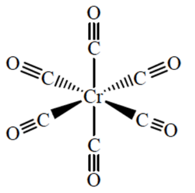
## Spectroscopic Evidence for Bonding in Complexes :

- IR spectroscopy of carbonyl complexes

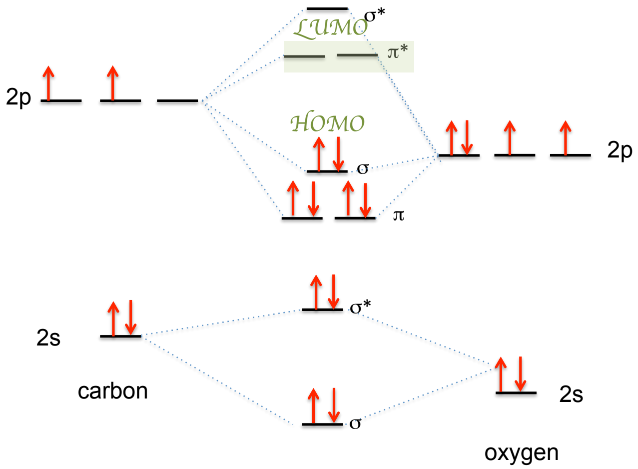
If we look at the MO diagram for CO we remember that the molecule has a σ MO is the HOMO and a π* as the LUMO. We have already seen that these ligands can forms bonding via the lone pair on the molecule or π back-bonding from the metal into the π * orbital. The stretching modes for uncoordinated and coordinated CO in complexes vary in IR spectroscopy. Based on what we have learned about the nature of the bonding, can we explain this ?



Cr-C = 195.5 pm
C-O = 114.0 pm
ν(C-O) = 1984 $cm^{-1}$

$C\equiv O$

C-O = 112.8 pm
ν(C-O) = 2143 $cm^{-1}$

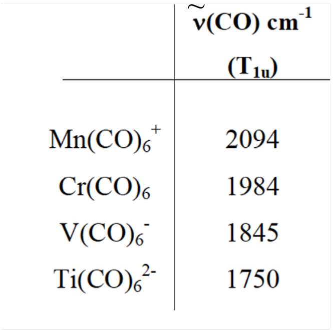


Bond Order is = 3.0.
B. O. = ((# bonding e-) –(# nonbonding e-))/ 2

Exercise : In **classical carbonyl complexes** there is an IR shift to lower wavenumbers. E= hc$\tilde{\nu}$ Can we explain?

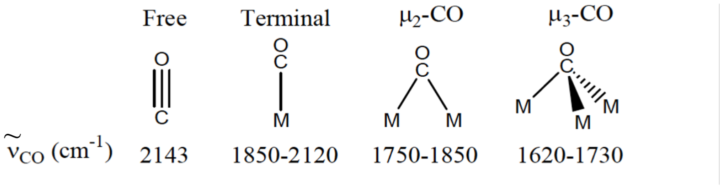
**Answer :** Well first of all lets figure out how to convert between wavenumber to energy, then we can understand whether the stretch is getting easier (lower energy, **red shift**) or harder (higher energy, **blue shift**). For spectroscopic wavenumbers, they can be converted into energy using the following equation. $E = hc\tilde{\nu}$. So we see they are proportional. As the stretching frequency ($\tilde{\nu}$) increases so does the energy of the stretch (E). So then what we see for the $[Cr(CO)_6]$ is that the stretch is getting easier. This should have been indicated by the increase in the length of the C-O bond, which indicates a decrease in bond order. This occurs because the electron density from the metal is donated into the $\pi^*$ orbital of the CO molecule. This decreases the bond order and increases the bond length making the C-O stretch shift to lower energy (red shift).

**Examples of classical carbonyls**



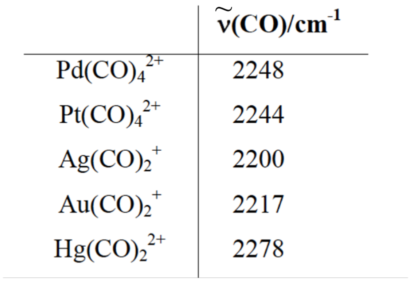
| | $\tilde{\nu}$(CO) cm$^{-1}$ ($T_{1u}$) |
|---|---|
| $Mn(CO)_6^+$ | 2094 |
| $Cr(CO)_6$ | 1984 |
| $V(CO)_6^-$ | 1845 |
| $Ti(CO)_6^{2-}$ | 1750 |

**Examples of carbonyl binding modes**



Exercise: Based on what we have learned about the nature of the bonding, can we explain what is meant by **non-classical carbonyls** and how they differ from the previous ones, see the table below?

Answer: In these complexes electron density is not transferred from the metal to the ligand $\pi^*$-orbitals. The major interaction is $\sigma$-donation from the CO anti-bonding, lone pairs to the metal. Therefore the CO stretching frequency is > free CO, meaning it is blue shifted.



| | $\tilde{\nu}$(CO)/cm$^{-1}$ |
|---|---|
| $Pd(CO)_4^{2+}$ | 2248 |
| $Pt(CO)_4^{2+}$ | 2244 |
| $Ag(CO)_2^{+}$ | 2200 |
| $Au(CO)_2^{+}$ | 2217 |
| $Hg(CO)_2^{2+}$ | 2278 |

## Chapter V. Magnetic and Optical Properties of Coordination Complexes

How do we determine if materials are high-spin or low-spin? How do we figure out the size of $\Delta o$?

### 1. Magnetic properties can indicate whether metals are high-spin or low-spin

When a compound is placed inside a magnetic field of strength (H) (amperes/meter), the magnetic flux density, B (Newton-meters/ampere or tesla), is given by

$B = \mu_0(H + M)$

where M is the intensity of magnetization induced in the sample

$\mu_0$ is the vacuum permittivity constant

Then the magnetic susceptibility, $\chi$, is

$\chi = M/H$

The molar magnetic susceptibility, $\chi$, is then given by

$\chi_m = \chi(MW)$/sample mass; where MW is the molecular weight.

- **Diamagnetic and Paramagnetic**

(a) If B is smaller than $\mu_0 H$, then the substance is diamagnetic. Such substance is slightly repelled by the magnetic field. Its susceptibility is negative, but only slightly.

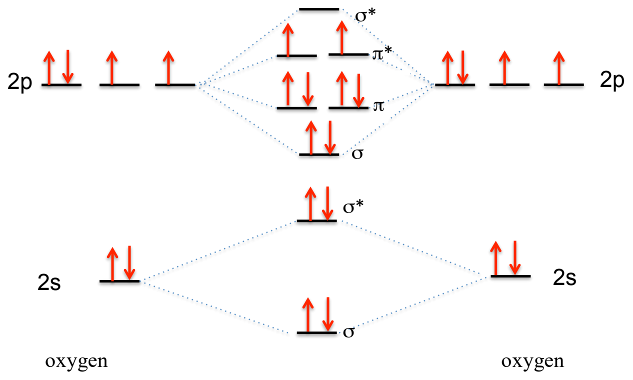
(b) If B is bigger than $\mu_0H$, then the substance is paramagnetic. Such substance is attracted into a magnetic field. Its susceptibility is positive.

(Recall your experiments with Gouy Balance)

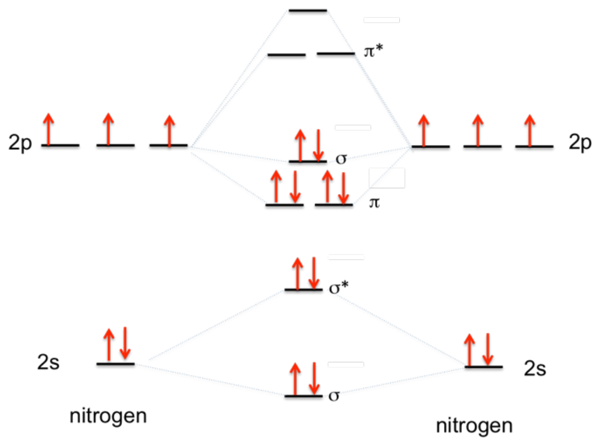
In general, diamagnetic compounds only have paired electrons. Where there are unpaired electrons, the compounds are paramagnetic. But keep in mind all materials have diamagnetic character. It is just that the signal from unpaired electrons is very large and offsets what would be observed from the paired electrons.

Simple example: Draw the MO diagram and show the difference in their magnetic properties of $O_2$; $N_2$ and classify as diamagnetic or paramagnetic.

Answer:



Bond Order is = 2.



Bond Order is = 3.0.

Ligands and metals can be paramagnetic. From the MO diagram of $O_2$ and $O_2^-$ (which we looked at in ligand field theory), then you remember it has two and three unpaired electrons in the π* orbitals, respectively. Whereas $N_2$, is diamagnetic.

## ➢ Magnetic susceptibility and moment

**Magnetic susceptibility** describes how sensitive a material is to an applied magnetic field and is proportional to the magnetic moment of the material, μ.

Molar susceptibility is defined as:

$\chi_m = (N\mu^2)/3RT$

N is the Avogadro number ($6.02 \times 10^{23}$ $mol^{-1}$), R is the ideal gas constant (8.31 j $mol^{-1}$ $K^{-1}$), T is the absolute temperature (in Kelv, and μ is the magnetic moment, in the unit of **Bohr Magneton** (B.M.).

Therefore, μ can be calculated from $\chi_m$:

$\mu = ((\chi_m \times 3RT)/N)^{1/2} = 2.83\ (\chi_m \times T)^{1/2}$

For **most transition metal ions**, quantum theories predict that:

$\mu_{S+L} = (4S(S+1)+L(L+1))^{1/2}$

**S** is the total spin angular momentum quantum number S = n/2

**L** is the total orbital angular momentum quantum number = |sum $m_l$|

i.e. for a High Spin $d^4$ octahedral complex has S=2 and L=2.

S = (4/2) and L = |-2 -1 + 0 +1| = 2

And for **first-row transition metal complexes**, the contribution from the orbital angular momentum is wholly or partially quenched, so

$\mu_s = (4S(S+1))^{1/2}$

This is the so-called **spin-only formula** for magnetic moment. For octahedral complexes, the only exceptions are low spin $d^5$, high spin $d^6$ and high spin $d^7$ complexes.

Because $S = n/2$, where n is the number of unpaired electrons,

$\mu((\text{spin-only}) = (n(n+2))^{1/2}$

Therefore, magnetic moments correspond to the number of unpaired electrons in fist-row transition metal complexes.

Ligand-field/crystal-field theory can be used to explain magnetic properties of complexes.

Example:

(1)For h.s. $Co^{2+}$ and (2) $Cr^{3+}$ calculate S and L.

Answer:

$Co^{2+}$ is $d^7$, L = 3 and S = 3/2

$Cr^{3+}$ is $d^3$, L=3 and S=3/2

The following table shows that indeed for most first-row transition metal ions, the measured magnetic moments are close to the calculated spin-only values. The examples are for high-spin complexes, but the same is true for low-spin complexes.

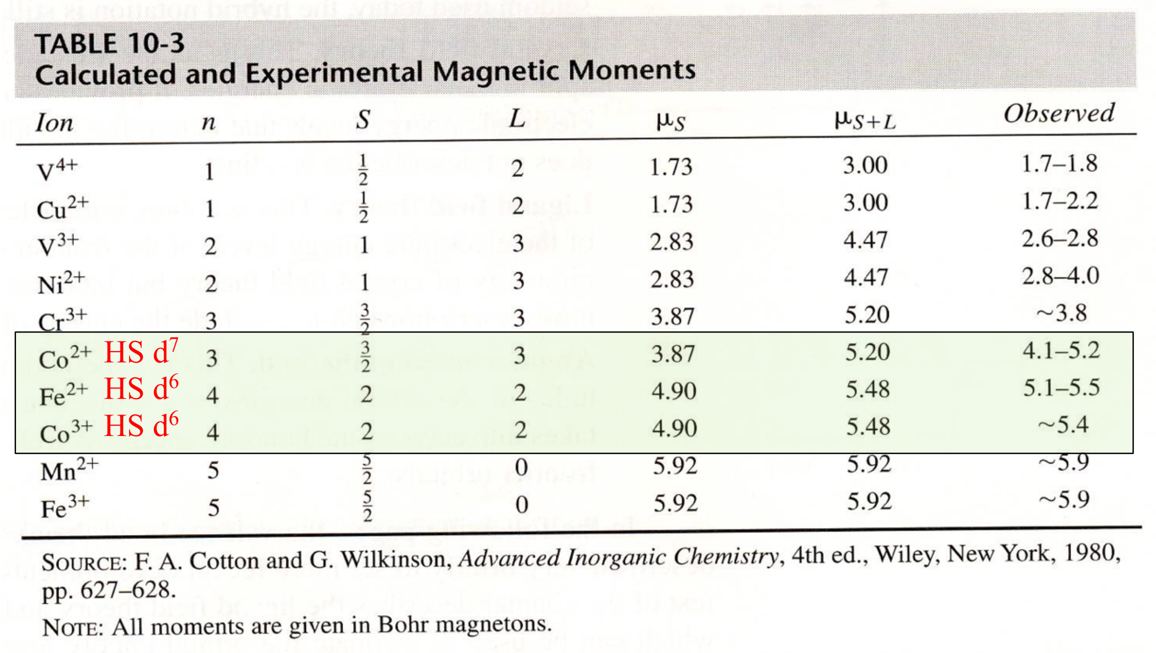


**TABLE 10-3**
**Calculated and Experimental Magnetic Moments**

| *Ion* | *n* | *S* | *L* | $\mu_S$ | $\mu_{S+L}$ | *Observed* |
|---|---|---|---|---|---|---|
| $V^{4+}$ | 1 | $\frac{1}{2}$ | 2 | 1.73 | 3.00 | 1.7–1.8 |
| $Cu^{2+}$ | 1 | $\frac{1}{2}$ | 2 | 1.73 | 3.00 | 1.7–2.2 |
| $V^{3+}$ | 2 | 1 | 3 | 2.83 | 4.47 | 2.6–2.8 |
| $Ni^{2+}$ | 2 | 1 | 3 | 2.83 | 4.47 | 2.8–4.0 |
| $Cr^{3+}$ | 3 | $\frac{3}{2}$ | 3 | 3.87 | 5.20 | ~3.8 |
| $Co^{2+}$ HS $d^7$ | 3 | $\frac{3}{2}$ | 3 | 3.87 | 5.20 | 4.1–5.2 |
| $Fe^{2+}$ HS $d^6$ | 4 | 2 | 2 | 4.90 | 5.48 | 5.1–5.5 |
| $Co^{3+}$ HS $d^6$ | 4 | 2 | 2 | 4.90 | 5.48 | ~5.4 |
| $Mn^{2+}$ | 5 | $\frac{5}{2}$ | 0 | 5.92 | 5.92 | ~5.9 |
| $Fe^{3+}$ | 5 | $\frac{5}{2}$ | 0 | 5.92 | 5.92 | ~5.9 |

SOURCE: F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980, pp. 627–628.
NOTE: All moments are given in Bohr magnetons.

Exercise. Are the following complexes diamagnetic or paramagnetic? If paramagnetic, what are their magnetic moments? For those 6-coordinate, assume it is a purely octahedral environments.

(1) $[Fe(H_2O)_6]^{2+}$

(2) $[Fe(CN)_6]^{4-}$

(3) $[CoCl_4]^{2-}$

(4) $[Ni(H_2O)_6]^{2+}$

(5) $[Pt(NH_3)_2Cl_2]$ (square planar)

(6) $VCl_4$

Answer:

(1) $d^6$ high spin, so S = 2, therefore it is paramagnetic. Then the calculated μ value is 4.9 $\mu_B$.

(2) $d^6$ low spin, so S=0, therefore it is diamagnetic. Then the calculated μ value is 0 $\mu_B$.

(3) $Co^{2+}$ is $d^7$, is tetrahedaral therefore it is paramagnetic S=3/2, 3.87 $\mu_B$

(4) $Ni^{2+}$ is $d^8$, therefore it is paramagnetic S=1, 2.83 $\mu_B$

(5) $Pt^{2+}$ is $d^8$, and square planar diamagnetic S=0, 0 $\mu_B$

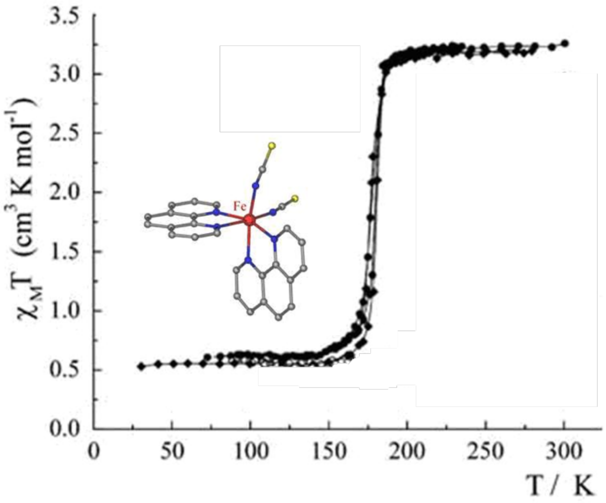
(6) $V^{4+}$ is $d^1$, therefore it is paramagnetic S=1/2, 1.73 $\mu_B$

**Spin-crossover.** We have learned that the spin state of a metal complex depends on the ligand field splitting energy Δ and the paring energy. If $\Delta < P$ **(**pairing energy), the complex prefers the high spin configuration; if $\Delta > P$, the complex prefers the low spin configuration.

**Question:** What happens if $\Delta \cong P$?

**Answer:** In this situation, the high spin and low spin configurations have similar energies. A small external stimulus can change the complex from high spin to low spin, or vice versa. Common stimuli are the variation of temperature, pressure, light irradiation, etc. The change of the spin state is called spin crossover.

The most well known example is Fe(II) complex [Fe(Phen)$_2$(NCS)$_2$]. d$^6$ complex.



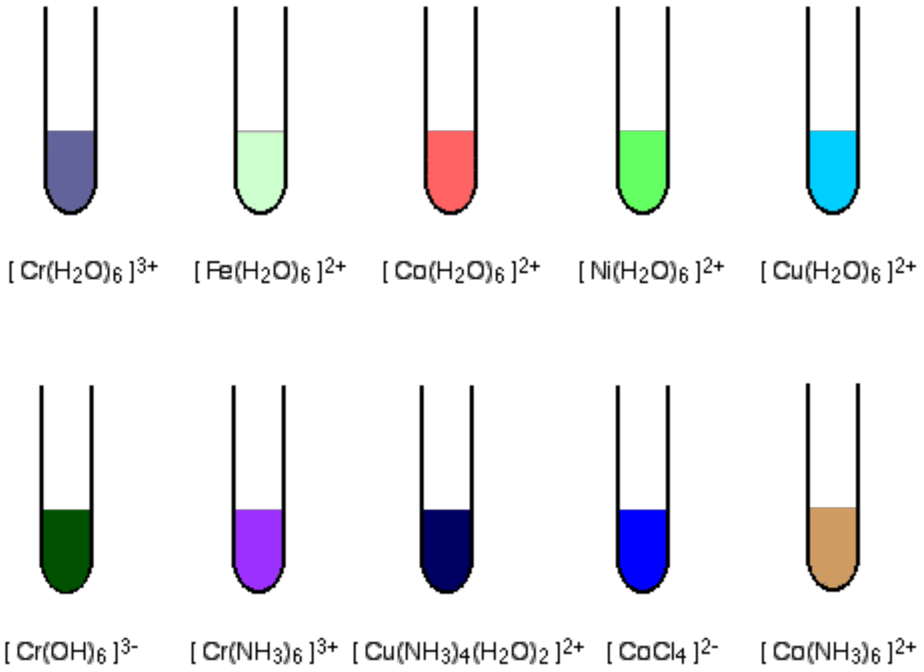
This complex is high spin at a temperature higher than 200 K; and low-spin at a temperature lower than 175 K.

Exercise: Based on what we have learned thus far, what complexes are most likely to undergo a transition from high spin to low-spin configurations, or vice versa?

Answer: Well only d$^4$ to d$^7$ can exist as both and heavier 4d and 5d transition metals are low-spin bc of low pairing energy. So we assume this can happen with d$^4$ to d$^7$ of 3d transition metals and often in an octahedral environment.

## 2. Optical Properties of Complexes

Transition metal complexes are colorful.



**Question:** Where does the color come from?

**Answer:** d-d transitions which have energies in the visible regime.

For a compound, if it absorbs light, one would see a color. If the compound absorbs a certain color of light, one sees its compliment color, what is reflected.

What is compliment color?

Green is the compliment color of red, yellow is the compliment color of violet.

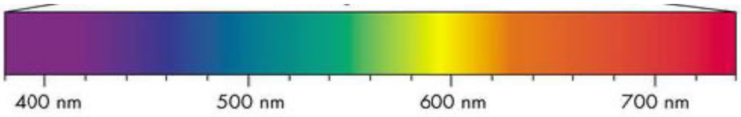
Keep in mind that white light contains all colors. Its compliment color is black.

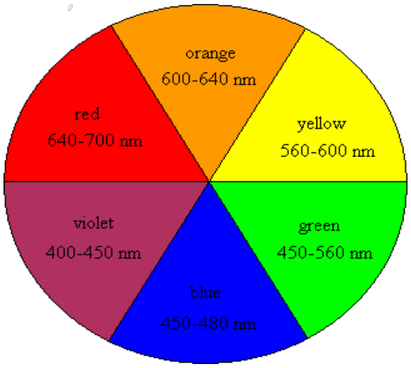
Numerically speaking, color is correlated to the wavelength of the light.

$\lambda$ = wavelength (nm)

$1/\lambda$ = wavenumber ($cm^{-1}$)

The following table shows the wavenumbers and wavelengths of lights corresponding to each color. The compliment colors are also shown.





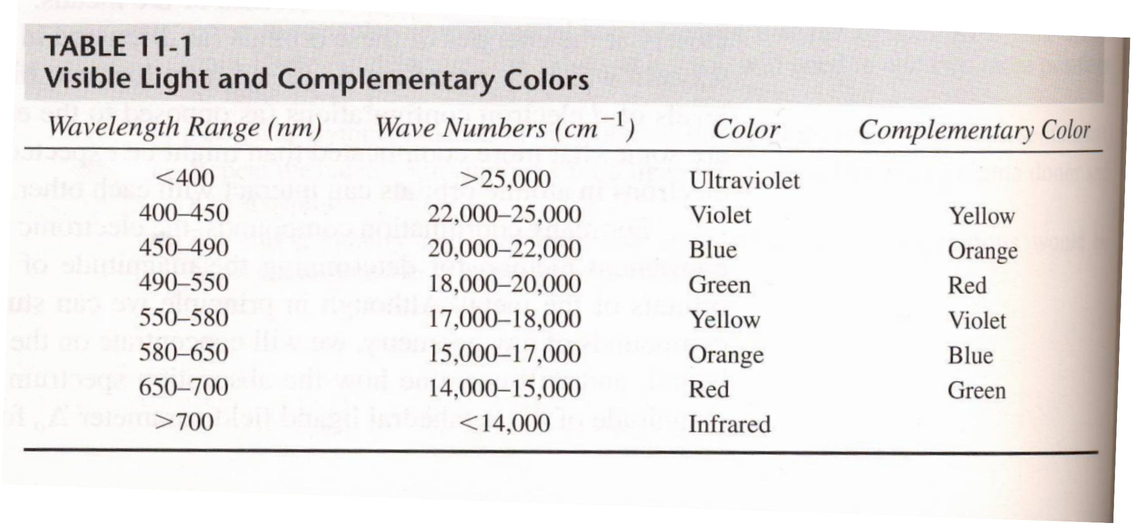


**TABLE 11-1**
**Visible Light and Complementary Colors**

| *Wavelength Range (nm)* | *Wave Numbers ($cm^{-1}$)* | *Color* | *Complementary Color* |
|---|---|---|---|
| <400 | >25,000 | Ultraviolet | |
| 400–450 | 22,000–25,000 | Violet | Yellow |
| 450–490 | 20,000–22,000 | Blue | Orange |
| 490–550 | 18,000–20,000 | Green | Red |
| 550–580 | 17,000–18,000 | Yellow | Violet |
| 580–650 | 15,000–17,000 | Orange | Blue |
| 650–700 | 14,000–15,000 | Red | Green |
| >700 | <14,000 | Infrared | |

Wavelength or wavenumber is an indication of the energy of the light.

Recall that

$E = \hbar\nu = \hbar\, c/\lambda = \hbar\, c\, (1/\lambda) = hc\tilde{\nu}$

E = energy

$\hbar$ = Planck's constant = $6.626 \times 10^{-34}$ J s c = speed of light = $2.998 \times 10^8$ m $s^{-1}$

$\nu$ = frequency

$\lambda$ = wavelength

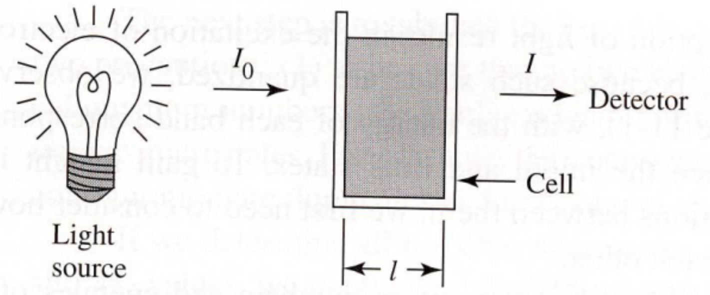
$1/\lambda$ = wavenumber

**When a complex absorbs a certain color of light, it means it absorbs the photon of certain energy.**

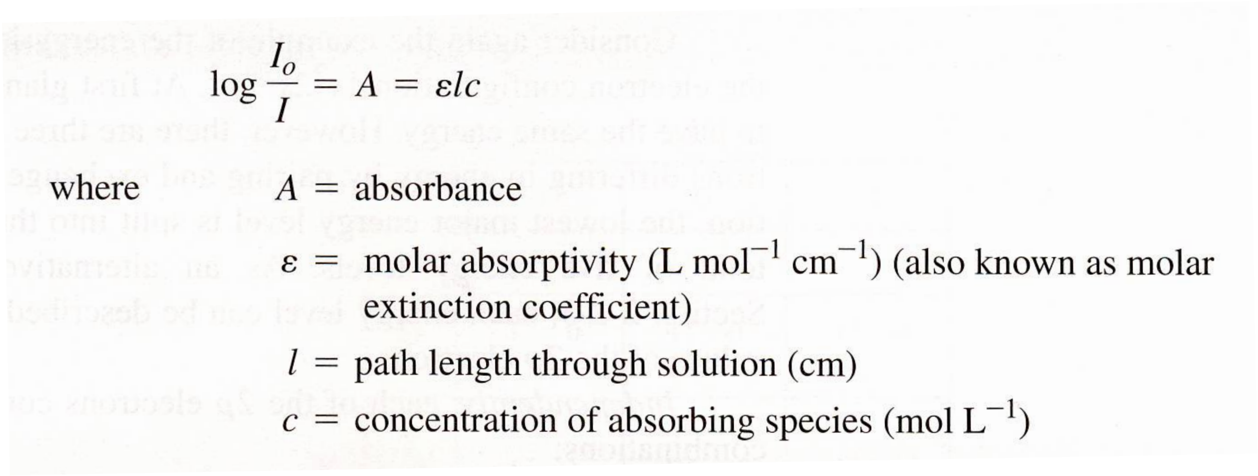
How do we measure the absorption of light in a quantitative manner?

We use spectroscopy.

A basic set-up.



It turns out that the absorption of the light follows the Beer-Lambert law.



$$\log \frac{I_o}{I} = A = \varepsilon l c$$

where $A$ = absorbance

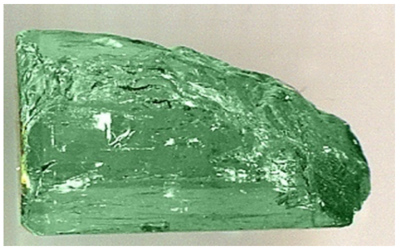
$\varepsilon$ = molar absorptivity (L mol$^{-1}$ cm$^{-1}$) (also known as molar extinction coefficient)

$l$ = path length through solution (cm)

$c$ = concentration of absorbing species (mol L$^{-1}$)

Let's now look at some examples on transition metal complexes.

Prussian blue, one of the first synthetic pigment, and the first coordination compound used as pigment. Formula $Fe_4[Fe(CN)_6]_3$. Absorbs orange and emits blue.



Emerald - $Be_3A_{l2}(SiO_3)_6$ absorbs red, emits green

Amethyst – $Fe^{3+}$ substituted silicate

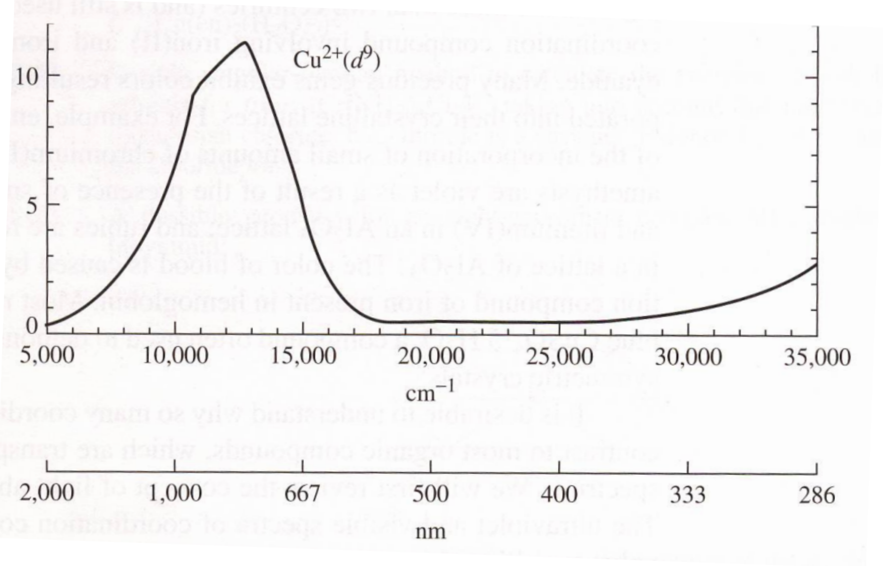
Absorbs yellow, emits violet.

Ruby – $Cr^{3+}$ aluminum oxide

Absorbs yellow-green region

Emits red

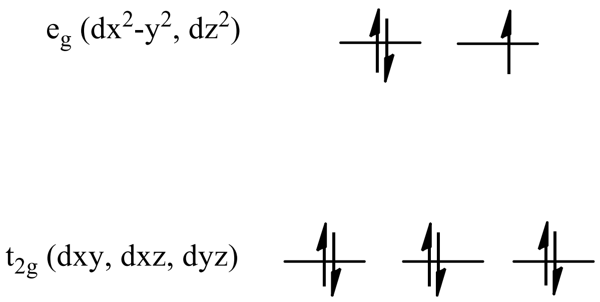
$[Cu(H_2O)_6]^{2+}$ absorbs orange-red, emits blue.



**Why does $[Cu(H_2O)_6]^{2+}$ absorb this light?**

To understand this, we need crystal/ligand field theory. (The two theories are equivalent here)

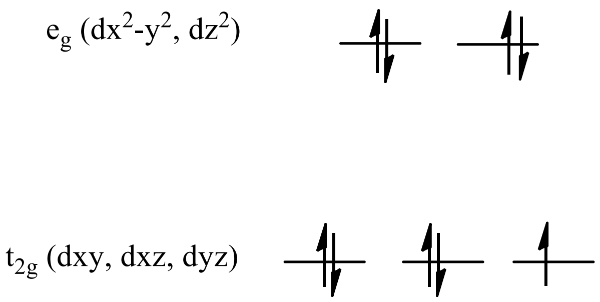
The ground state electronic configuration is:



in an octahedral field

The energy of the system is $E^0$

The electron in the $t_{2g}$ orbital can jump up to the $e_g$ orbital to form an excited state:



in an octahedral field

The energy of this state is $E^1$.

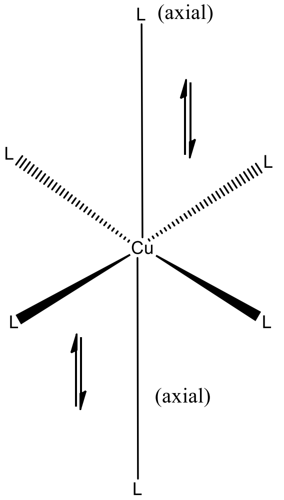
The difference of the energy is $\Delta E = (E^1 - E^0) = \Delta o$ = Crystal field splitting energy

Therefore, the Cu complex can absorb the light with an energy of $\Delta o$. By this absorption, it gives rise to the blue color we see.

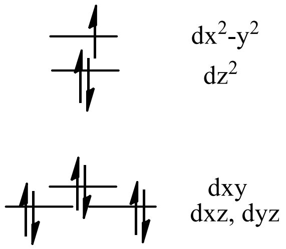
**For your information.** If we look carefully the absorption spectrum, we can see that this broad peak is better described by the combination of two closely spaced peaks. That is, the complex absorbs two different lights. Why?

Recall the Jahn-Teller distortion (Chapter IV).

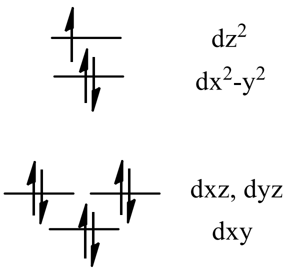
For a Cu(II) complex, a Jahn-Teller distortion makes the axial Cu-ligand distances different from the equatorial Cu-ligand distances.



By doing so, it gives rise to one of the following two electronic configurations:



axial elongation



axial compression

The energies of the (dxz, dyz, and dxy) orbitals are close but not the same. Likewise, the energies of ($dz^2$, $dx^2$-$y^2$) are not equivalent. In the case of elongation, an electron can jump from dxy or (dxz, dyz) to $dx^2$-$y^2$. For this reason, we see two closely packed absorption peaks. In the case of compression, an electron can jump from either dxy or (dxz, dyz); again we will see two absorption peaks.

**Selection rules for light absorption**

Not all transitions between different electronic states (orbitals) are allowed. Here are two important rules.

**A. Laporte selection rule**

Transitions between states of the same parity (symmetry with respect to a center of inversion) are forbidden. u to g or go to u.

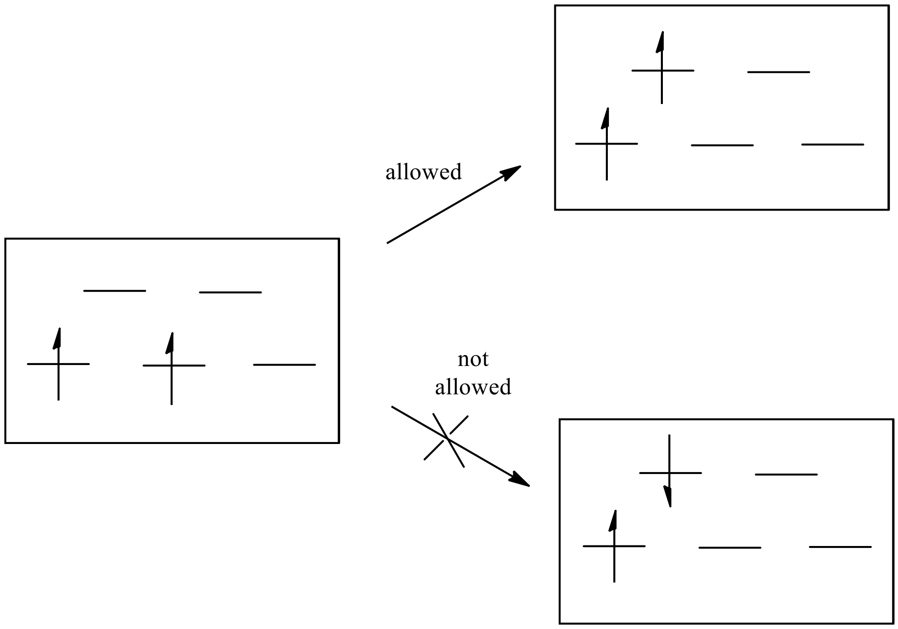
According to this rule, transitions between d orbitals are forbidden because they are both g, $t_{2g}$ and $e_g$. Transitions between d and p orbitals are allowed. Now, why do we see colors of complexes which arise from the d-d transitions?

This is because the bonds in complexes are not rigid. They undergo vibrations that may temporarily remove the center symmetry. Under such circumstances, d-d transitions can be observed, as they do not violate the selection rule. However, such transition is weak. In octahedral complexes, they are very weak, and generally have ε = 10 – 50 $M^{-1}$ $cm^{-1}$. But it is strong enough to be observed by eyes and it is responsible for the bright color of the complexes. A tetrahedral complex normally has much higher ε because it does not have a center of symmetry. Its ε is in the order of thousands. For comparison, a parity-allowed transition, for examples, transition between d and p orbitals, has a ε of about 10000 to 100000 $M^{-1}$ $cm^{-1}$.

**B. Spin selection rule**

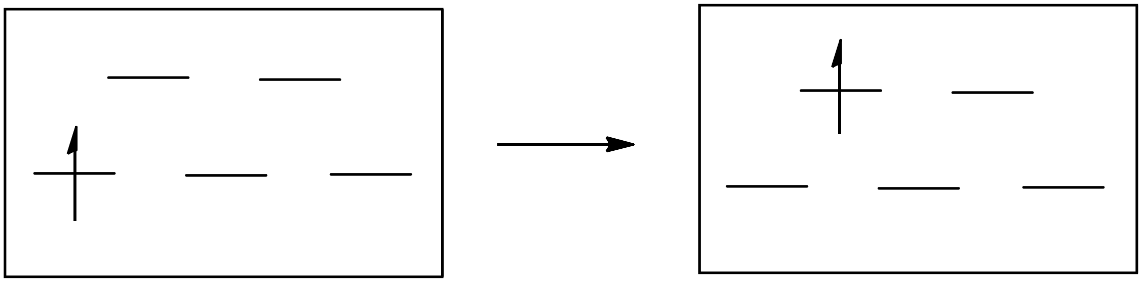
Transitions between states of different spin multiplicities are forbidden. Spin multiplicity is 2S+1 or also shown as n+1, b/c S = n/2

For example:



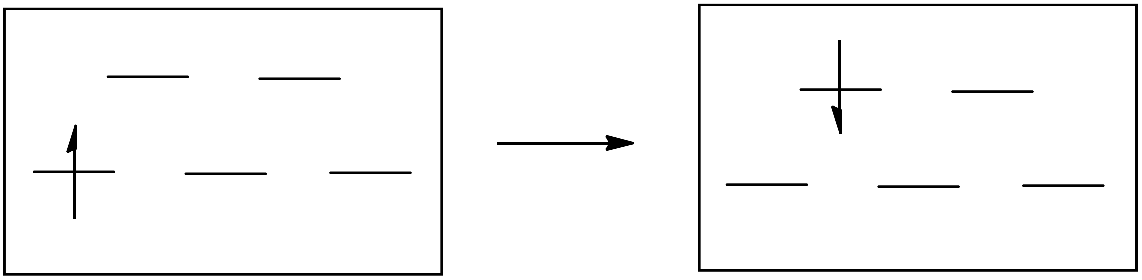
Exercise.

Judge whether the following transitions are spin-allowed. Note all of the following are disallowed according to the Laporte selection rule due to the similarity in parity between $t_2$g and eg.



(a)

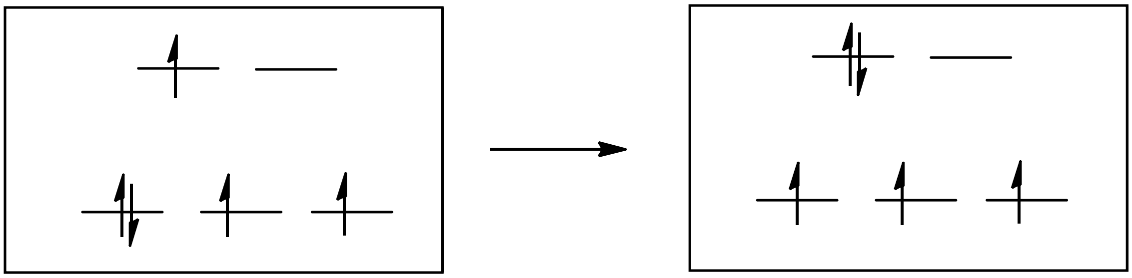
Answer: allowed.



(b)

Answer: disallowed , b/c spin multiplicity goes from 2 to 0.

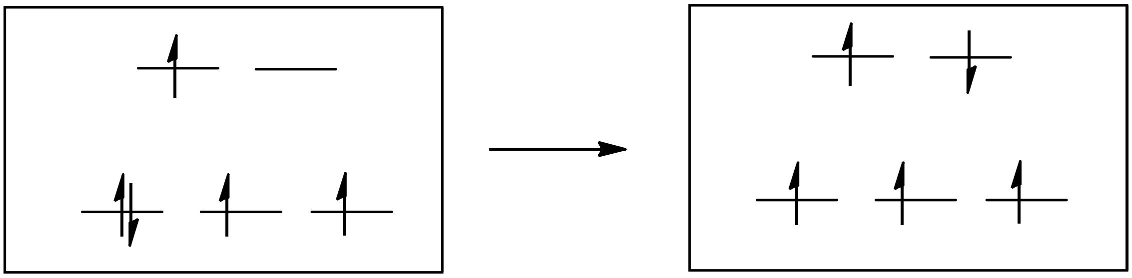
1+1 vs -1+1.



(c)

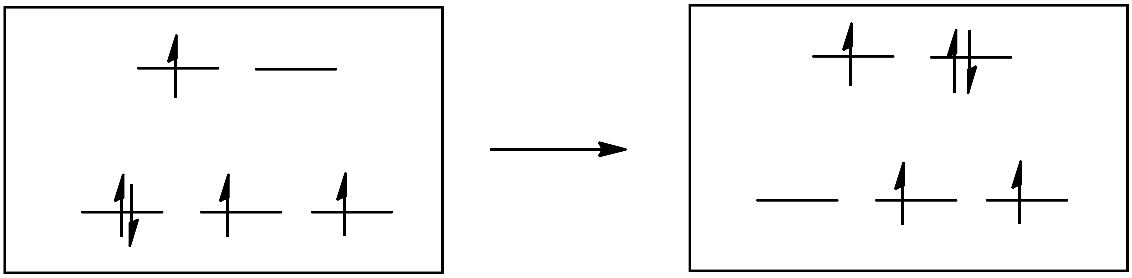
Answer: allowed. Spin multiplicity = 4.

(d)



Answer: allowed. Spin multiplicity = 4.

(e)



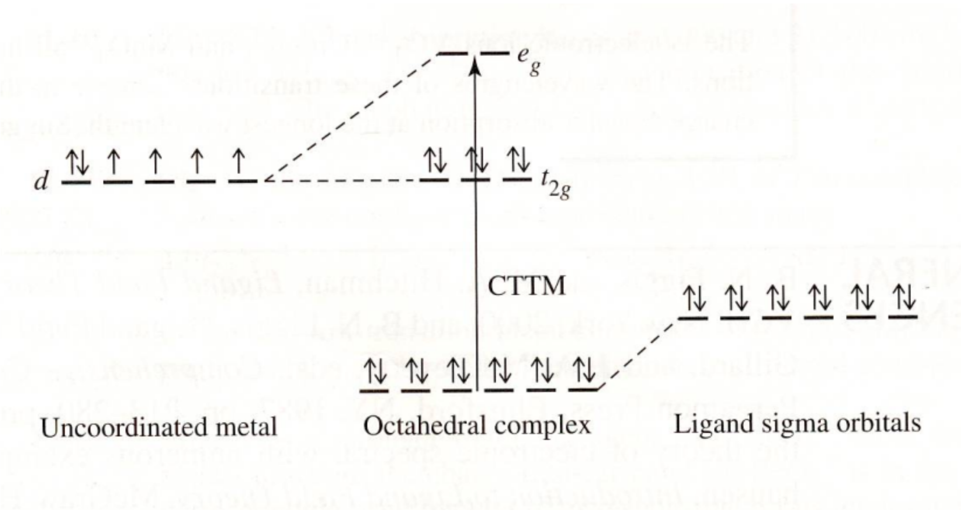
Answer: allowed. Spin multiplicity = 4.

### ➢ Charge-transfer transition

So far we have seen transitions between metal d-d orbitals. How about transitions from ligand orbitals to metal orbitals, and vice versa?

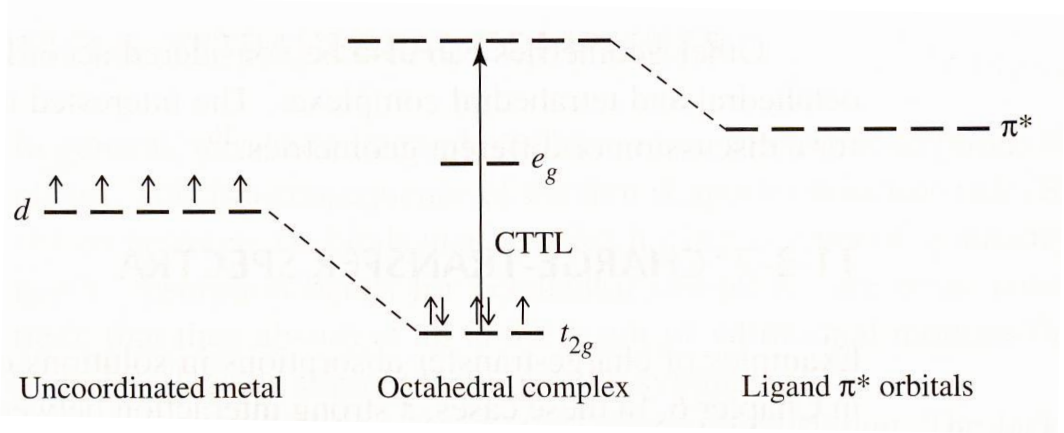
These are called **charge-transfer** transitions, which are common in metal complexes. They are parity-allowed, and have high intensities (often 50000 $M^{-1}$ $cm^{-1}$ or above). They can be in UV or visible region.

For examples, for a $d^6$ low-spin complex.



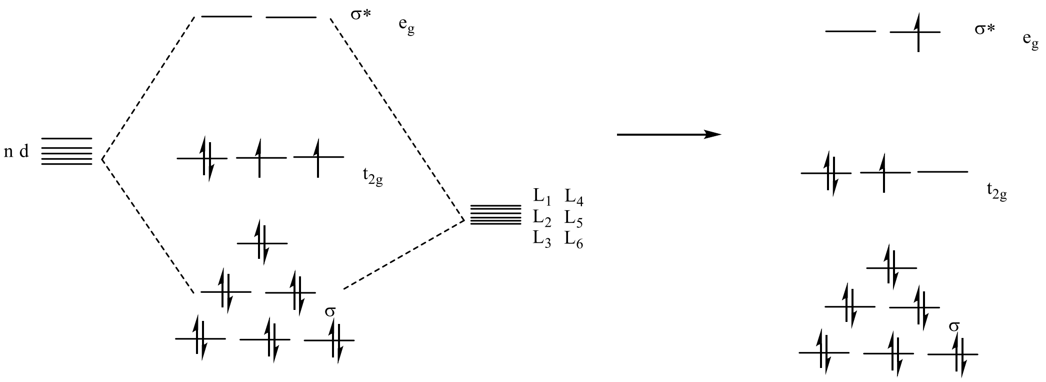
This is often called ligand to metal charge transfer (LMCT). CTTM: charge transfer to metal.

An opposite situation is also possible, where the transition is from the orbitals that are predominately metal in nature. This is called metal to ligand charge transfer (MLCT), or CCTL (charge transfer to ligand). This situation most often occurs in complexes with empty π* orbitals, such as CO, CN$^-$, SCN$^-$, pyridine, bipyridine, etc. For example:



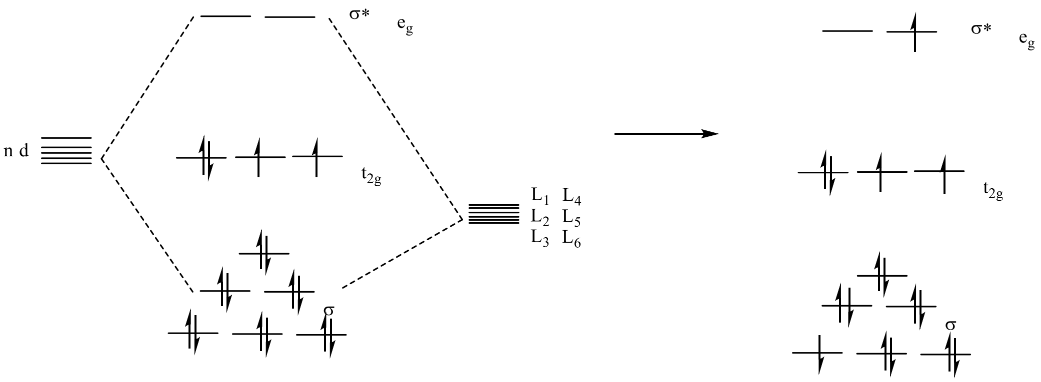
Exercise. Predict whether the following transition is strong or weak.

(a)



This transition will be very weak as it is Laporte (or parity) forbidden. It will be spin allowed.

(b)



This transition will be strong as it is Laporte (or parity) allowed as it comes from t1u and goes to the eg. It will be spin allowed as well.