Atomic Term Symbols

The Stationary States of the Many-Electron Atom are determined by the *overall* properties of the Atom, not those of the individual electrons that exist in the atom.

What are these overall properties?
- The total orbital angular momentum of the electrons, L
- The total spin angular momentum of the electrons, S
- The total angular momentum of the atom, J

S = Total spin quantum no.
L = Orbital quantum number
J = Total angular momentum quantum number

The 'definition' of the term symbol:

$$^{2S+1}L_J$$

Note: In the symbol L must be replaced with its alphabetic 'code':

L=0 is S,
L=1 is P,
L=2 is D,
L=3 is F,
L=4 is G,
L=5 is H...
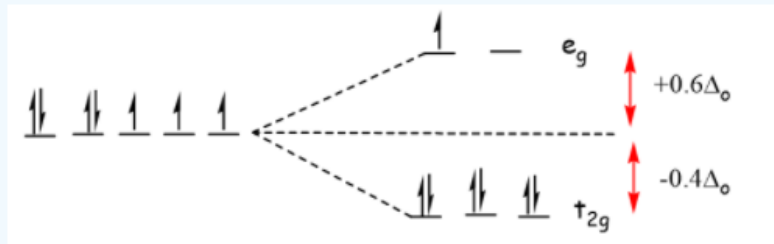
J is the vector sum of **L** and **S**:
J = (L+S), (L+S-1), (L+S-2), ...|L-S|

Determine the ground state term of free ion d1, d2, d3, d5, d6.

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.

The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand\) field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P$$
$$= -9/5\Delta_o + 3P$$

So via Equation 20.3B.1, the CFSE is

$$CFSE = E_{\text{ligand field}} - E_{\text{isotropic field}}$$
$$= (-9/5\Delta_o + 3P) - 2P$$
$$= -9/5\Delta_o + P$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin d^7 configuration in Example 20.3B. 1, but we have then to take into consideration the Pairing energy P to know definitely, which varies between $200 - 400 \ kJ \ mol^{-1}$ depending on the metal.

Total d-electrons	Isotropic Field	Octahedral Complex				Crystal Field Stabilization Energy	
		High Spin		**Low Spin**			
	$E_{\text{isotropic field}}$	**Configuration**	$E_{\text{ligand field}}$	**Configuration**	$E_{\text{ligand field}}$	**High Spin**	**Low Spin**
d^0	0	$t_{2g}0e_g0$	0	$t_{2g}{}^0e_g{}^0$	0	0	0
d^1	0	$t_{2g}1e_g0$	-2/5 Δ_o	$t_{2g}{}^1e_g{}^0$	-2/5 Δ_o	-2/5 Δ_o	-2/5 Δ_o
d^2	0	$t_{2g}2e_g0$	-4/5 Δ_o	$t_{2g}{}^2e_g{}^0$	-4/5 Δ_o	-4/5 Δ_o	-4/5 Δ_o
d^3	0	$t_{2g}3e_g0$	-6/5 Δ_o	$t_{2g}{}^3e_g{}^0$	-6/5 Δ_o	-6/5 Δ_o	-6/5 Δ_o
d^4	0	$t_{2g}3e_g1$	-3/5 Δ_o	$t_{2g}{}^4e_g{}^0$	-8/5 Δ_o + P	-3/5 Δ_o	-8/5 Δ_o + P
d^5	0	$t_{2g}3e_g2$	0 Δ_o	$t_{2g}{}^5e_g{}^0$	-10/5 Δ_o + 2P	0 Δ_o	-10/5 Δ_o + 2P
d^6	P	$t_{2g}4e_g2$	-2/5 Δ_o + P	$t_{2g}{}^6e_g{}^0$	-12/5 Δ_o + 3P	-2/5 Δ_o	-12/5 Δ_o + P
d^7	2P	$t_{2g}5e_g2$	-4/5 Δ_o + 2P	$t_{2g}{}^6e_g{}^1$	-9/5 Δ_o + 3P	-4/5 Δ_o	-9/5 Δ_o + P
d^8	3P	$t_{2g}6e_g2$	-6/5 Δ_o + 3P	$t_{2g}{}^6e_g{}^2$	-6/5 Δ_o + 3P	-6/5 Δ_o	-6/5 Δ_o
d^9	4P	$t_{2g}6e_g3$	-3/5 Δ_o + 4P	$t_{2g}{}^6e_g{}^3$	-3/5 Δ_o + 4P	-3/5 Δ_o	-3/5 Δ_o
d^{10}	5P	$t_{2g}6e_g4$	0 Δ_o + 5P	$t_{2g}{}^6e_g{}^4$	0 Δ_o + 5P	0	0

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital. For a given metal ion P (pairing energy) is constant, but it does not vary with ligand and oxidation state of the metal ion).

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

Coulomb repulsion
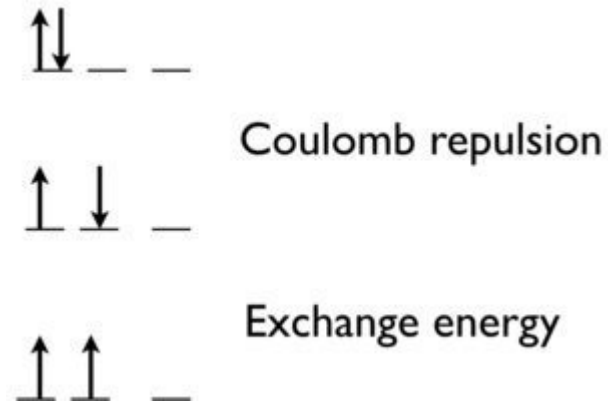
Exchange energy

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The exchange energy (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state, we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we gain the exchange energy, because these two electrons are indistinguishable.

**Hund's Second Rule (Maximize Orbital Angular Multiplicity)**

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the relative momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Jahn-Teller effect

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t2g (dxz , dyz , dxy) and eg (dz2 and dx2−y2). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure 1 below:


Elongated   Compressed
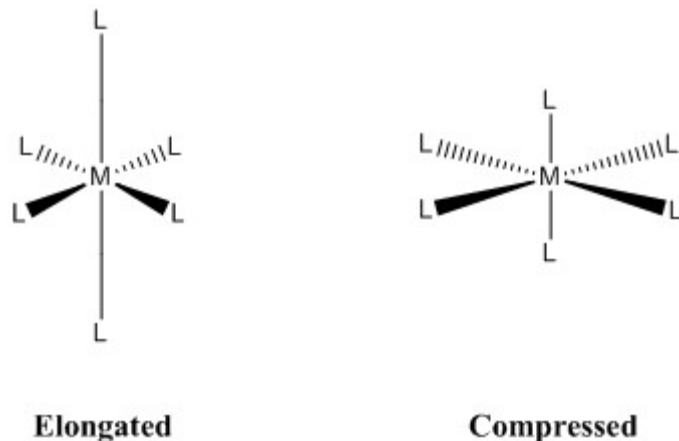
When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy) as shown in Figure 2 below:
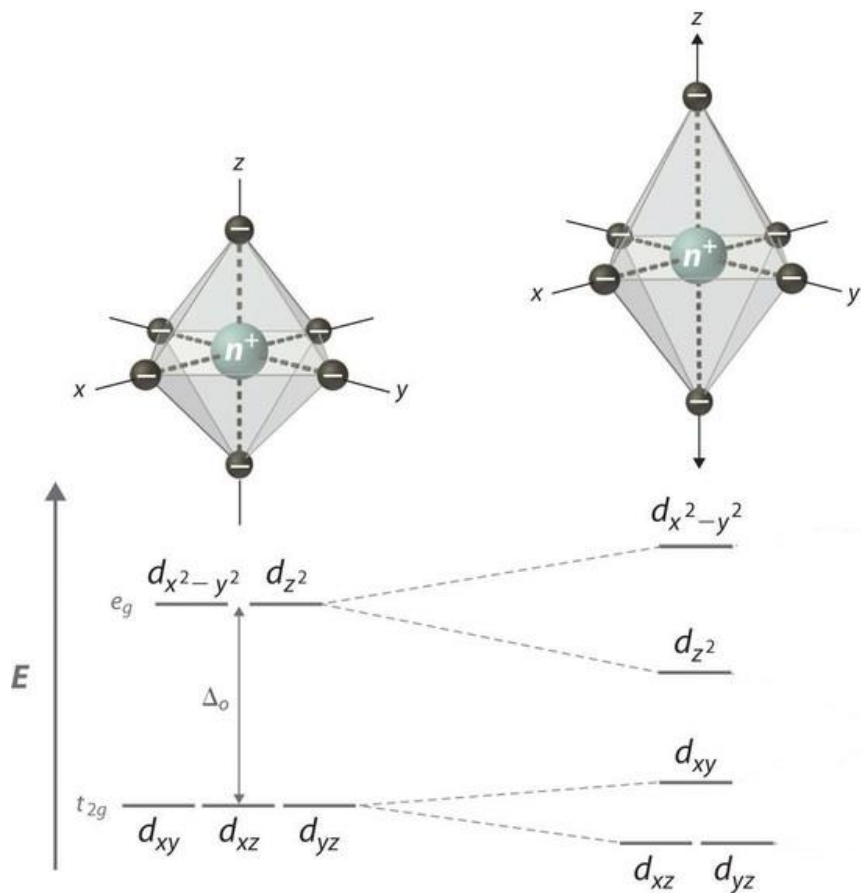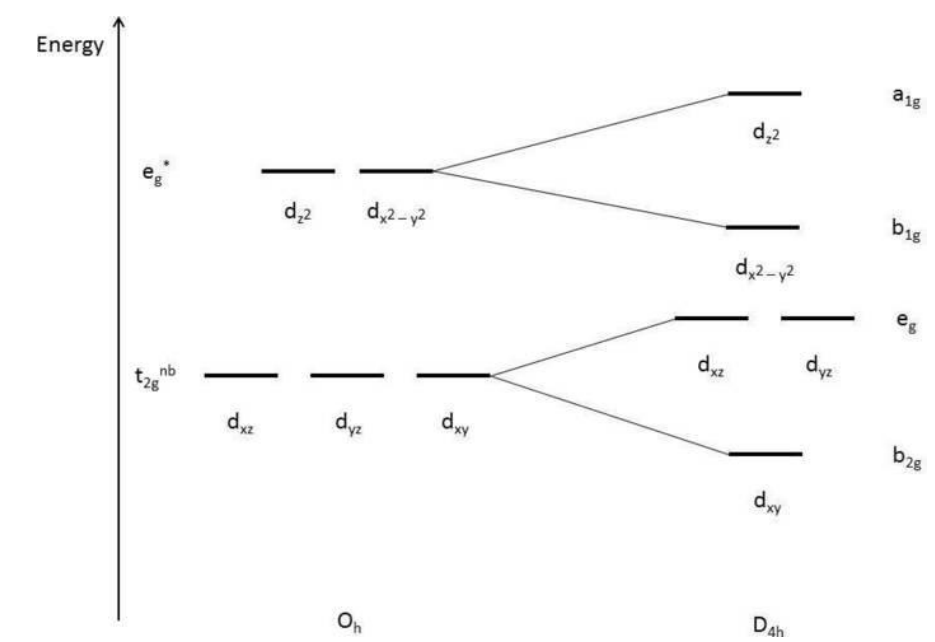
This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure 3.
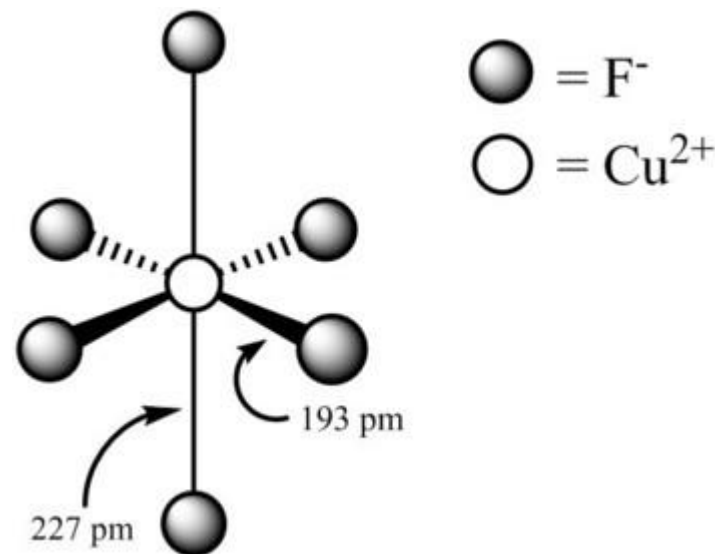
Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals without a z component, while the orbitals with a z component are destabilized (higher in energy) as shown in Figure 4 below:

This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the dz2 orbital is antibonding, it is expected to increase in energy due to compression. The dxz and dyz orbitals are still nonbonding, but are destabilized due to the interactions.
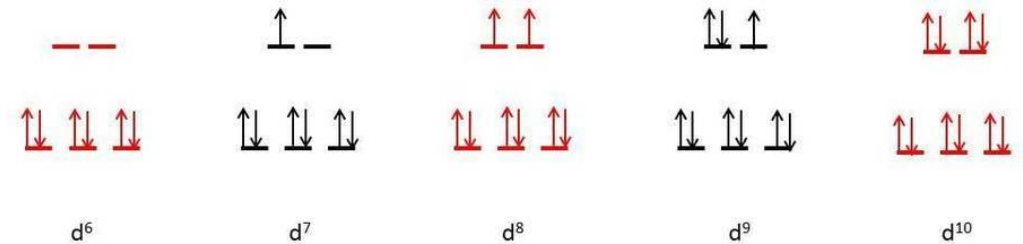
Electronic Configurations

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t2g or eg orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, Δ. When Δ is large and is greater than the energy required to pair electrons, electrons pair in t2g before occupying eg. On the other hand, when Delta small and is less than the pairing energy, electrons will occupy eg before pairing in t2g. The Δ of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If there electron configurations for any d-electron count is different depending on Δ, the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.
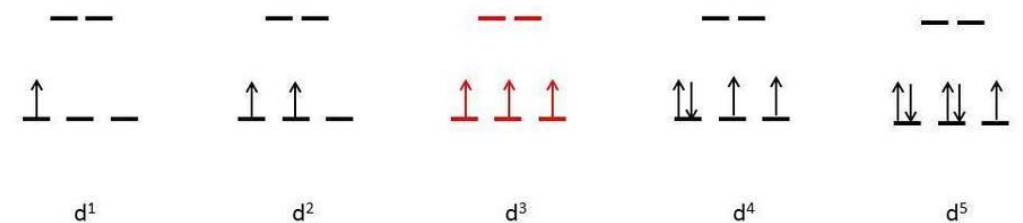
The electron configurations diagrams for d1 through d10 with large and small δ are illustrated in the figures below. Notice that the electron configurations for d1, d2, d3, d8, d9, and d10 are the same no matter what the magnitude of Δ. Low spin and high spin configurations exist only for the electron counts d4, d5, d6, and d7.

Large Δ

Figure shows the various electronic configurations for octahedral complexes with large $\Delta\Delta$, including the low-spin configurations of d^4, d^5, d^6, and d^7:

The figure illustrates the electron configurations in the case of large Δ. The electron configurations highlighted in red (d3, low spin d6, d8, and d10) do not exhibit Jahn-Teller distortions. On the other hand d1, d2, low spin d4, low spin d5, low spin d7, and d9, would be expected to exhibit Jhan-Teller distortion. These electronic configurations correspond to a variety of transition metals. Some common examples include Cr3+, Co3+, and Ni2+.

Small Δ

Figure 6 (below) shows the various electronic configurations for octahedral complexes with small Δ, including the high-spin configurations of d4, d5, d6, and d7::

The figure illustrates the electron configurations in the case of small Δ. The electron configurations highlighted in red (d3, high spin d5, d8, and d10) do not exhibit Jahn-Teller distortions. In general, degenerate electronic states occupying the eg orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the eg set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.

↑↓	↑↓	↑↓	↑↓↑	↑↓↑↓
↑↓↑↑	↑↓↑↓↑	↑↓↑↓↑↓	↑↓↑↓↑↓	↑↓↑↓↑↓
d⁶	d⁷	d⁸	d⁹	d¹⁰

			↑	↑↑
↑	↑↑	↑↑↑	↑↑↑	↑↑↑
d¹	d²	d³	d⁴	d⁵
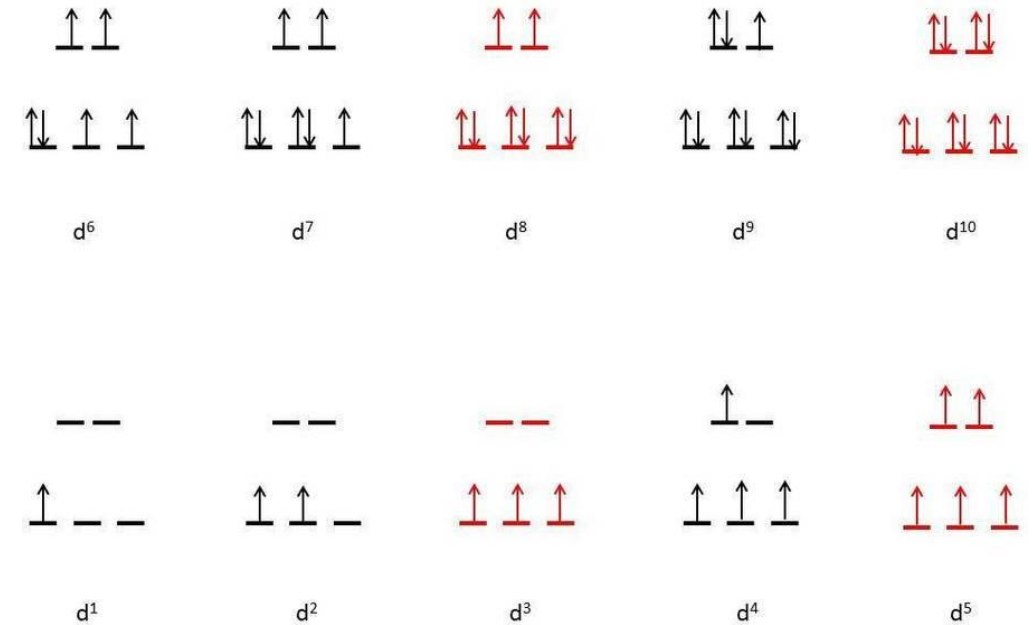
Spectroscopic Observation

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (Oh to D4h). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in Figure
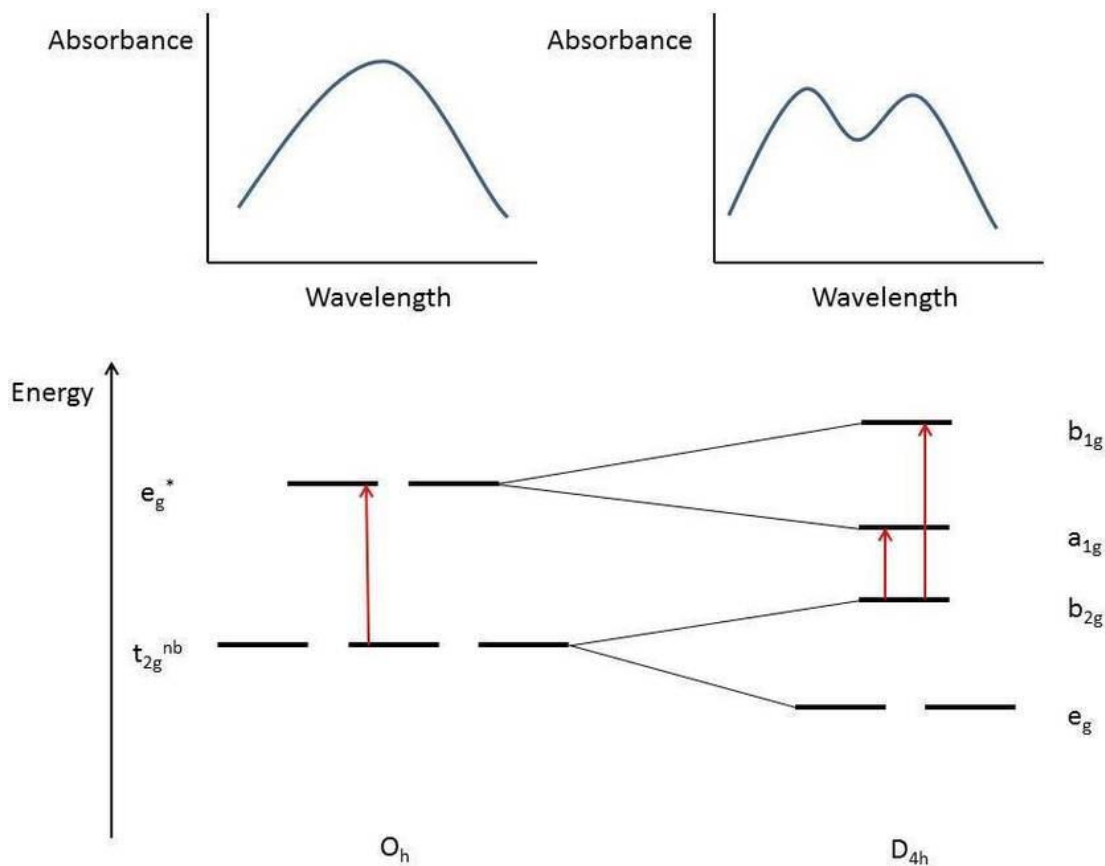
Table 1: Examples of Jahn-Teller distorted complexes

Complex	Bond lengths
$CuBr_2$	4 Br at 240 pm 2 Br at 318 pm
$CuCl_2$	4 Cl at 230 pm 2 Cl at 295 pm
$CuCl_2.2H_2O$	2 O at 193 pm 2 Cl at 228 pm 2 Cl at 295 pm
$CsCuCl_3$	4 Cl at 230 pm 2 Cl at 265 pm
CuF_2	4 F at 193 pm 2 F at 227 pm
$CuSO_4.4NH_3.H_2O$	4 N at 205 pm 1 O at 259 pm 1 O at 337 pm
K_2CuF_4	4 F at 191 pm 2 F at 237 pm
$KCuAlF_6$	2 F at 188 pm 4 F at 220 pm
CrF_2	4 F at 200 pm 2 F at 243 pm
$KCrF_3$	4 F at 214 pm 2 F at 200 pm
MnF_3	2 F at 209 pm 2 F at 191 pm 2 F at 179 pm

The Jahn-Teller Theorem predicts that distortions should occur for any degenerate state, including degeneracy of the t2g level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the eg level.

· What is the ground state term symbol: $|| \underline{d^2}?$, $\textcircled{$d^3$}$, $\underline{\underline{d^5}}$, $\underline{\underline{d^6}}$

d^1

$\underline{2S+1}$

$\underset{\text{⌐}}{\text{∟}}$ J

$L=3, S=1$

+2 +1   0 -1 -2

$S=\frac{1}{2}$

$2S+1 = 2 \times \frac{1}{2} + 1 = 2$

$\boxed{^2D_{3/2}}$

$\boxed{J = (L+S) \ldots (L-S)}$

$L+S = 3+1 = 4$
$L-S = 3-1 = 2$

$J = |(L+S)| \ldots |(L-S)|$

$= (L+\frac{1}{2}) \ldots (2-\frac{1}{2})$

$= \frac{5}{2} \ldots \textcircled{$\frac{3}{2}$}$

$^3F_2$ $S=0$
 $P=1$
 $D=2$
 $\underline{F=3}$
 $G=4$
 $H=5$

$L=3, S=1$

$L=+2$, $\boxed{D}$

Lower than half-filled, then $J = |(L-S)|$, for g. s.

More than half-filled, then $J = L+S$, for g. s.

d^5 $S=\frac{5}{2}$ $2 \times \frac{5}{2}+1 = 6$

+2 +1   0 -1 -2 $J = L-S$
 $= 3-3/2$

$L=0$ $S_{5/2}$

$d^3 = $

+2 +1   0 $S = 2 \times \frac{3}{2} + 1 = 4$

$\boxed{^4F_{3/2}}$

① The CFT considers the M—L bond as — ⓐ covalent, ⓑ ionic, ⓒ polar ⓓ Hydrogen ?

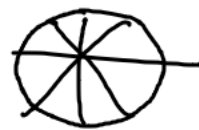② In CFT, which of the following gr/ligand will be treated as 'point dipole'
ⓐ Cl^-, ⓑ NO_2^- ⓒ CN^-, ⓓ NO |

$Cl^{\ominus} \Rightarrow$ anions → pt. change $\Big\}$ H_2O.

neutral → pt. dipole

CO, NO.

③ A th. complex absorbs at 545 nm. what is the respective octahedral splitting? What is the color of the complex?

Ans.

$$\Delta_t = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J. s})(3 \times 10^8 \text{ ms}^{-1})}{545 \times 10^{-9} \text{ m}}$$
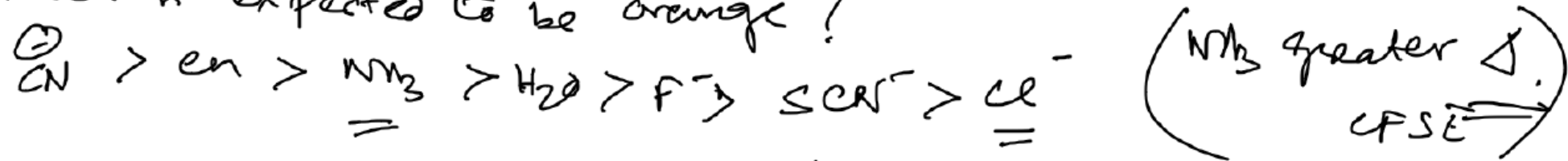

$$= 3.65 \times 10^{-19} \text{ J}$$

$$\Delta_0 = \frac{\Delta_t}{0.44} = \frac{3.65 \times 10^{-19}}{0.44} \text{ J} = 8.3 \times 10^{-18} \text{ J} \quad || \quad \underline{red}$$

④ Determine paramagnetic/diamagnetic

$$\left[Ti(H_2O)_6\right]^{3+}, \quad \left[NiCl_4\right]^{2-}, \quad \left[CoF_6\right]^{3-}, \quad \left[Co(NH_3)_6\right]^{3+}$$

sq. planar complex are usually low spin (✓)

⑤ An octahedral complex absorbs light at 535 nm. What is Δ_o? What will be the color?

⑥ There are two sol^n., one orange and one blue. Both sol^n are known to be made from Co-complex, however, one has Cl^- and one has NH_3. Which in expected to be orange?

$$\overset{\ominus}{CN} > en > NH_3 > H_2O > F^- > SCN^- > Cl^-$$

$\left(\begin{array}{c} NH_3 \text{ greater } \Delta. \\ CFSE \longrightarrow \end{array}\right)$

high energy photon → lower energy color

orange has low energy color than <u>blue</u>
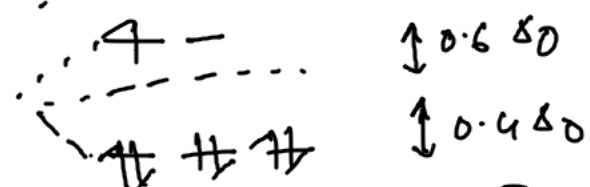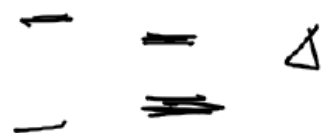
① What color absorbs light at 600 nm?   =)

② If $\Delta_0 = 3.75 \times 10^{-19}$ J, $h = 6.6 \times 10^{-34}$ J·s, $c = 3 \times 10^8$ m s^{-1}, then what is the color of the complex?

③ Would you expect a violet soln. to be high spin or low spin? What about red soln.?

High spin => complementary color of violet is yellow, which has high wavelength of ~570 $\underline{nm}$. For a red color, the complementary color → green. → 530 nm => so it would be $\underline{low\ spin}$

④ What is the CFSE for d^7? (low spin) => strong field ligand) include P. value?

$$\underline{\underline{4}} - \qquad \uparrow 0.6\,\delta_0 \qquad E_{Ligand\ field} = \left[6 \times \left(-\tfrac{2}{5}\Delta_0\right)\right] + \left(1 \times \tfrac{3}{5}\Delta_0\right)$$

$$\text{⇈⇈ 4 4 ⊢} \qquad \text{⇅ ⇅ ⇅} \qquad \uparrow 0.4\,\delta_0 \qquad = -\tfrac{9}{5}\Delta_0 + 3P \qquad + 3P$$

$$E_{isotropic\ field} = 7\times0 + 2P \qquad CFSE = E_{LF} - E_{11} = -\tfrac{9}{5}\Delta_0 + 3P - 2P = \boxed{-\tfrac{9}{5}\Delta_0 + P}$$
$$= 2P$$