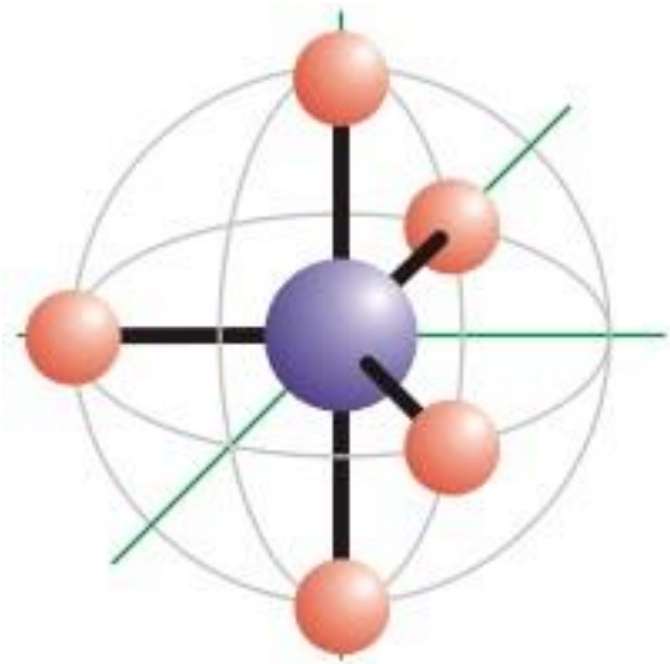
How many d-electrons are OK for square-planar ?

- d-orbital energy split according to the ligand coordination:

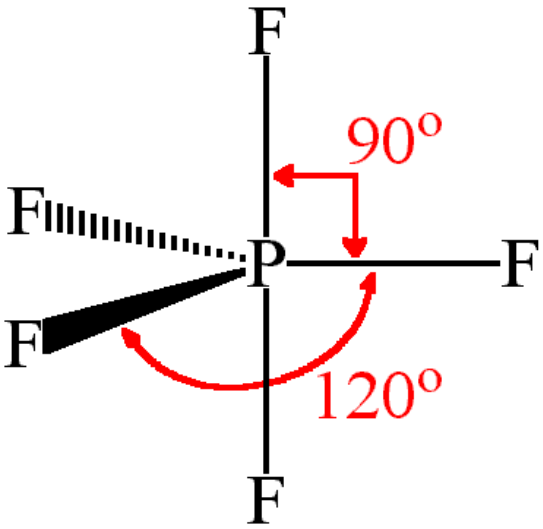


Identify the d-orbitals for each coordination !

Trigonal bipyramidal ML_5



For example
(refer to VSEPR Theory !)



High spin and low spin complexes

- A method to determine the spin of a complex is to look at its field strength and the wavelength of color it absorbs.
- If the field is strong, it will have few unpaired electrons and thus low spin.
- If the field is weak, it will have more unpaired electrons and thus high spin.
- In terms of wavelength, a field that absorbs high energy photons (in other words, low wavelength light) has low spin and a field that absorbs low energy photons (high wavelength light) has high spin.
- Once again, whether a complex is high spin or low spin depends on two main factors:
  1. The crystal field splitting energy and the pairing energy. The electrons will take the path of least resistance, the path that requires the least amount of energy.
  2. If the paring energy is greater than Δ, then electrons will move to a higher energy orbital because it takes less energy. If the pairing energy is less than Δ, then the electrons will pair up rather than moving singly to a higher energy orbital

Example

Question:

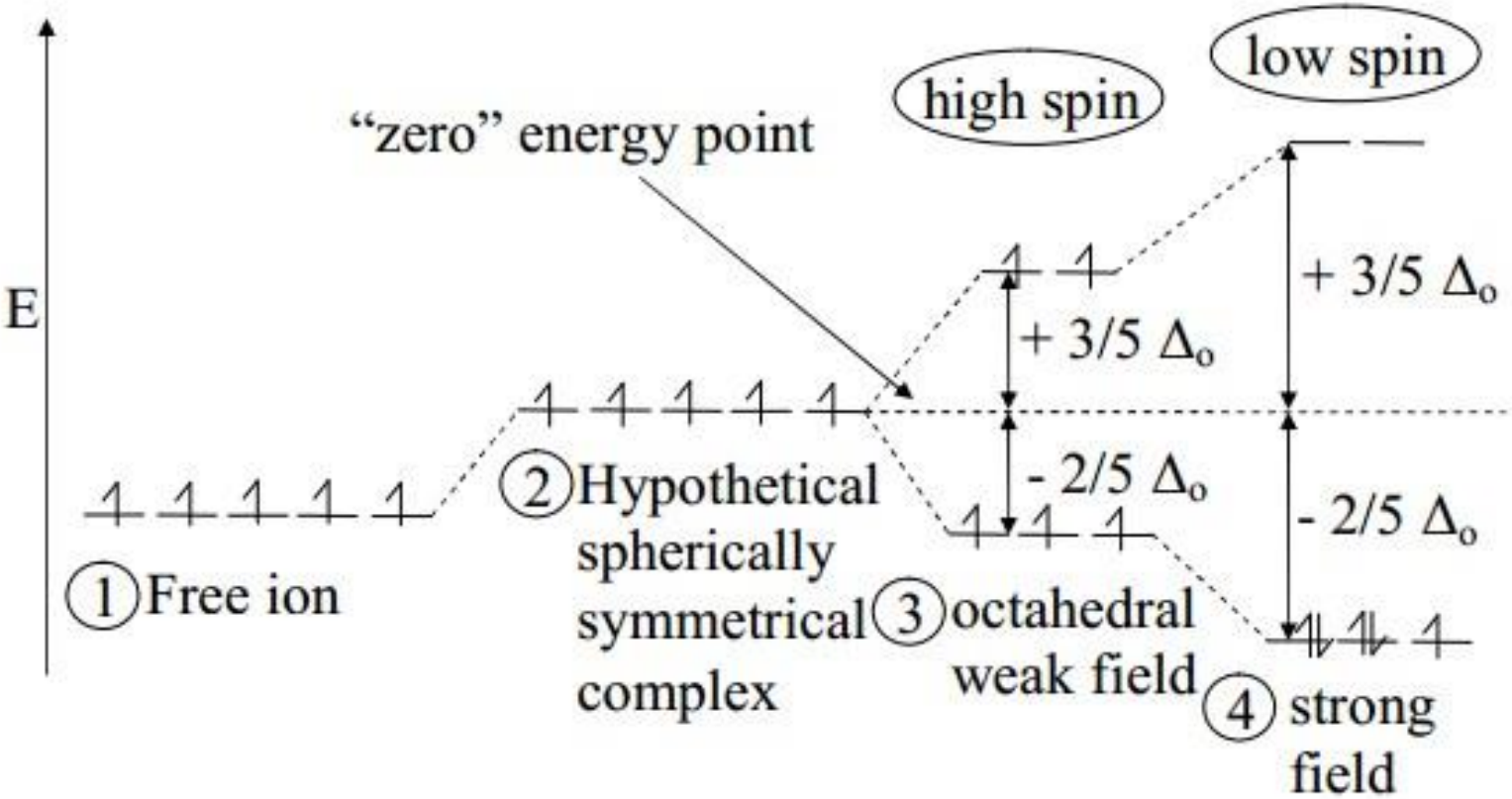
Is the $[Co(H_2O)_6]^{3+}$complex ion expected to be high or low spin?

SOLUTION:

- What do we know?
- The complex has an octahedral shape
- The aqua ligand (H_2O) is typically regarded as weak-field ligand
- The d electron configuration for Co is d^6
- The splitting energy is small
- Therefore, the complex is expected to be high spin.

Crystal Field Splitting Energy (CFSE)

High – spin Fe(III) example $[Fe(H_2O)_6]^{3+}$
Low – spin Fe(III) example $[Fe(CN)_6]^{3-}$



(CFSE)

What is the difference in the energies of the electrons in $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ → called **Crystal Field Splitting Energy (CFSE)**

$t_{2g}^{3}\ e_g^{2}$ versus $t_{2g}^{5}\ e_g^{0}$

$$\begin{array}{r} 3x(-2/5\Delta_o) \\ \underline{+\ 2x(3/5\Delta_o)} \\ 0 \end{array} \qquad \begin{array}{r} 5x(-2/5\Delta_o) \\ \underline{+\ 0x(3/5\Delta_o)} \\ -2\Delta_o \end{array}$$

So it depends on the magnitude of Δ and P which configuration is more stable

Summary

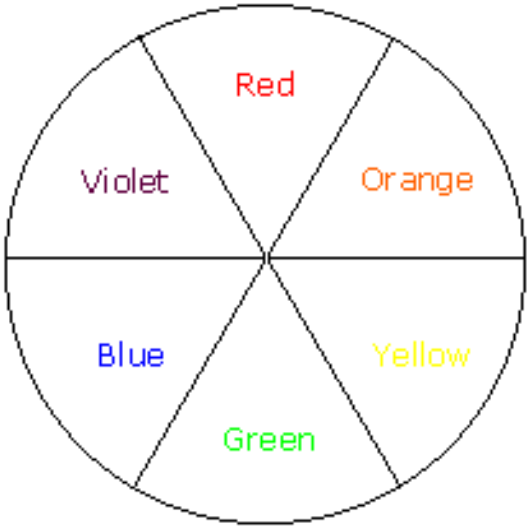
- Two factors determine the geometry of a compound:
  - CFSE
  - Steric influences

- Most common compounds are octahedral ML_6 (middle of the TM block) and trigonal-bipyramidal
- Tetrahedral ML_4 are common for the first row TM's
- Square-planar ML_4 are typical for 2nd and 3rd row TM's
- d^{10} ions arrange ligands according to their ox. numbers and max. distance of the ligands to each other

UV-VIS Spectroscopy

Light absorption by electron transfers

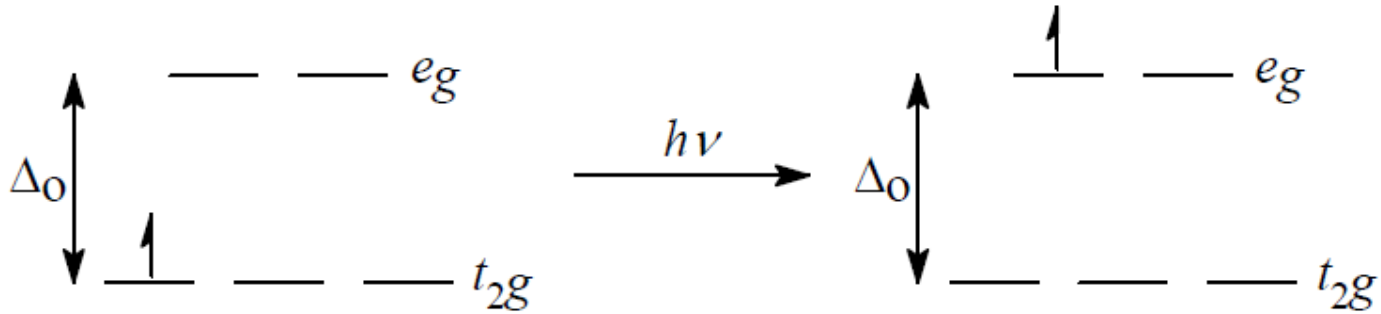
Visible Colors



Colour of light *absorbed*	**Approximate wavelength ranges / nm**	**Colour of light *transmitted***
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow

Spectrum of d^1 complex

Only one allowed electron transition:



Ground state:

- triple degenerated => "**T**"
- Spin ½ => S= (2s+1) = **2**
- Name: "$^2\mathbf{T_{2g}}$"

Excited state:

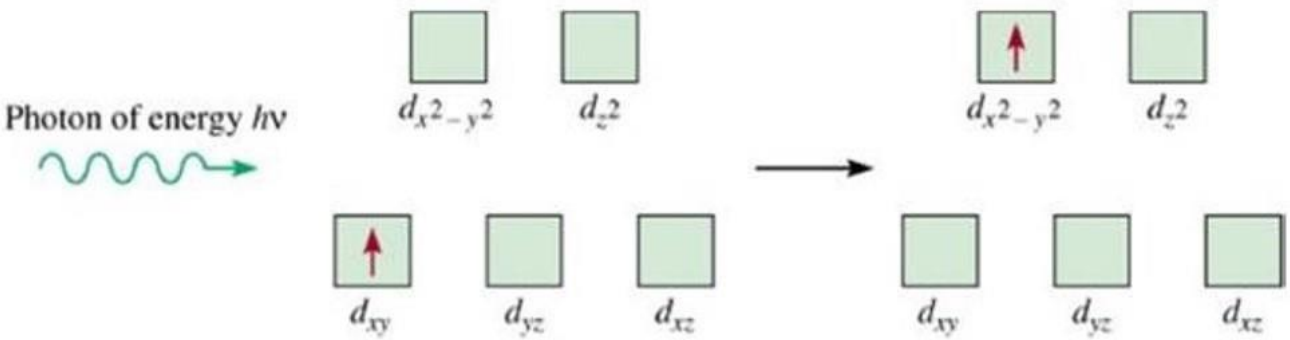
- double degenerated => "**E**"
- Spin ½ => S= (2s+1) = **2**
- Name: "$^2\mathbf{E_g}$"

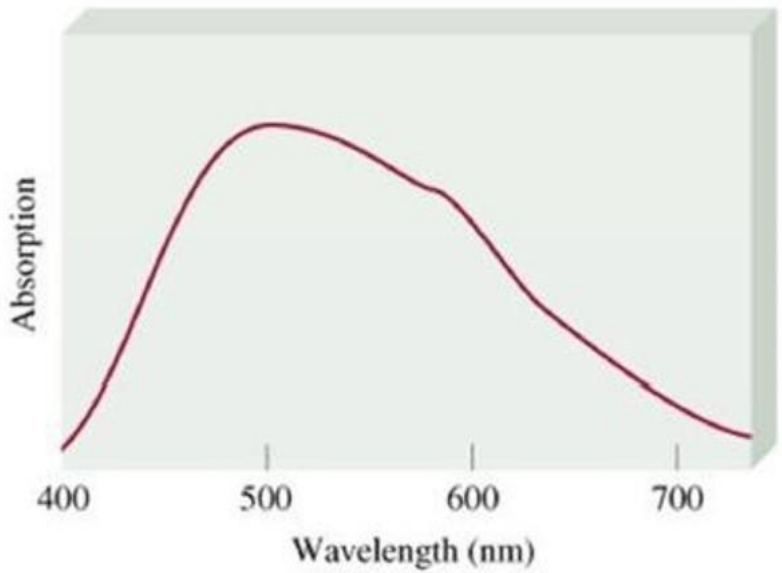
Selection Rules

a) Laporte rule:
we should have a change in parity (g→u , u→g)

b) Spin selection rule:
spin multiplicity must not change ($^3A \rightarrow {}^3T$ ok)

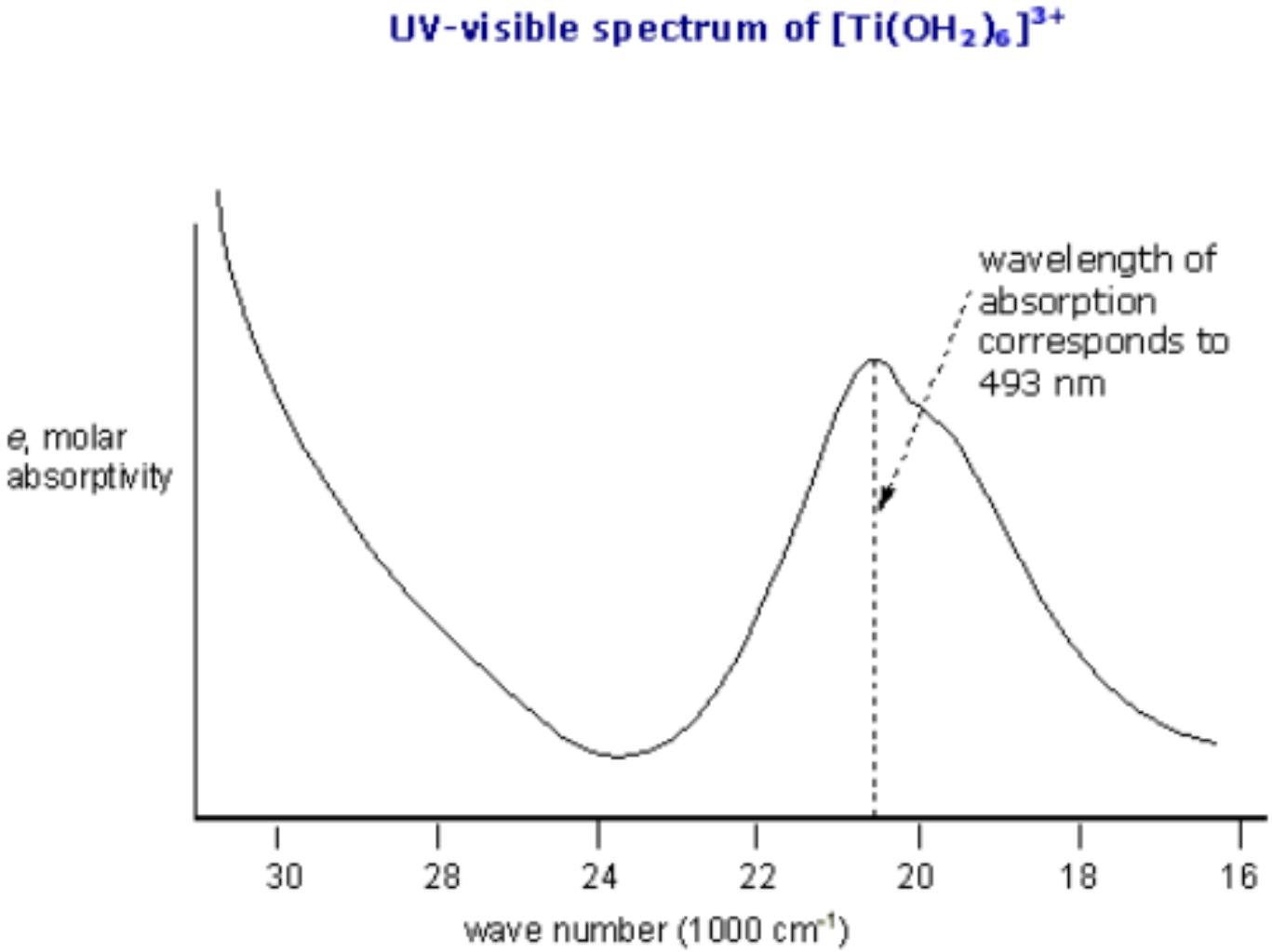
- Rule (a) is always NOT fulfilled for d-d transitions; therefore, these are only of moderate intensity !


Photon of energy hν
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{yz}
d_{xz}
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{yz}
d_{xz}


Absorption
400
500
600
700
Wavelength (nm)

$$\Delta = h\nu$$

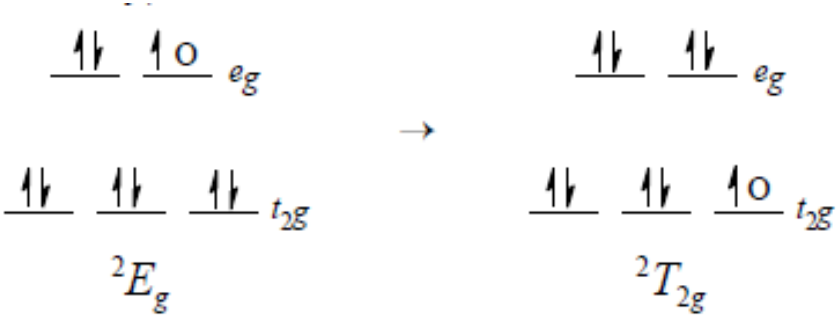
How to convert between cm^{-1} and nm ?



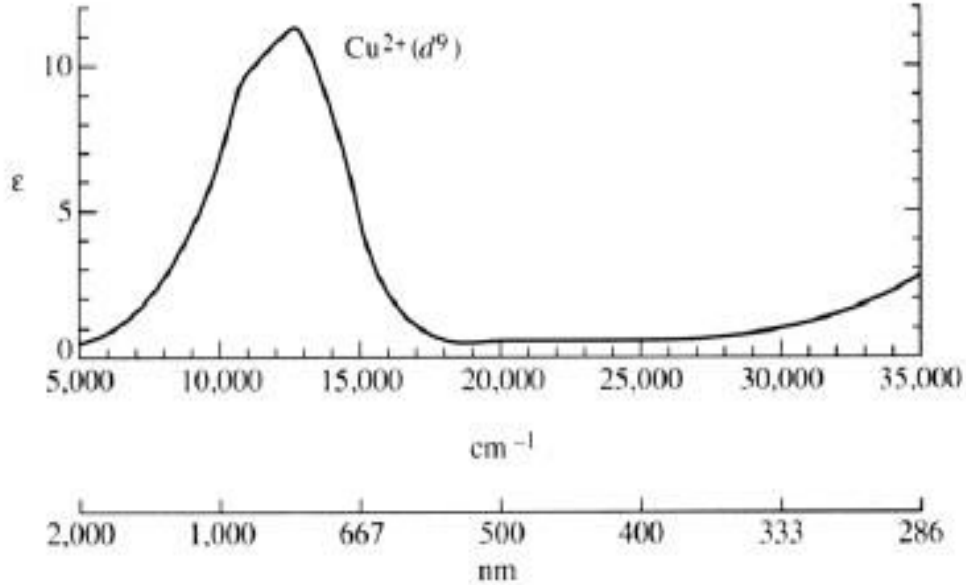
d^1 and d^9

Electronic states in Cu^{2+}:

We look at the state of the electron-hole



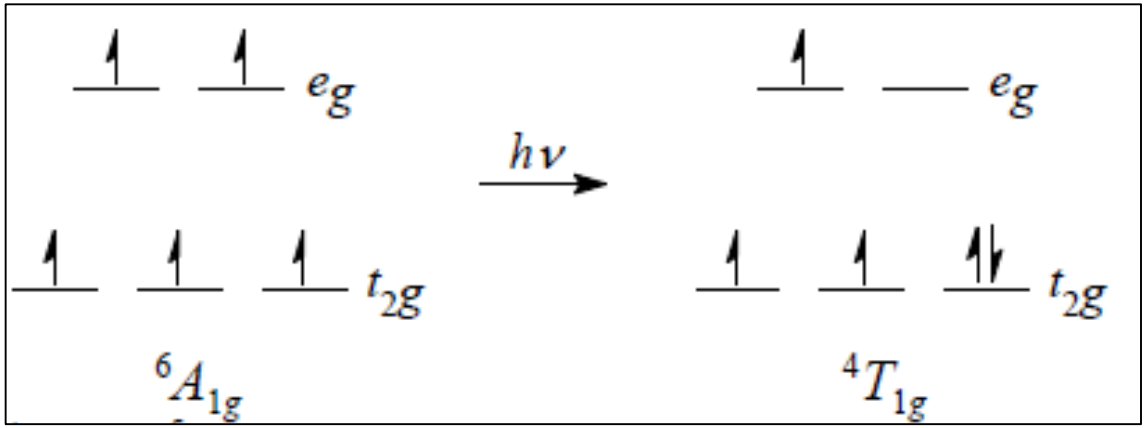
$Cu(H_2O)_6^{2+}$ has a blue color due to the single $^2E_g \rightarrow {}^2T_{2g}$ electronic transition at ~800 nm.



d^5 high spin case

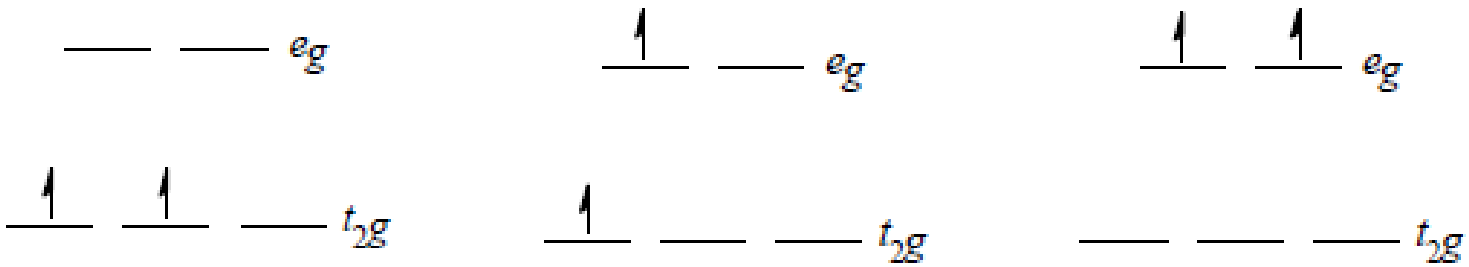
- The only possible transition is “spin-forbidden”
- Only very small peak in the spectrum
- Only weak color of the compound

- Which transitions are possible for the low spin case?



$$^2T_{2g} \rightarrow (^2A_{2g}, {}^2T_{1g}) \quad ^2T_{2g} \rightarrow {}^2E_g \quad ^2T_{2g} \rightarrow {}^2A_{1g}$$

d^2 case



$t_{2g}^{\,2} \rightarrow {}^3T_{1g}(F)$ $\quad$ $t_{2g}^{\,1}e_g^{\,1} \rightarrow {}^3T_{1g}(P) + {}^3T_{2g}$ $\quad$ $e_g^{\,2} \rightarrow {}^3A_{2g}$

$${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$$

$${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$$

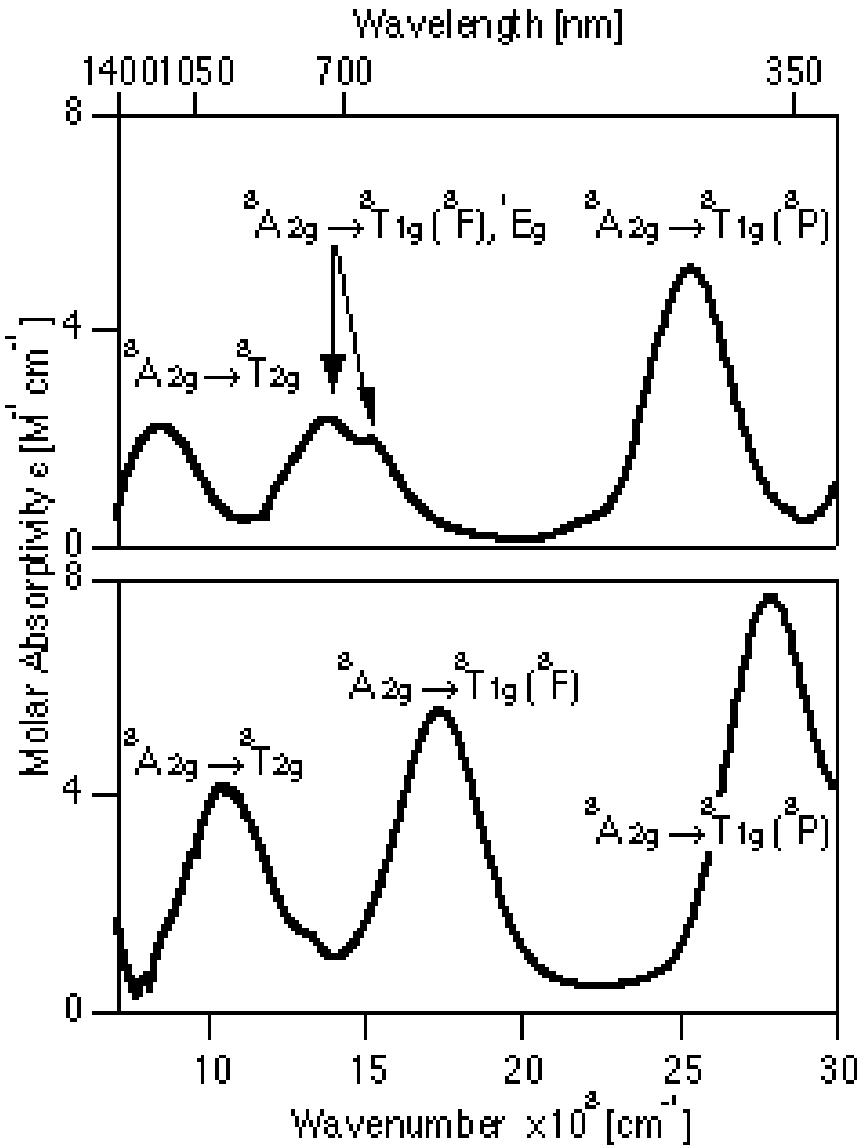
the 2 electrons are in orthogonal orbitals

the 2 electrons are in orbitals in the same plane

=> 2 different energies of the 2 states !

Compare 2 Ni-compounds

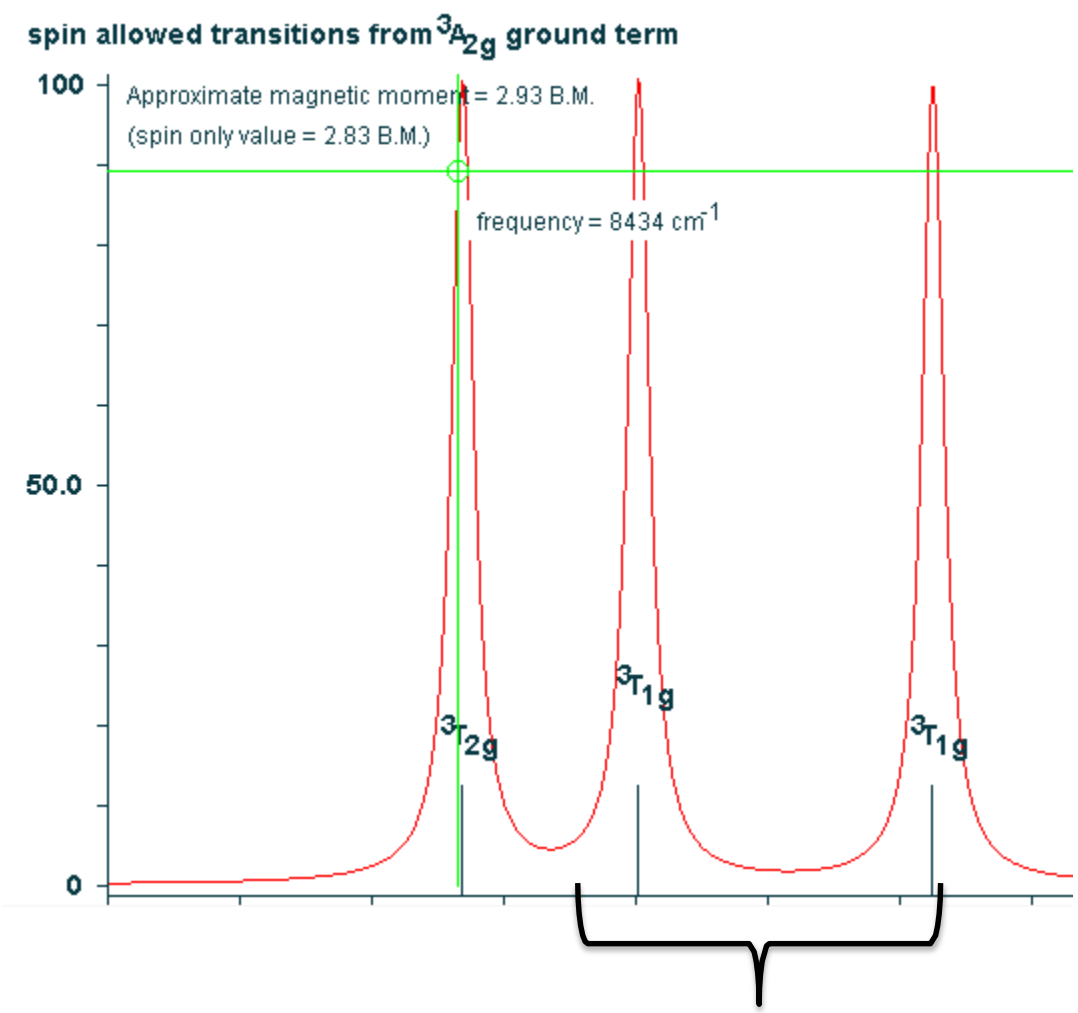
- $Ni(H_2O)_6$ (2+) Color:
- $Ni(NH_3)_6$ (2+) Color:
- Which compound absorbs light at higher energy ?
- Find the ground- and excited electron states



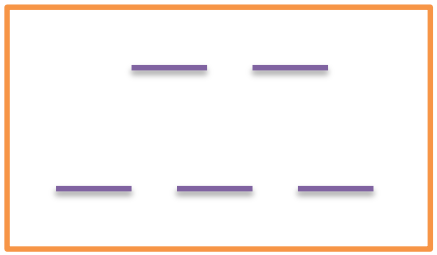
http://jchemed.chem.wisc.edu/JCEWWW/Articles/JCENi/JCENi.html

Simulation

http://firstyear.chem.usyd.edu.au/calculators/dd.shtml

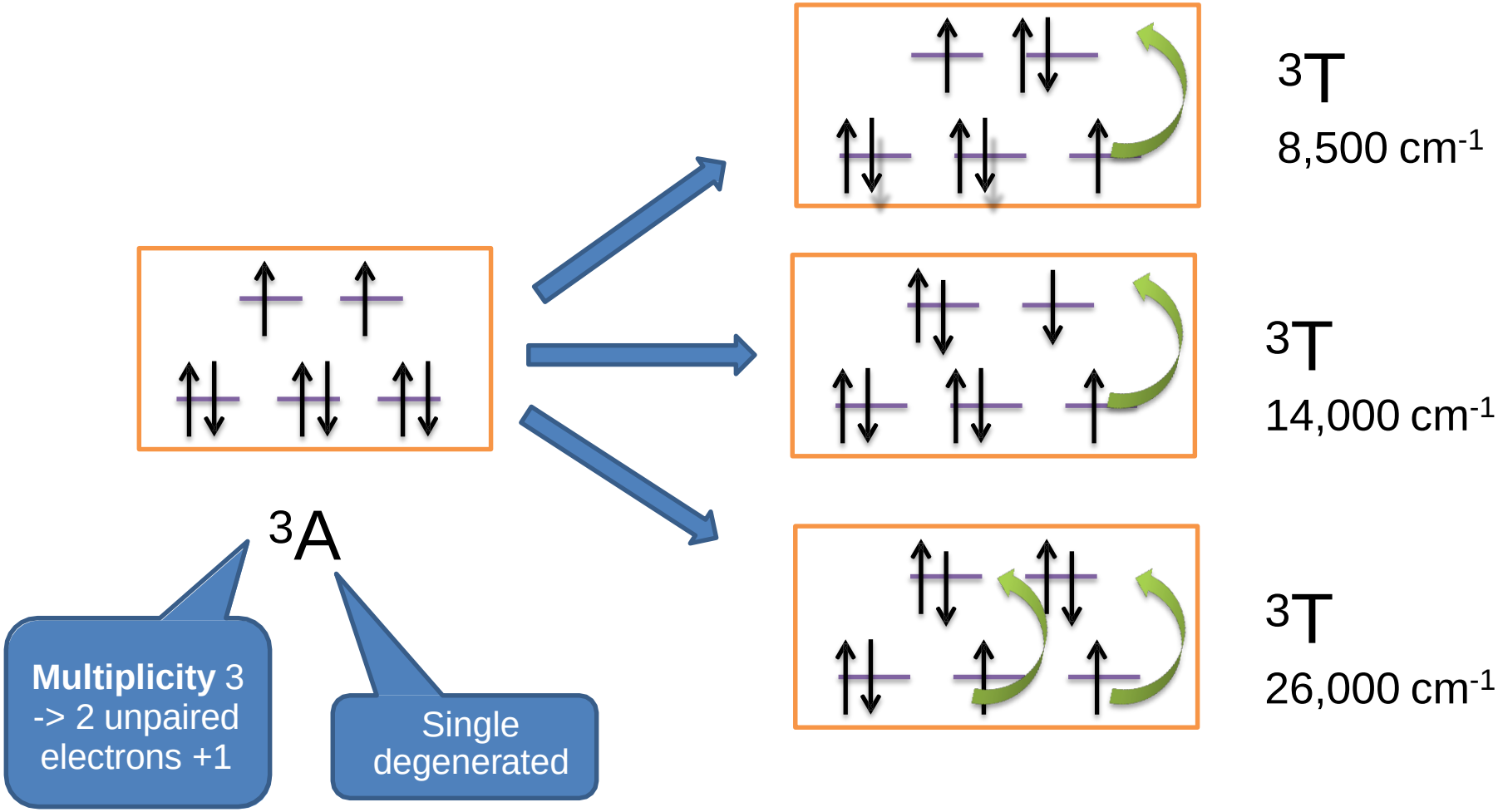


Ground state d^8:



Excited states d^8:

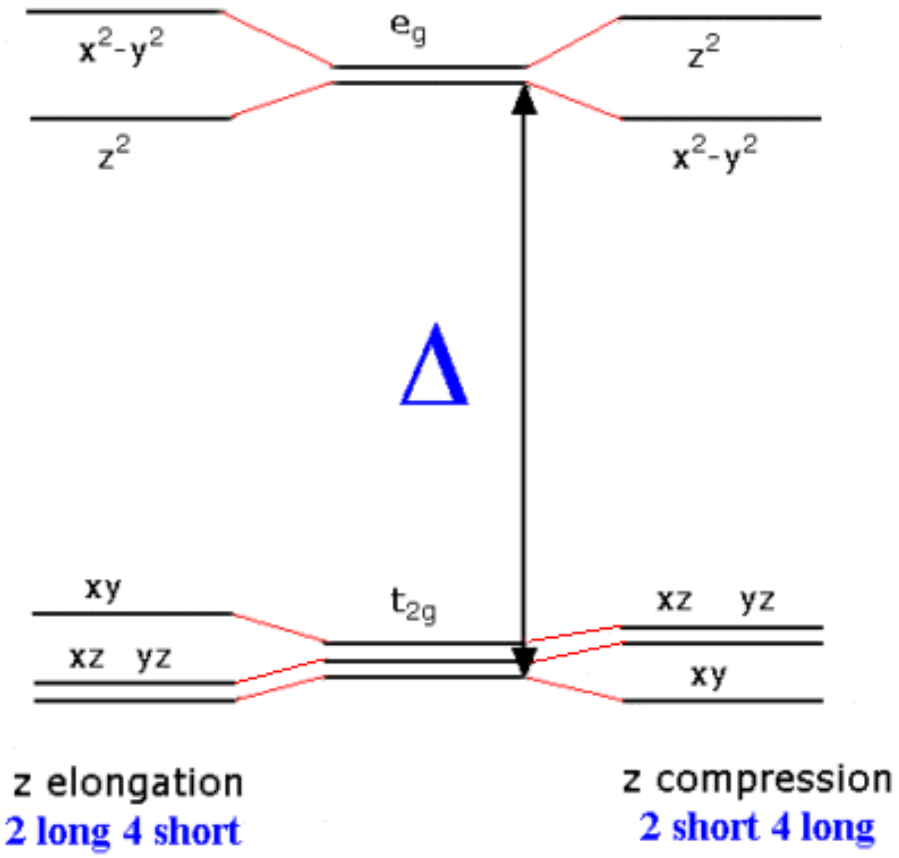
Possible d^8 d-d transitions



Jahn-Teller Effect

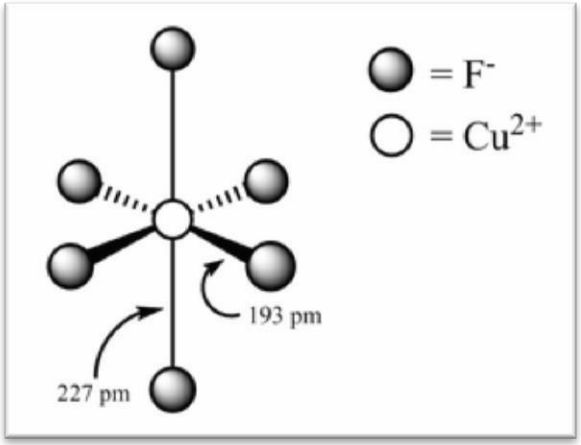
The Jahn-Teller effect is generally only important for odd number occupancy of the e_g level.

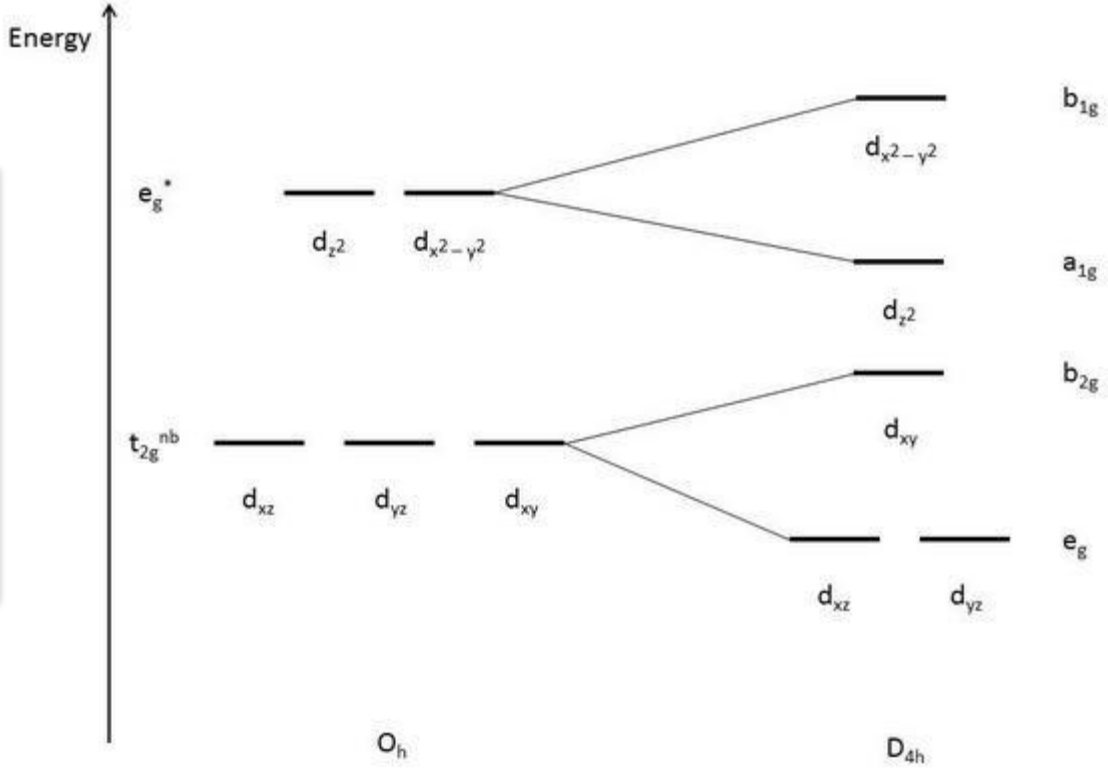
The effect of Jahn-Teller distortions is best documented for Cu(II) complexes (with 3 electrons in the e_g level) where the result is that most complexes are found to have elongation along the z-axis.

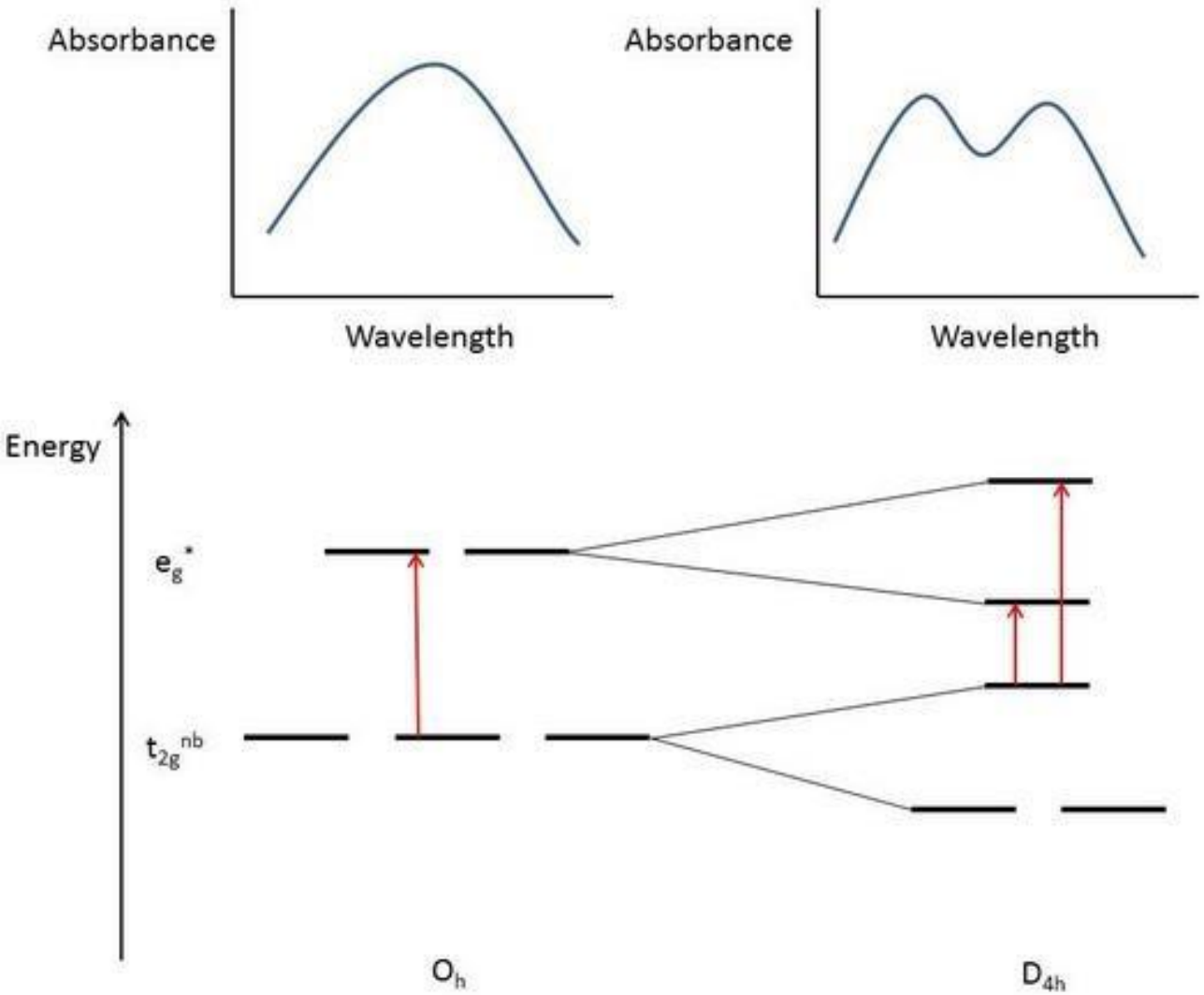


Cu(II) complexes

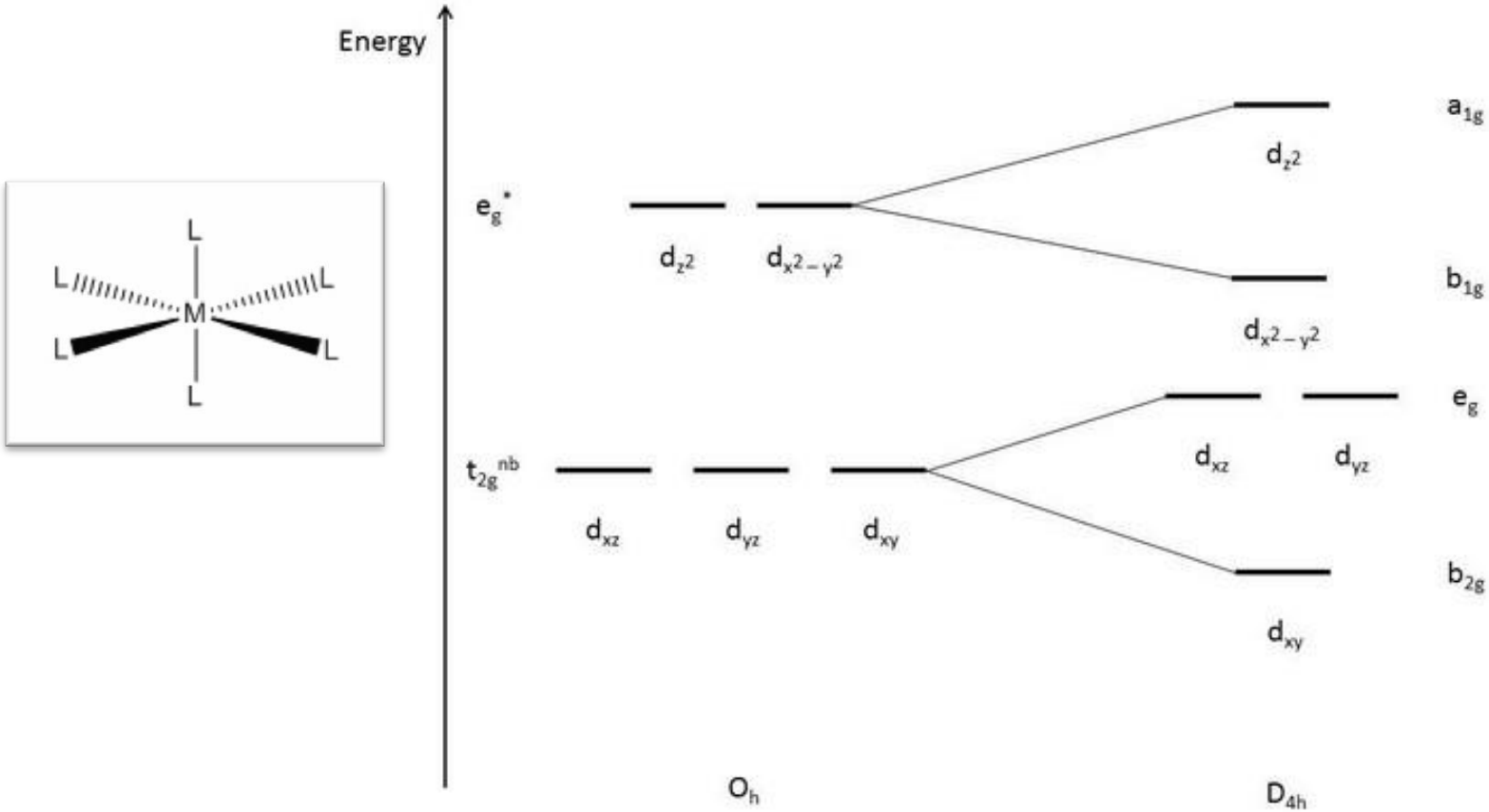
Elongation:






Absorbance
Wavelength
Absorbance
Wavelength
Energy
e_g^*
t_{2g}^{nb}
O_h
D_{4h}

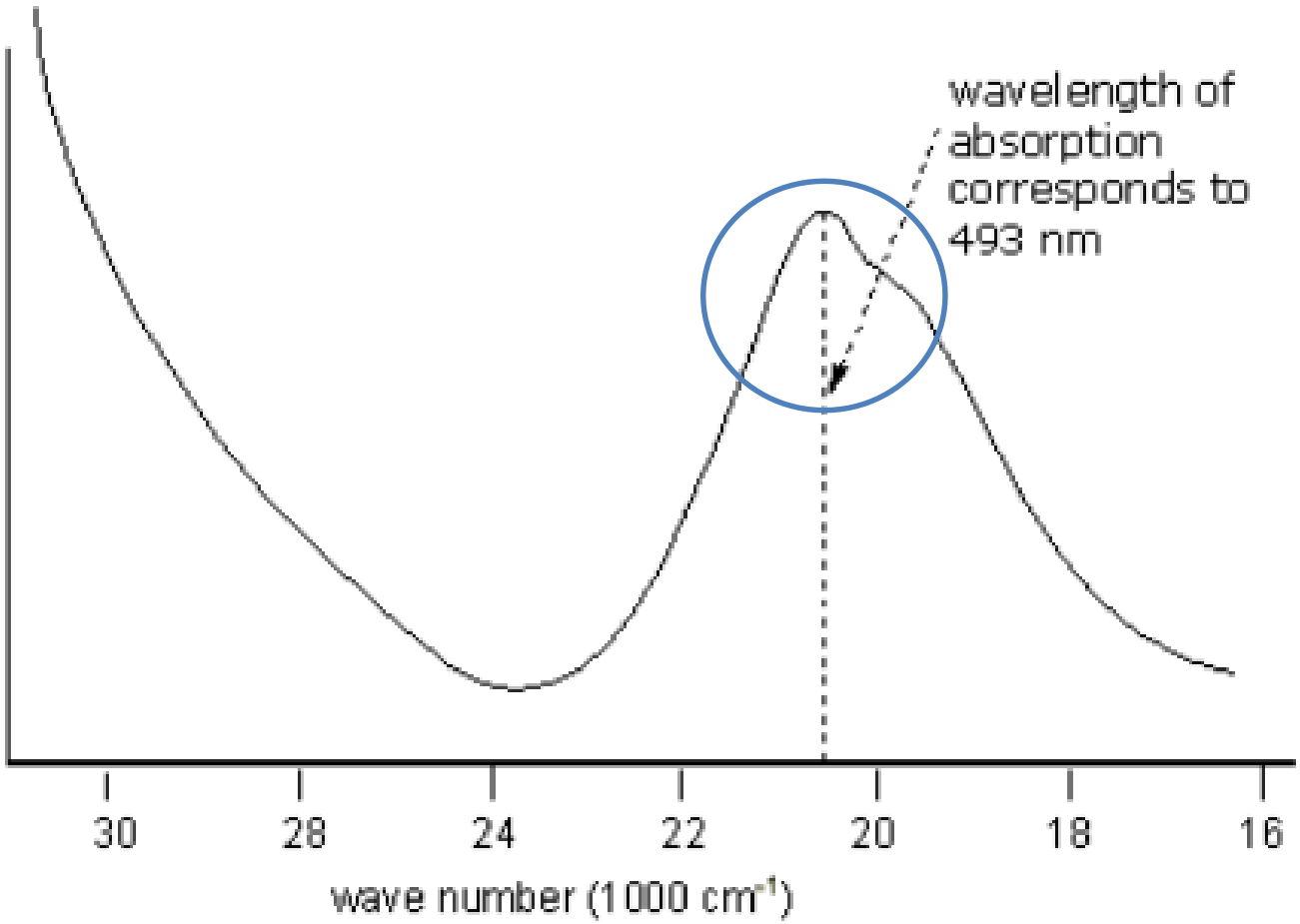
Compression



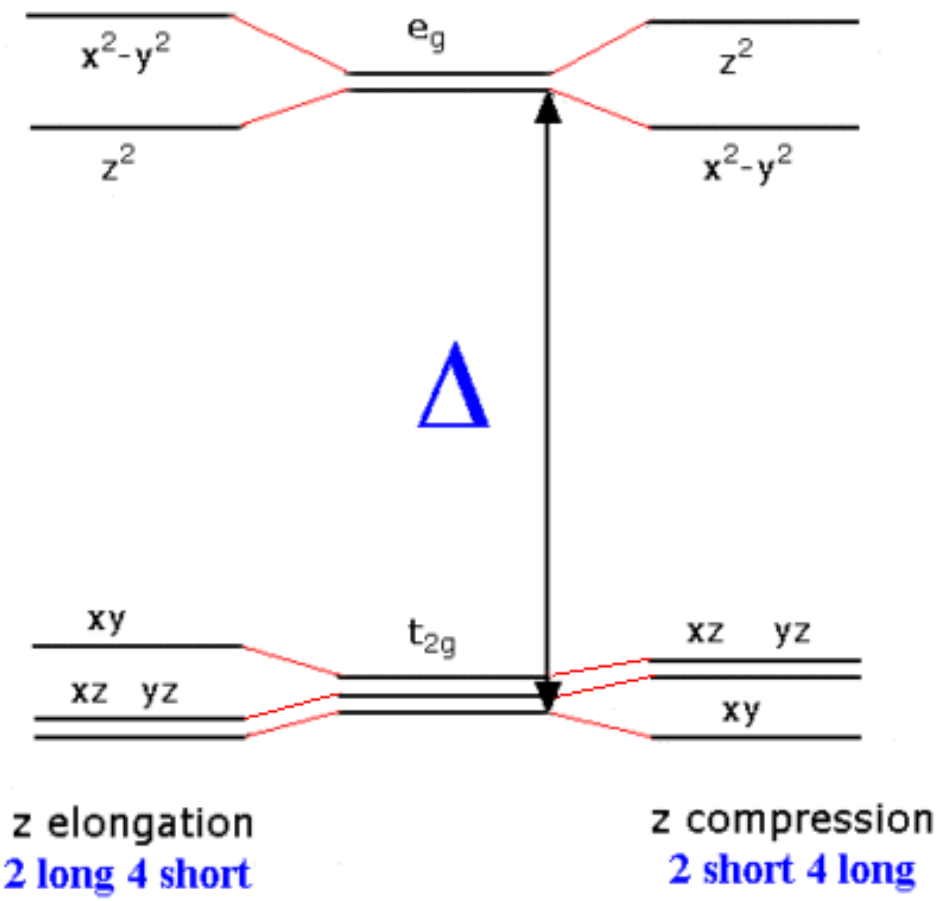
Why could we expect ***elongation*** *instead of* ***compression*** *for d^9 compounds ?*

Example Ti ($^{3+}$)

If we look carefully, we detect 2absorptions in the VIS spectrum:



- Which kind of Jahn-Teller Effect do you expect for a d^1 complex ?
- And which electron transitions can be observed then ?

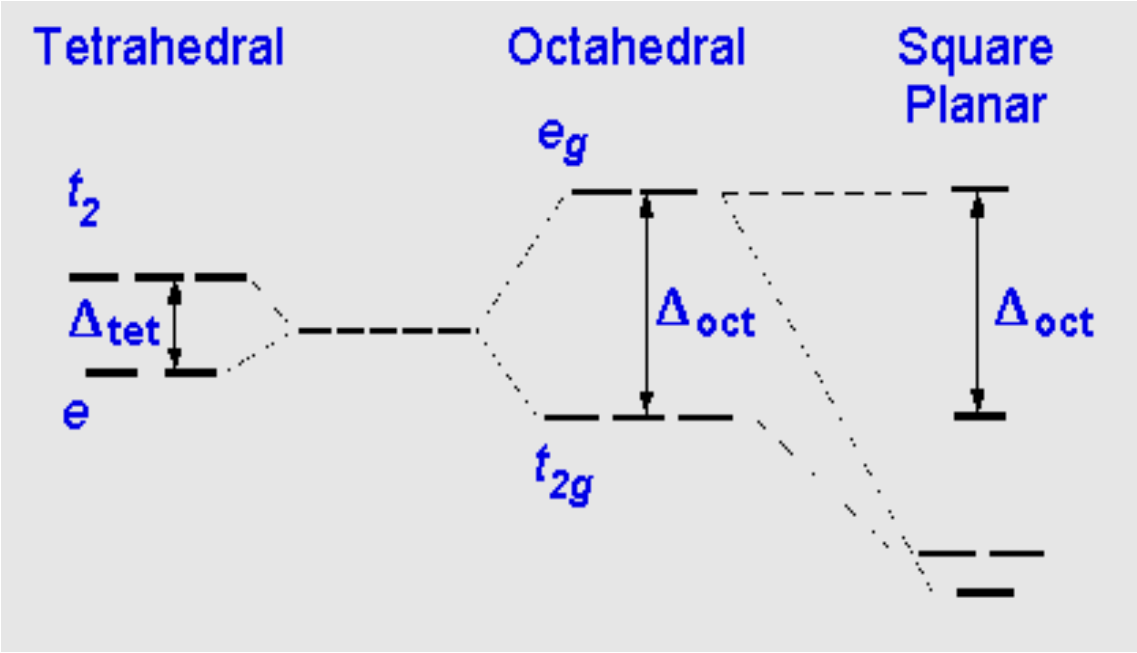


Problem solving

Compare the 2 compounds: $Fe(H_2O)_6^{2+}$ and $Fe(CN)_6^{4-}$
Δo = 10,400 cm^{-1} and 32,850 cm^{-1}
Paring energy P is 17,600 cm^{-1} for both
Which is the electron configuration (low- or high-spin) for both compounds ?

Compare the 2 compounds: $Co(F)_6^{3-}$ and $Co(NH_3)_6^{3+}$
Δo = 13,000 $^{cm-1}$ and 23,000 $^{cm-1}$ Paring energy P is 21,000 $^{cm-1}$ for both
Which is the electron configuration (low- or high-spin) for both compounds ?

Which d-electron configuration(s) always have zero CFSE ?

Consider a d^8 compound (like Pt(II)). What is more likely to form a 4-coordinate or a 6-coordinate compound.

Explain using VB theory and CFT.