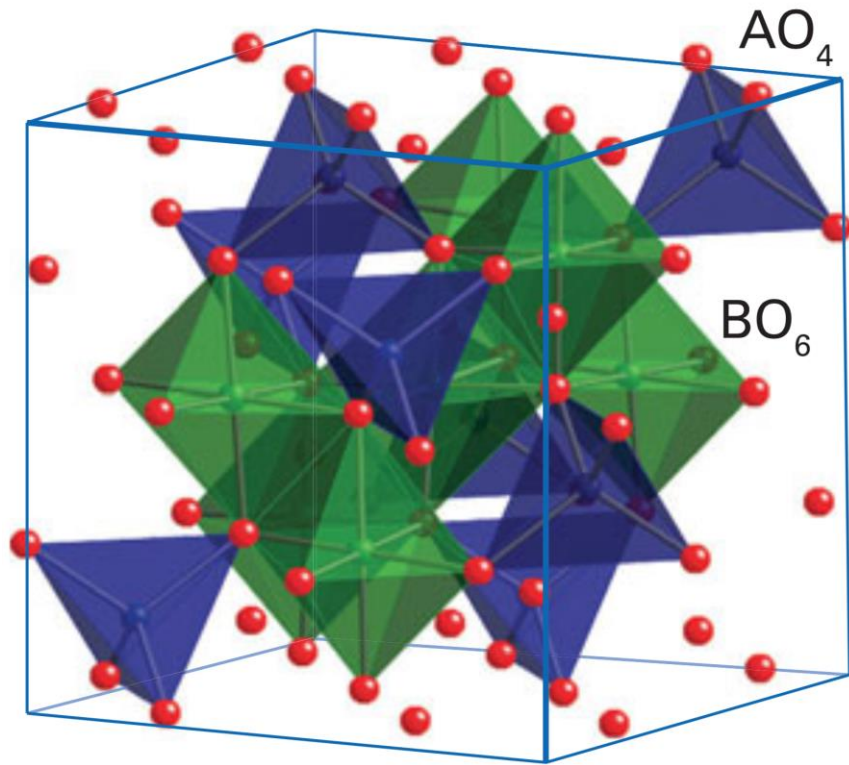# Lecture 3

Crystal Field Theory

# Site preference of Spinels and Inverse Spinels

AO$_4$

BO$_6$

A segment of the spinel (AB$_2$O$_4$) unit cell showing the tetrahedral environment of A ions and the octahedral environments of B ions.

Spinels are a class of crystalline solids of the general formula AB$_2$O$_4$ (A^{II}B$^{III}_2$O$_4$) where

The weak field oxide ions provide a cubic close-packed lattice. In one unit cell of AB$_2$O$_4$ there are 8 tetrahedral and 4 octahedral holes
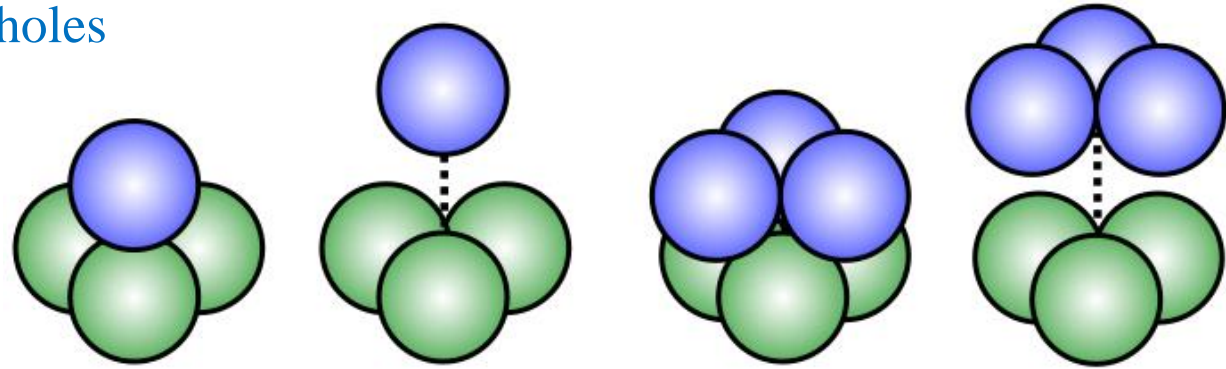
Normal Spinel: A^{2+} ions occupy the T$_d$ holes and both B^{3+} ions occupy the octahedral holes

Inverse Spinel: One B^{3+} ions occupy the T$_d$ holes, and the (A^{2+} and one B^{3+}) ions occupy the octahedral holes

Eg. MgAl$_2$O$_4$
Mg^{2+} Tetrahedral
Al^{3+} octahedral

Eg. Fe$_3$O$_4$ (Magnetite)
Fe^{3+} Tetrahedral
Fe$^{2+,}$ Fe^{3+} octahedral

Uses of Spinels:
- Manganese spinels used as the cathode in rechargeable batteries.
- Mixed-metal spinels, such as $ZnFe_2O_4$, have very useful magnetic properties.
- Several spinels—such as chromite, magnetite, and franklinite are important ores of metals

Question: Why does some AB_2O_4 compounds having transition elements as A and /or B prefer the inverse Spinel structure and some others normal Spinel structure?

ANS: Crystal Field Stabilization Energy in an octahedral site [Also given as Octahedral site stabilization energy (OSSE) in some books]

$Mn_3O_4 = Mn^{II}Mn^{III}_2O_4$

O^{2-} = a weak field ligand
$Mn^{2+} = d^5$ HS : CFSE = 0
$Mn^{3+} = d^4$ HS : CFSE = $-0.6\ \Delta_o$
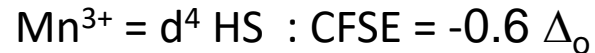
Mn^{2+} by exchanging positions with Mn^{3+} in an octahedral hole is not going to gain any extra crystal field stabilization energy. While Mn^{3+} by being in the octahedral hole will have CFSE.

Therefore Mn_3O_4 will be Normal Spinel

Spinels or Inverse Spinels

$Fe_3O_4 = Fe^{II}Fe^{III}_2O_4$

$Fe^{2+} = d^6$ HS : CFSE $= -0.4 \Delta_o$
$Fe^{3+} = d^5$ HS: CFSE $= 0$

Fe^{2+} by exchanging positions with Fe^{3+} to an
octahedral hole is going to gain extra crystal field
stabilization energy. While Fe^{3+} by being in the
octahedral hole will not have any CFSE.
Therefore Fe_3O_4 will be Inverse Spinel
$(Fe^{III})^{tet}[Fe^{II}Fe^{III}]^{oct}O_4$

If A and B of AB_2O_4 are both s or p block elements (e.g. $CaAl_2O_4$), why it always show
Spinel structure?

Home work

$Zn^{II}Fe^{III}_2O_4$

Zn^{2+} (d^{10}): CFSE = 0
Fe^{III} (d^5 high-spin): CFSE = 0

$Fe^{II}Cr^{III}_2O_4$

Fe^{2+} (d^6 high-spin): CFSE = $-0.4\Delta_O$
Cr^{III} (d^3 high-spin): CFSE = $-1.2\Delta_O$
Cr(III) has a greater CFSE compared to Fe(II);
Therefore, prefers to occupy octahedral site

Co_3O_4 is a normal spinel, whereas Fe_3O_4 (magnetite) is an inverse spinel. Explain.

$Ni^{II}Ga^{III}_2O_4$

Ni^{2+} (d^8 high-spin): CFSE = $-1.2\Delta_O$
Ga^{III} (d^{10}): CFSE = 0
Ni(II) has CFSE, therefore more stabilized in an octahedral site. Therefore the compound is inverse spinal: $(Ga^{III})^{tet}[Ni^{II}Ga^{III}]^{oct}O_4$

$Co^{II}Fe^{III}_2O_4$

Co^{2+} (d^7, high-spin): CFSE = $-0.8\Delta_O$
Fe^{III} (d^5, high-spin): CFSE = 0
Co(II) has CFSE, more stabilized in an octahedral site. Therefore the compound is inverse spinal: $(Fe^{III})^{tet}[Co^{II}Fe^{III}]^{oct}O_4$

Distortion of some octahedral complexes

All six Ni-O bonds equal at 2.05 Å

two long axial Cu-O bonds = 2.45 Å

four short in-plane Cu-O bonds = 2.00 Å

$[Ni(H_2O)_6]^{2+}$
no distortion

$[Cu(H_2O)_6]^{2+}$
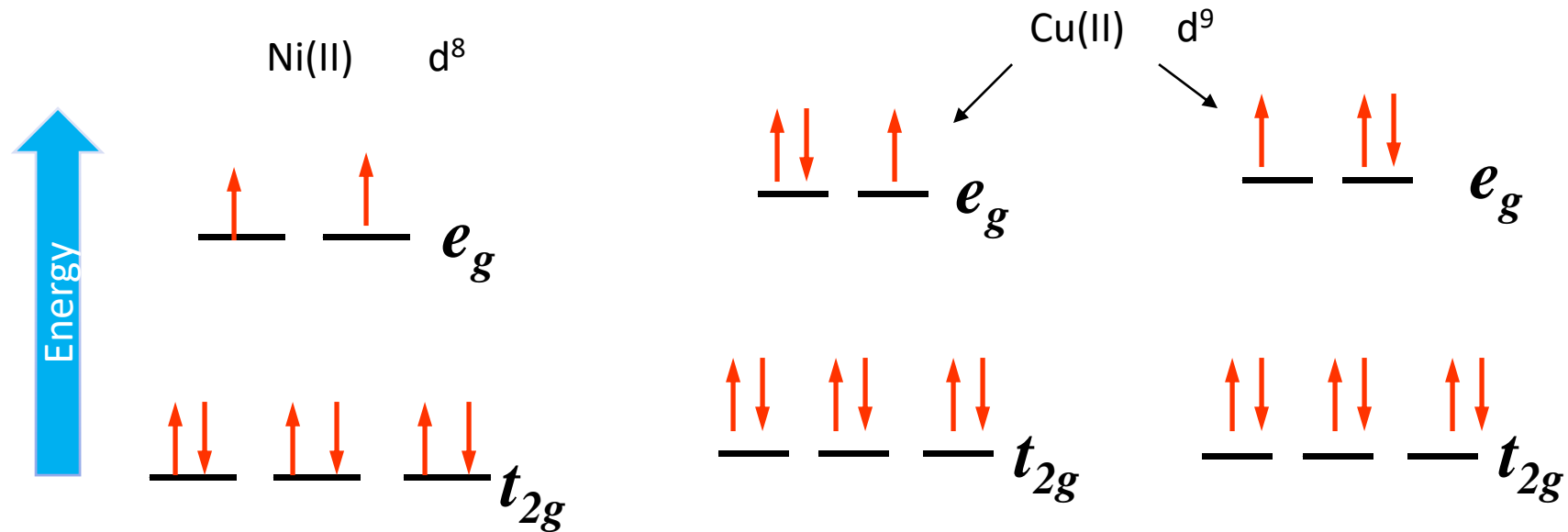distortion lengthens axial Cu-O's
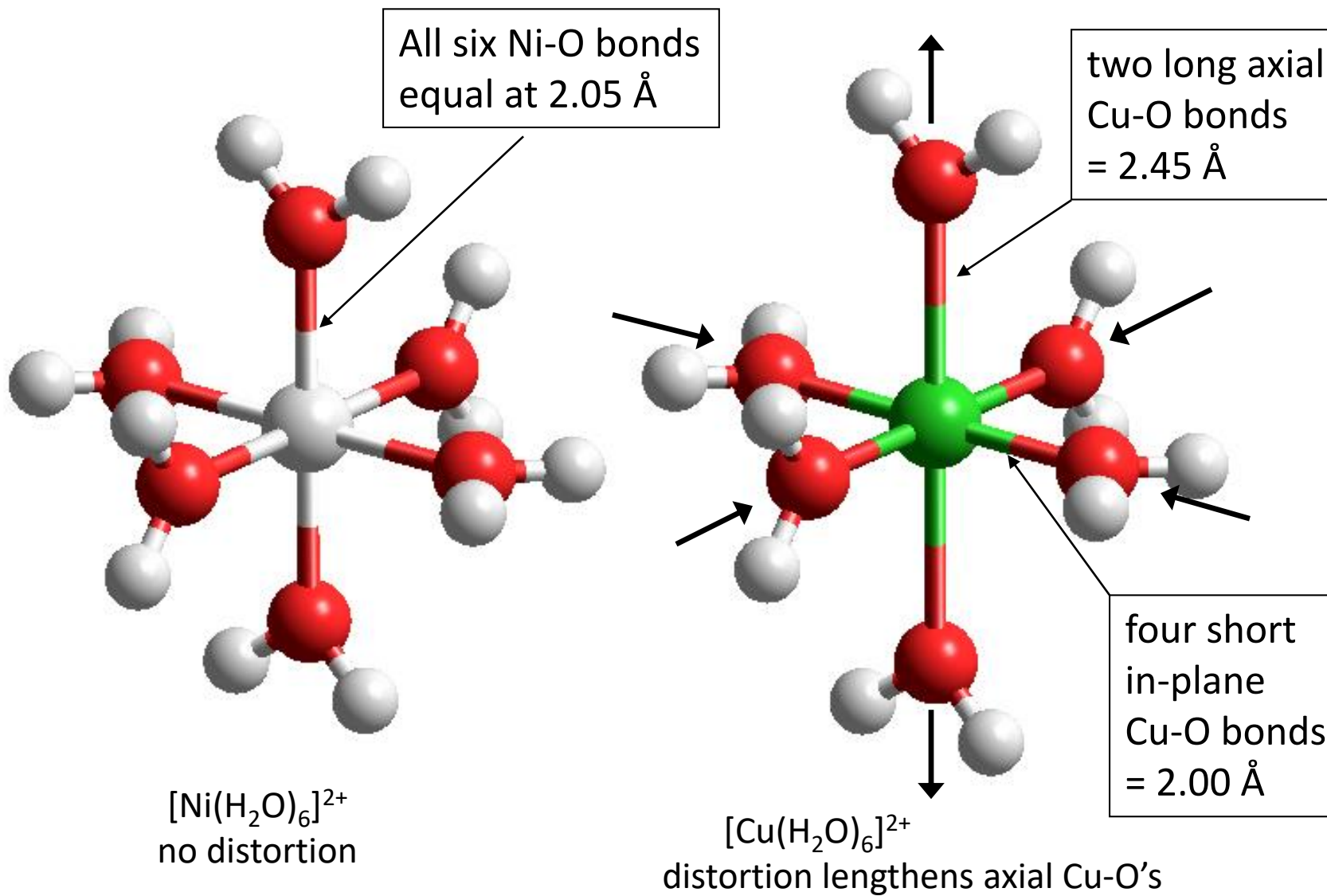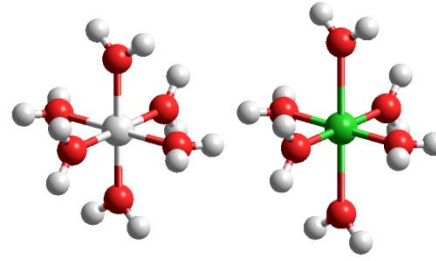
Ni(II) Cu(II)

High-spin Ni(II) – only one way of filling the e_g level – not electronically degenerate

Cu(II) – two ways of filling the e_g level – it is electronically degenerate

Ni(II) d^8

Cu(II) d^9

Energy

e_g

t_{2g}

e_g

t_{2g}

e_g

t_{2g}

What is the consequence of ELECTRONIC DEGENERACY ?

Jahn-Teller Distortion in d^9 Complexes

That principle states that *if a system has unequally populated degenerate orbitals, the system will distort to remove the degeneracy.* When the degeneracy is removed, the state of lower energy will be populated first.

Before Jahn-Teller Distortion

$- 0.4\Delta_0 \times 6 + 3 \times 0.6\,\Delta_0 = -0.6\,\Delta_0$

After Jahn-Teller Distortion

CFSE $= -(0.6\,\Delta_0 + \delta_1/2)$

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

$\dfrac{\delta_1}{2}$

e_g $d_{x^2-y^2}$ d_{z^2} δ_1

$\dfrac{\delta_1}{2}$

d_{z^2}

E

Δ_o

d_{xy}

$\dfrac{2\delta_2}{3}$ δ_2

t_{2g} d_{xy} d_{xz} d_{yz} $\dfrac{\delta_2}{3}$

d_{xz} d_{yz}

Elongated

$\Delta o \gg \delta 1 > \delta 2.$
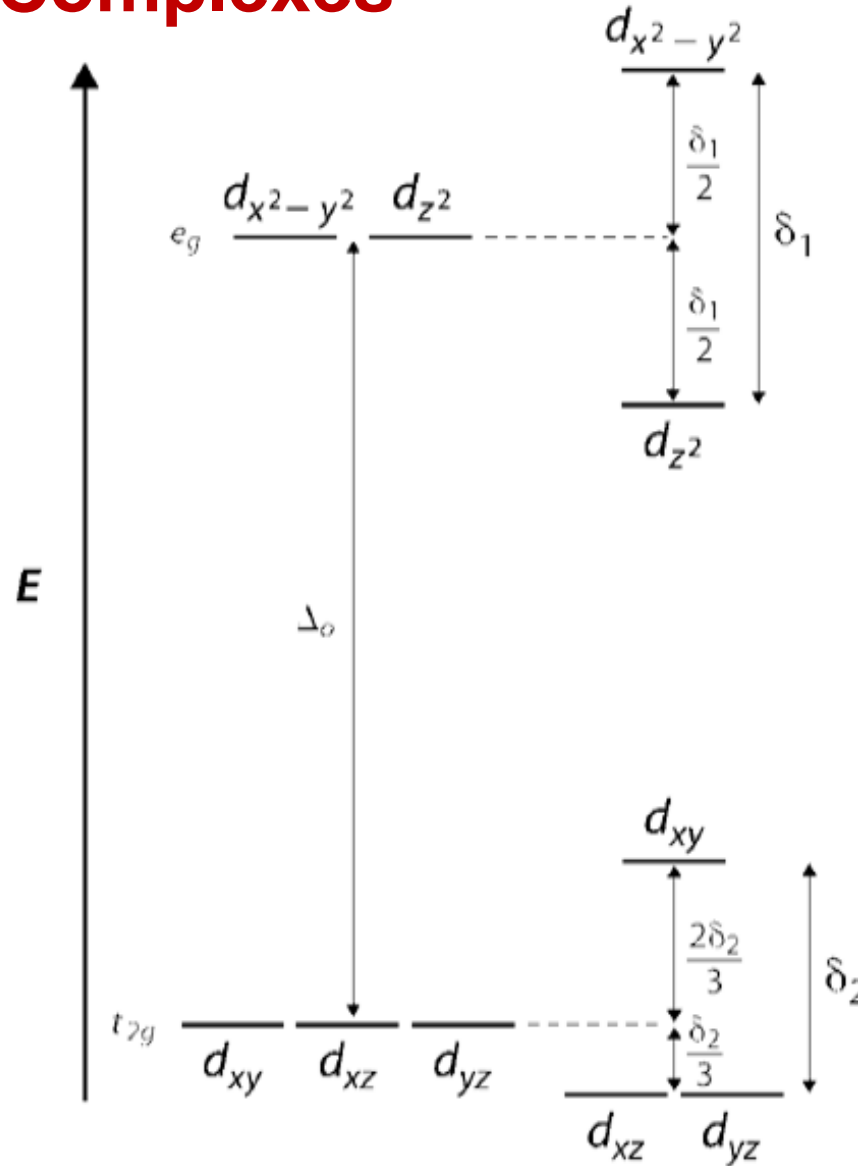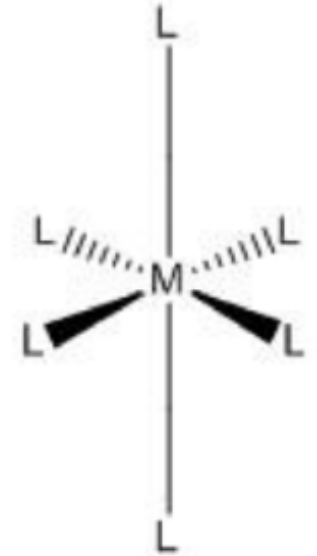
Jahn-Teller Distortion

➤ **That principle states that** *if a system has unequally populated degenerate orbitals, the system will distort to remove the degeneracy.* **When the degeneracy is removed, the state of lower energy will be populated first.**
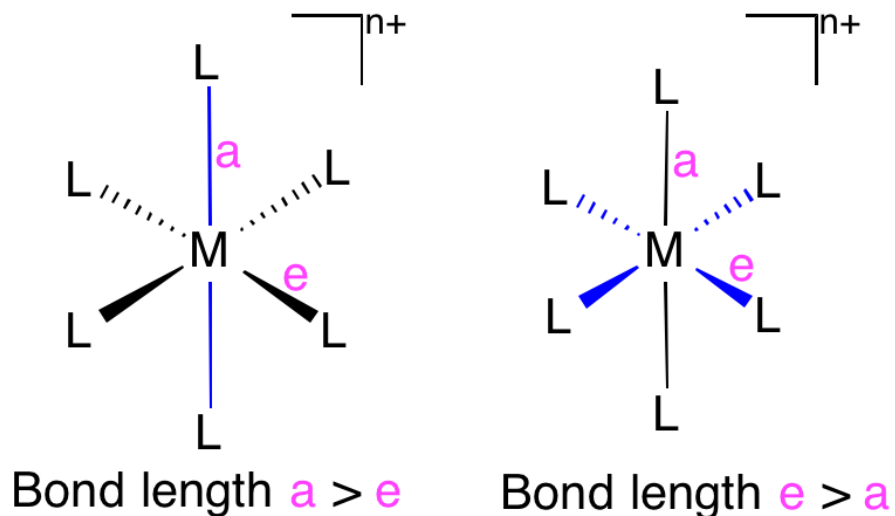
(a) **Elongated octahedron**   (b) **Compressed octahedron**

Bond length $a > e$ Bond length $e > a$

The Jahn-Teller effect predicts which structures will distort. It does not predict the nature or extent of the distortion. The effect is more significant when the electronic degeneracy is in the orbitals that point directly towards the ligands.
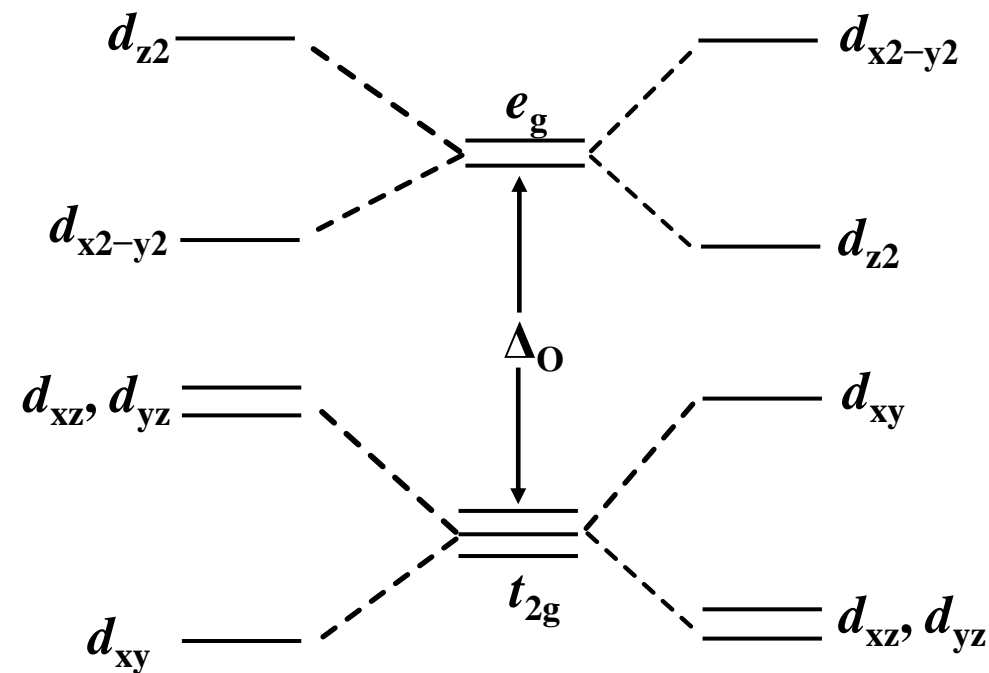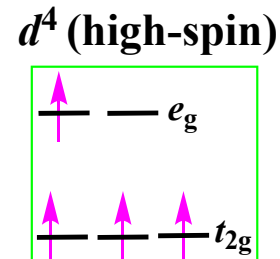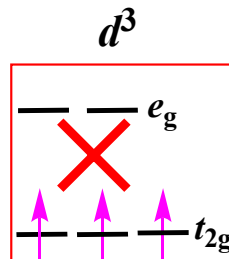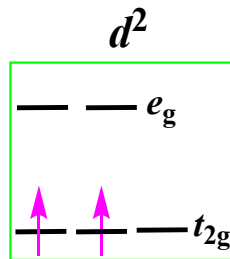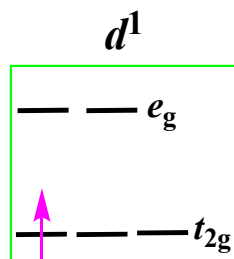
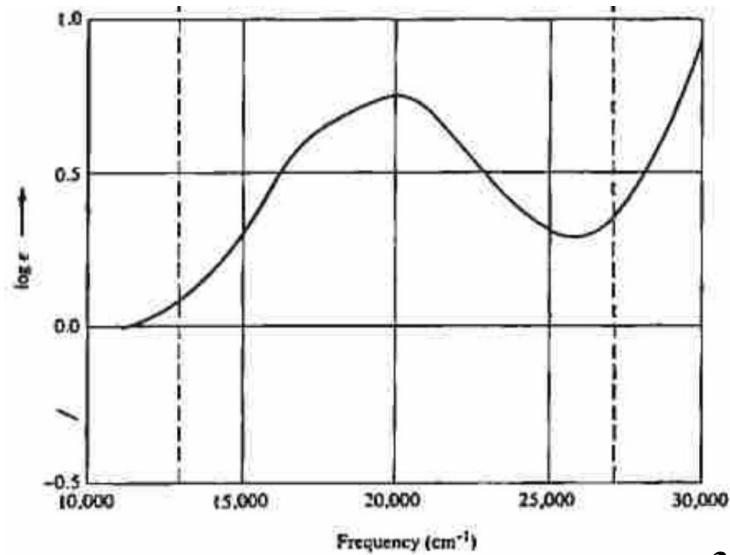

Tetragonal Compression   Octahedral   Tetragonal Elongation

Jahn-Teller Distortion
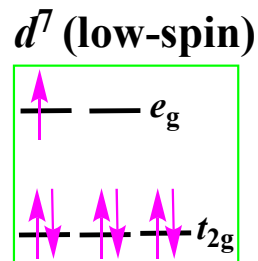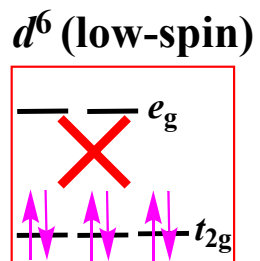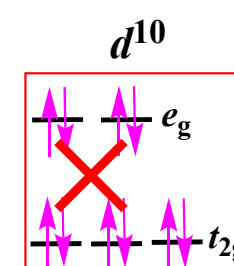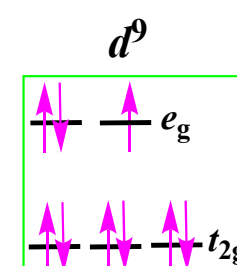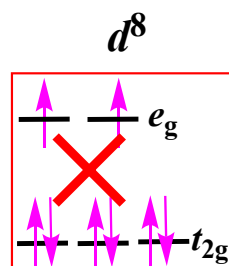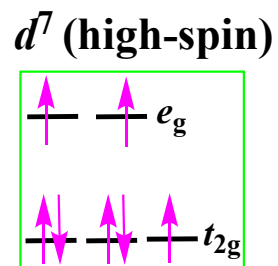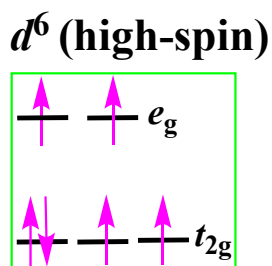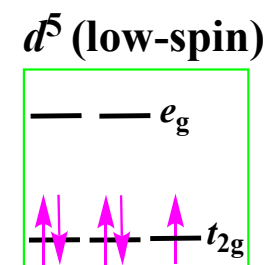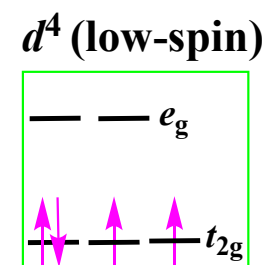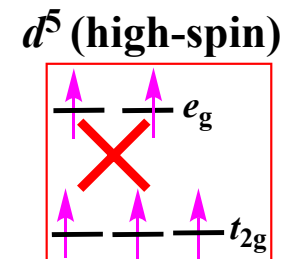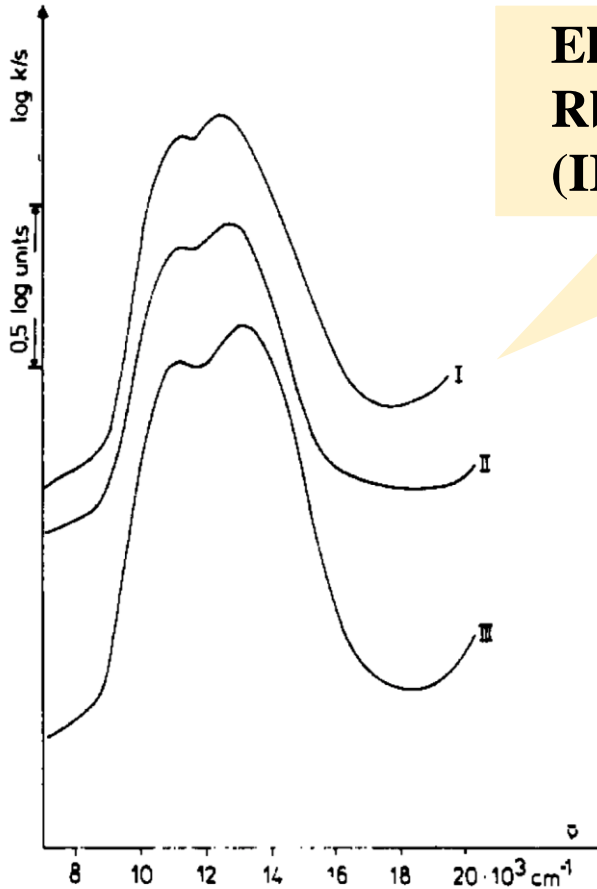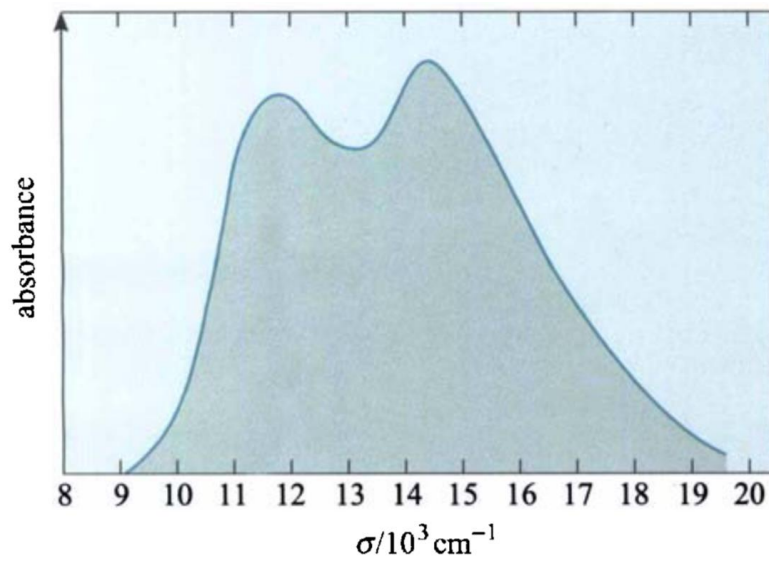

Configurations for which Jahn−Teller distortions are expected in ML$_6$ complexes

Jahn-Teller Distortion

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

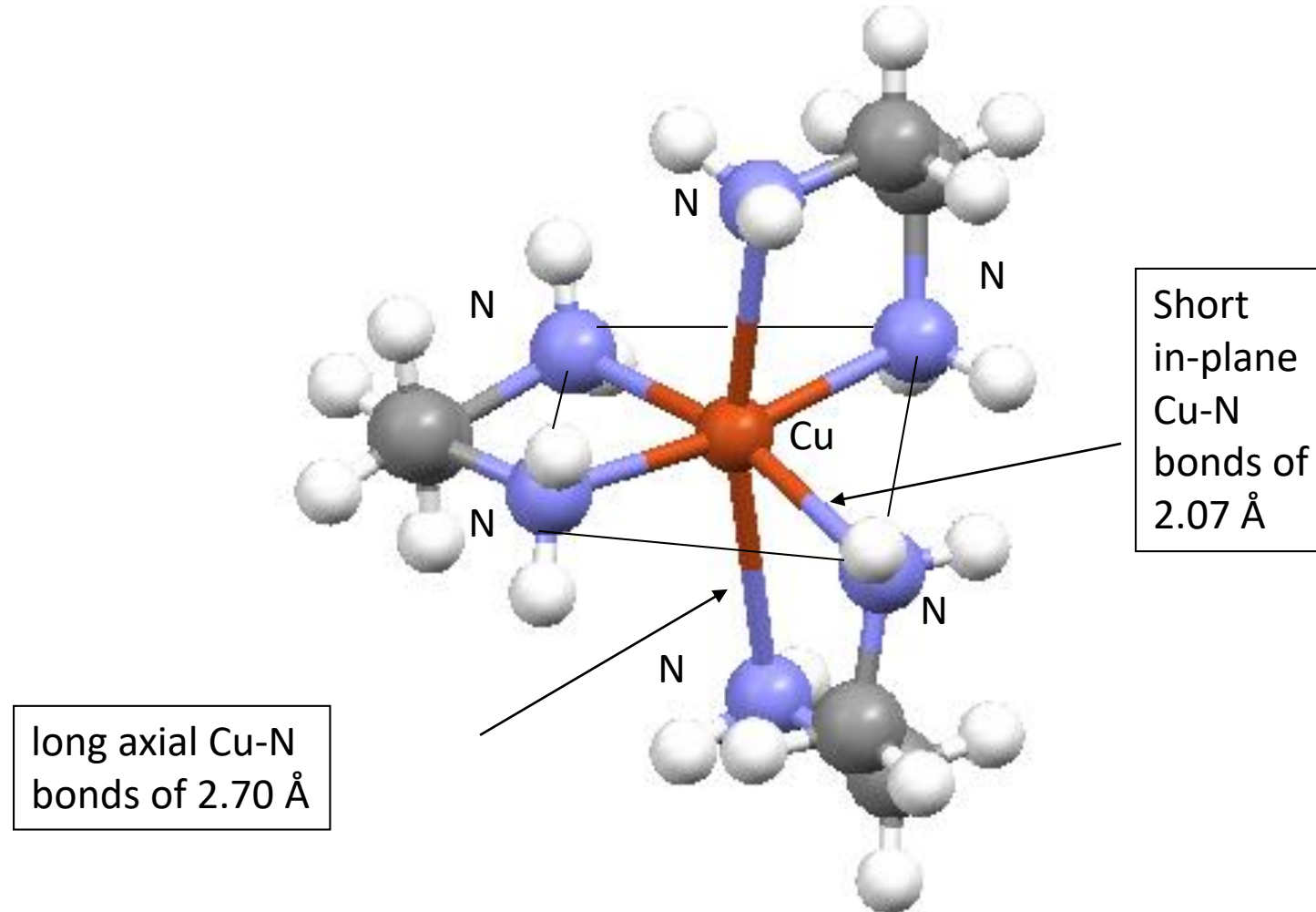Electronic spectra of $Rb_2Na[TiCl_6]$ (I), $Cs_2K[TiCl_6]$ (II), $Rb_3[TiCl_6]$ (III)
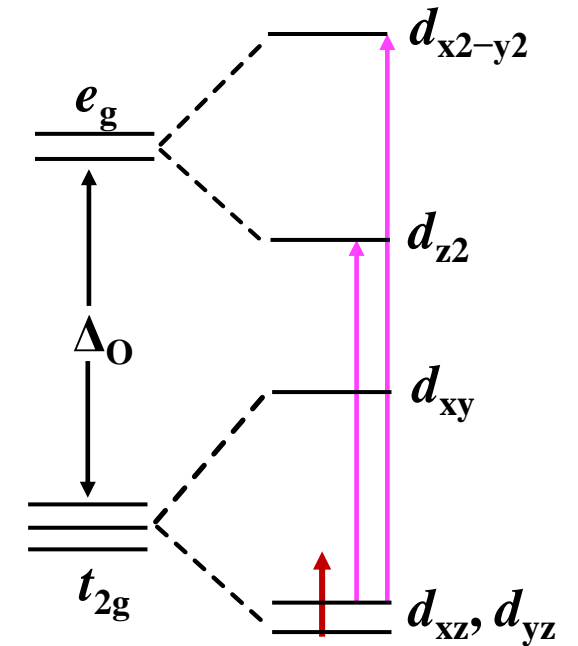
Splitting of d-orbitals for Ti^{3+} ion


The electronic absorption spectrum of the $[CoF_6]^{3-}$ ion, showing the two peaks due to the Jahn-Teller splitting of the excited state

Structural effects of Jahn-Teller distortion on [Cu(en)$_3$]$^{2+}$

Short in-plane Cu-N bonds of 2.07 Å

long axial Cu-N bonds of 2.70 Å

Chelation versus Jahn Teller distortion : Two opposing forces **consequence: low stability of such complexes**

Problem solving! (Home work)

$$[Co(en)_3]^{2+}, \quad [Fe(CN)_6]^{4-}, \quad [Fe(CN)_6]^{3-}, \quad [CrF_6]^{4-}$$
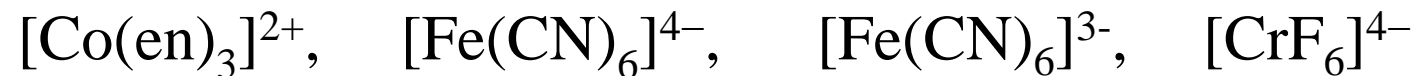
Classify the above given octahedral complexes and write in the boxes below as those

Having no tetragonal distortion	Having slight tetragonal distortion which is seen from UV Visible spectral studies	Having significant tetragonal distortion indicated as varying bond distances in their structure

Magnetic properties of metal complexes

Magnetism is caused by moving charged electrical particles (Faraday, 1830s). These particles can be the current of electrons through an electric wire, or the movement of charged particles (protons and electrons) within an atom. These charged particles move much like planets in a solar system:
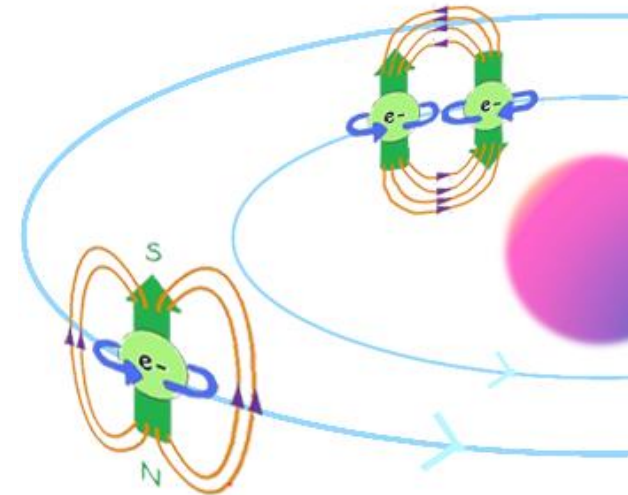
nucleus spin around its own axis, causing a **very weak** magnetic field.
electrons orbit around the nucleus, causing a **weak** magnetic field.
electrons spin around their own axis, causing a **significant** magnetic field .

Spinning electrons generate the bulk of the magnetism in an atom.

Within each orbit, electrons with opposite spins pair together, resulting in no net magnetic field. Therefore **only unpaired electrons** lead to magnetic moment

The **spin-only** formula (μ_s)

$$\mu_s = \sqrt{n(n+2)}$$