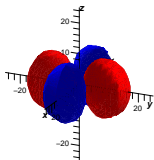
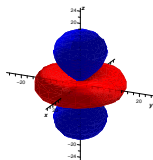
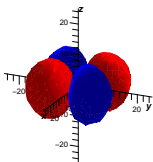
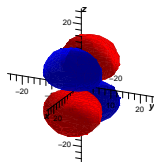
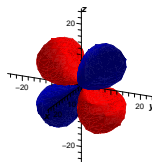


# Chemistry 1000 Lecture 26: Crystal field theory

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## The d orbitals

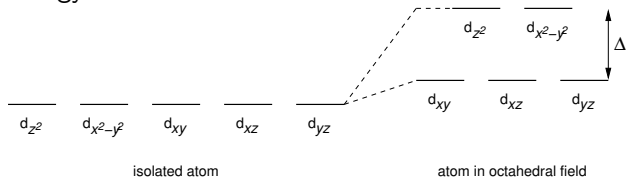
 $3d_{x^2-y^2}$  $3d_{z^2}$  $3d_{xy}$  $3d_{xz}$  $3d_{yz}$

# Crystal field theory

- In an isolated atom or ion, the d orbitals are all degenerate, i.e. they have identical orbital energies.
- When we add ligands however, the spherical symmetry of the atom is broken, and the d orbitals end up having different energies.
- The qualitative appearance of the energy level diagram depends on the structure of the complex (octahedral vs square planar vs. . . ).
- The relative size of the energy level separation depends on the ligand, i.e. some ligands reproducibly create larger separations than others.

# Octahedral crystal fields

- In an octahedral complex, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals point directly at some of the ligands while the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  do not.
- This enhances the repulsion between electrons in a metal  $d_{x^2-y^2}$  or  $d_{z^2}$  orbital and the donated electron pair from the ligand, raising the energy of these metal orbitals relative to the other three. Thus:



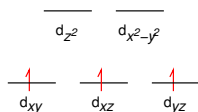
- $\Delta =$  crystal-field splitting

# Crystal-field splitting

**Note:** Sometimes we write  $\Delta_o$  instead of  $\Delta$  to differentiate the crystal-field splitting in an octahedral field from the splitting in a field of some other symmetry (e.g.  $\Delta_t$  for tetrahedral).

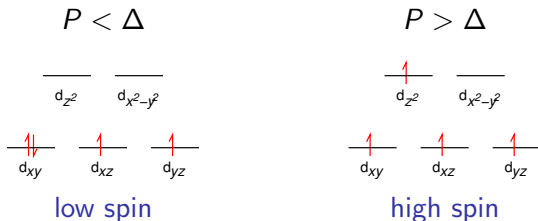
# Electron configurations

- At first, just follow Hund's rule, e.g. for a  $d^3$  configuration,



- $P$  = pairing energy = extra electron-electron repulsion energy required to put a second electron into a d orbital + loss of favorable spin alignment

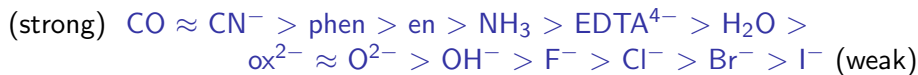
- For  $d^4$ , two possibilities:



- Experimentally, we can tell these apart using the paramagnetic effect, which should be twice as large for the high-spin  $d^4$  than for the low-spin  $d^4$  configuration.

# Spectrochemical series

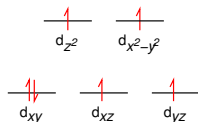
- We can order ligands by the size of  $\Delta$  they produce.  
 $\implies$  spectrochemical series
- A ligand that produces a large  $\Delta$  is a **strong-field ligand**.
- A ligand that produces a small  $\Delta$  is a **weak-field ligand**.



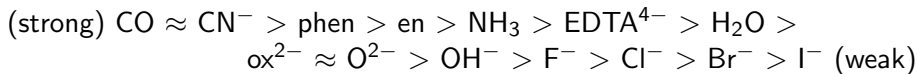


# Example: Iron(II) complexes

- Electronic configuration of  $\text{Fe}^{2+}$ :  $[\text{Ar}]3d^6$
- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is high spin:

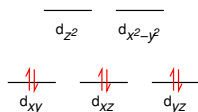


- From the spectrochemical series, we know that all the ligands after  $\text{H}_2\text{O}$  in octahedral complexes with  $\text{Fe}^{2+}$  will also produce high-spin complexes, e.g.  $[\text{Fe}(\text{OH})_6]^{4-}$  is high spin.

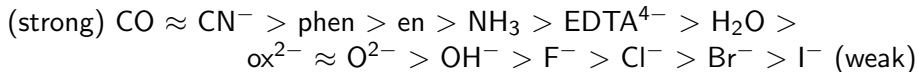


# Example: Iron(II) complexes (continued)

- $[\text{Fe}(\text{CN})_6]^{4-}$  is low spin:

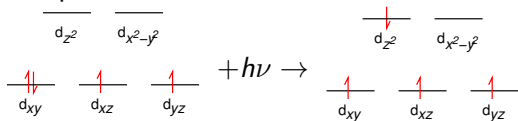


- Somewhere between  $\text{CN}^-$  and  $\text{H}_2\text{O}$ , we switch from low to high spin.



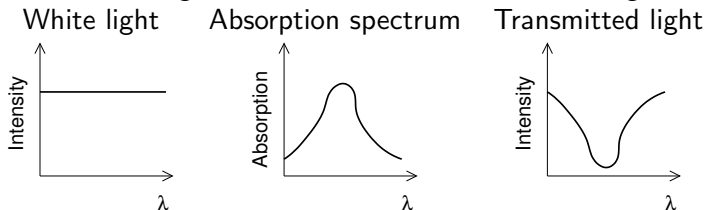
## Color

- Typically in the transition metals,  $\Delta$  is in the range of energies of visible photons.
- Absorption:

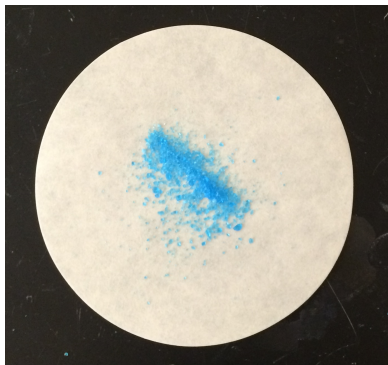
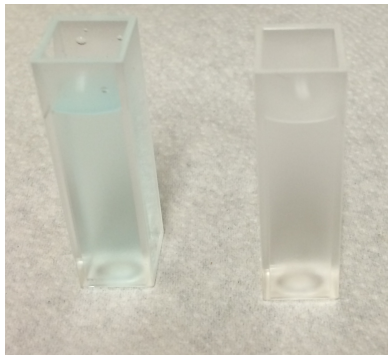


- Colored compounds absorb light in the visible range.

The absorbed light is subtracted from the incident light:

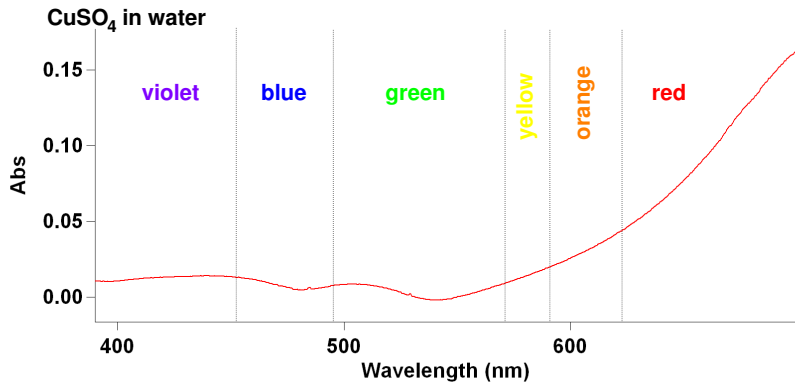


## Example: copper sulfate

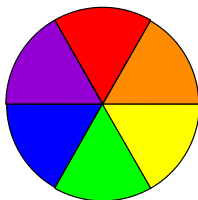
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  $\text{CuSO}_4$  solution vs blank

# Example: copper sulfate

## Visible spectrum

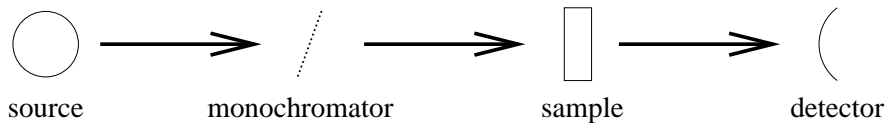


# The color wheel

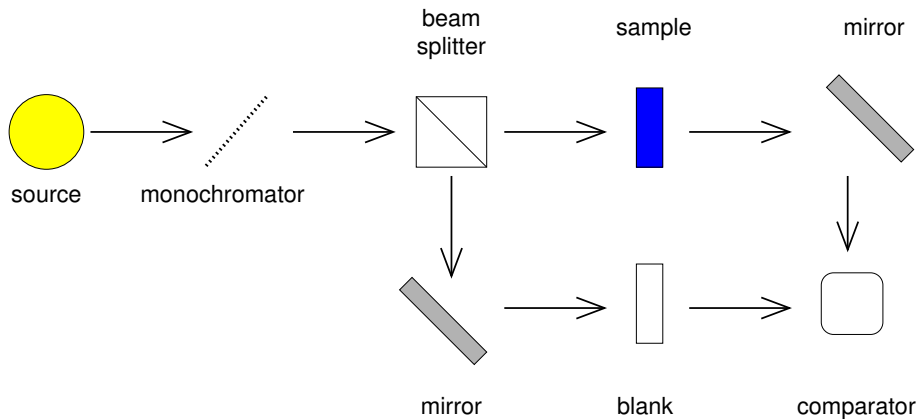


- Colors in opposite sectors are complementary.
- Example: a material that absorbs strongly in the red will appear green.

# Simple single-beam absorption spectrometer



# Dual-beam absorption spectrometer





## Example: Cobalt(III) complexes

- The  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  ion is green.  
From the color wheel, this corresponds to absorption in the red.
- The  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is yellow-orange.  
It absorbs in the blue-violet.
- The  $[\text{Co}(\text{CN})_6]^{3-}$  ion is pale yellow.  
It absorbs mostly in the ultraviolet, with an absorption tail in the violet.
- Note that these results are consistent with the spectrochemical series:  
The d level splitting is ordered  
 $\text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$ .

## Examples: Colorless ions

- Titanium(IV) ion  $\implies d^0$  configuration
  
  
  
  
  
  
  
  
  
  
- Zinc(II) ion  $\implies d^{10}$  configuration