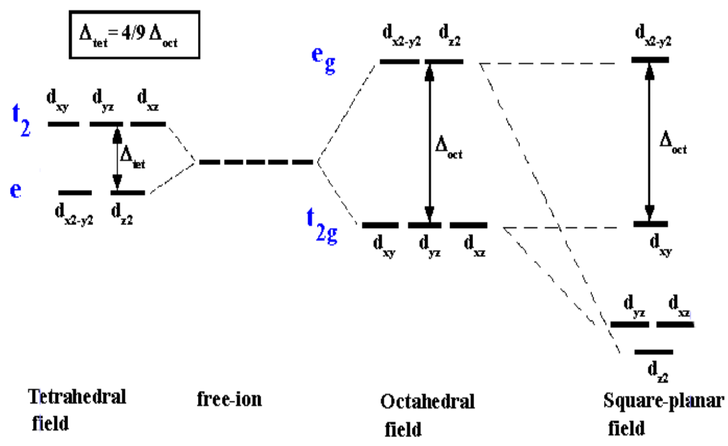
# Absorption involving *d* and *f* *electrons*

- **Lanthanide and Actinide Ions**
- Absorb in UV-V range
- Narrow, and well defined peaks
- Transitions involve for lanthanides 4*f* electrons for actinides 5*f* electrons
- **Transition metals**
- Absorb in V range
- Broad peaks
- Transitions involve *3d* and *4d* electrons

The color of transition metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. Most charge-transfer complexes involve electron transfer between metal atoms and ligands.

Absorption peaks of Lanthanide and Actinide series are little affected by the type of ligand associated with the metal ion.

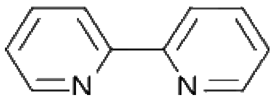
Crystal field d orbital splitting diagrams for common stereochemistries.

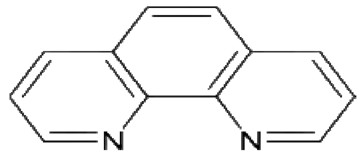



# Factors affecting Δ:

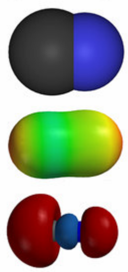
- 1-Stereochemistry
- $\Delta_{tet} = 4/9\ \Delta_{oct}$

- 2-Ligands (increasing ligand strength)
- $I^- < Br^- < SCN^- \sim Cl^- < F^- < OH^- \sim ONO^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 \sim$ pyr ~ en < bipy < phen < $CN^- \sim CO$

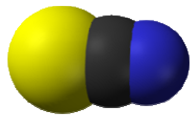




$[:C\equiv N:]^-$



$SCN^-$



en = $NH_2CH_2CH_2NH_2$

- 3-Nature of metal ion
- i- Δ increases as oxidation state increases
- ii-Transition row in which the metal is
  - Δ (3 th.) > Δ (2 nd.) > Δ ( 1 st)

Intensity of d-d transition peaks in UV-V spectroscopy:

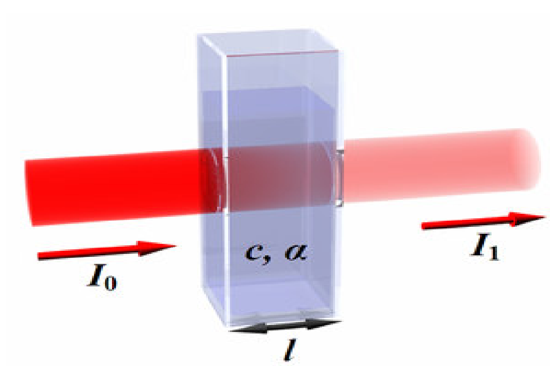
Tetrahedral, ε ~550

Non-centrosymetrical octahedral, ε ~ 50-100

Centrosymetrical octahedral, ε ~ 5

Effect of Ligands on $\lambda_{max}$

| | 6 $Cl^-$ | $6H_2O$ | $6NH_3$ | 3en | $6CN^-$ |
|---|---|---|---|---|---|
| Cr(III) | 736 | 573 | 462 | 456 | 380 |
| Co (III) | - | 538 | 435 | 428 | 294 |
| Co (II) | - | 1345 | 980 | 909 | - |
| Ni(II) | 1370 | 1279 | 925 | 863 | - |
| Cu (II) | - | 794 | 663 | 610 | - |
| | | | | | |




$$A = -\log_{10}\left(\frac{I}{I_0}\right) \qquad T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon \ell c}$$

$$A = \varepsilon \ell c = \alpha \ell \qquad A = -\log(T) = -\log\left(\frac{P}{P_0}\right)$$

A mixture in solution containing two components at concentrations **c1** and **c2**:

The absorbance at any wavelength, λ is, for unit path length, given by

$$A(\lambda) = c_1 \; \epsilon_1(\lambda) + c_2 \; \epsilon_2(\lambda)$$

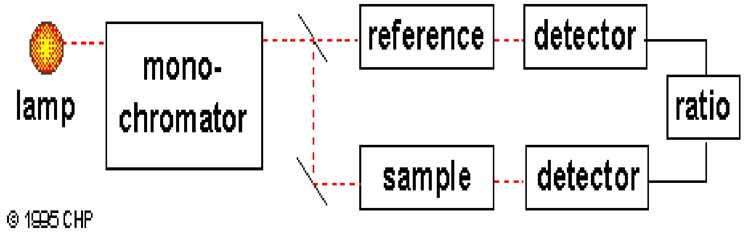
The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

1-deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity

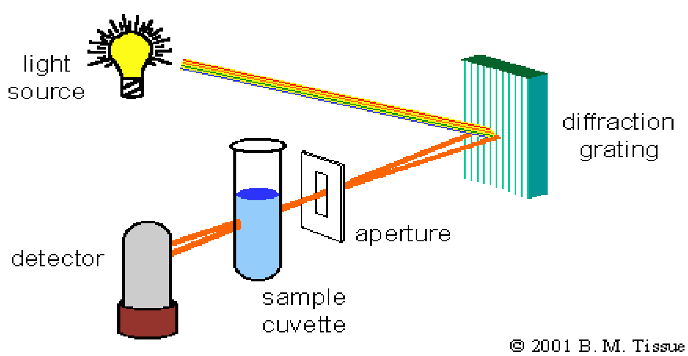
2-scattering of light due to particulates in the sample fluoresecence or phosphorescence of the sample

3-changes in refractive index at high analyte concentration shifts in chemical equilibria as a function of concentration

4-non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band stray light *dual-beam spectrophotometer*




single-beam spectrophotometer

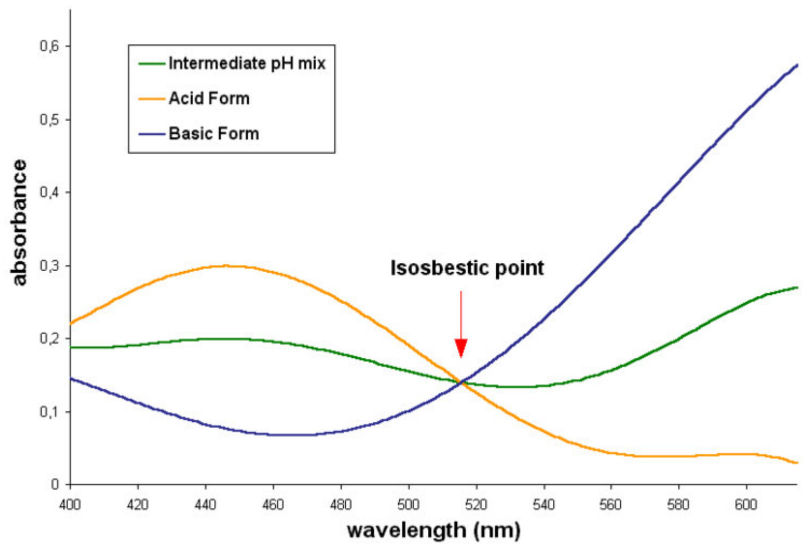


The light source is usually a *deuterium discharge lamp* for UV measurements and

*tungsten-halogen lamp* for visible and Near IR measurements.

**Isosbestic point** is a specific wavelength at which two (or more) chemical species have the same molar absorptivity (ε).

When an **isosbestic plot** is constructed by the superposition of the absorption spectra of two species (whether by using molar absorptivity for the representation, or by using absorbance and keeping the same molar concentration for both species), the **isosbestic point** corresponds to a wavelength at which these spectra cross each other.




For the reaction: $X \rightarrow Y$

$$c_X + c_Y = c$$

$$A = l \cdot (\epsilon_X c_X + \epsilon_Y c_Y)$$

$$\epsilon_X = \epsilon_Y = \epsilon$$

$$A = l \cdot (\epsilon_X c_X + \epsilon_Y c_Y) = l \cdot \epsilon \cdot (c_X + c_Y) = l \cdot \epsilon \cdot c$$

When a 1-to-1 (one mole of reactant gives one mole of product) chemical reaction involves a pair of substances with an isosbestic point, the absorbance of the reaction mixture at this wavelength remains invariant, regardless of the extent of reaction (or the position of the chemical equilibrium). This occurs because the two substances absorb light of that specific wavelength to the same extent, and the analytical concentration remains constant.