Ultraviolet-Visible Spectroscopy

- **Introduction to UV-Visible**
  - **Absorption spectroscopy from 160 nm to 780 nm**
  - **Measurement of transmittance**

    → Conversion to absorbance

    *** $A=-\log T=\varepsilon bc$**

- **Measurement of transmittance and absorbance**
- **Beer's law**
- **Noise**
- **Instrumentation**

Measurement

- Scattering of light
  - Refraction at interfaces
  - Scatter in solution
    - →Large molecules
    - →Air bubbles
- Normalized by comparison to reference cell
  - Contains only solvent
    - →Measurement for transmittance is compared to results from reference cell

Beer's Law

- **Based on absorption of light by a sample**
  - **$dP_x/P_x=dS/S$**
    - **→dS/S=ratio of absorbance area to total area**
      - * **Proportional to number of absorbing particles**
    - **→dS=adn**
      - * **a is a constant, dn is number of particles**
  - **n is total number of particles within a sample**

$$-\int_{P_o}^{P}\frac{dP_x}{P_x}=\int_{0}^{n}\frac{adn}{S}$$

$$-\ln\frac{P_o}{P}=\frac{an}{S}$$

$$\log\frac{P_o}{P}=\frac{an}{2.303S}$$

Beer's Law

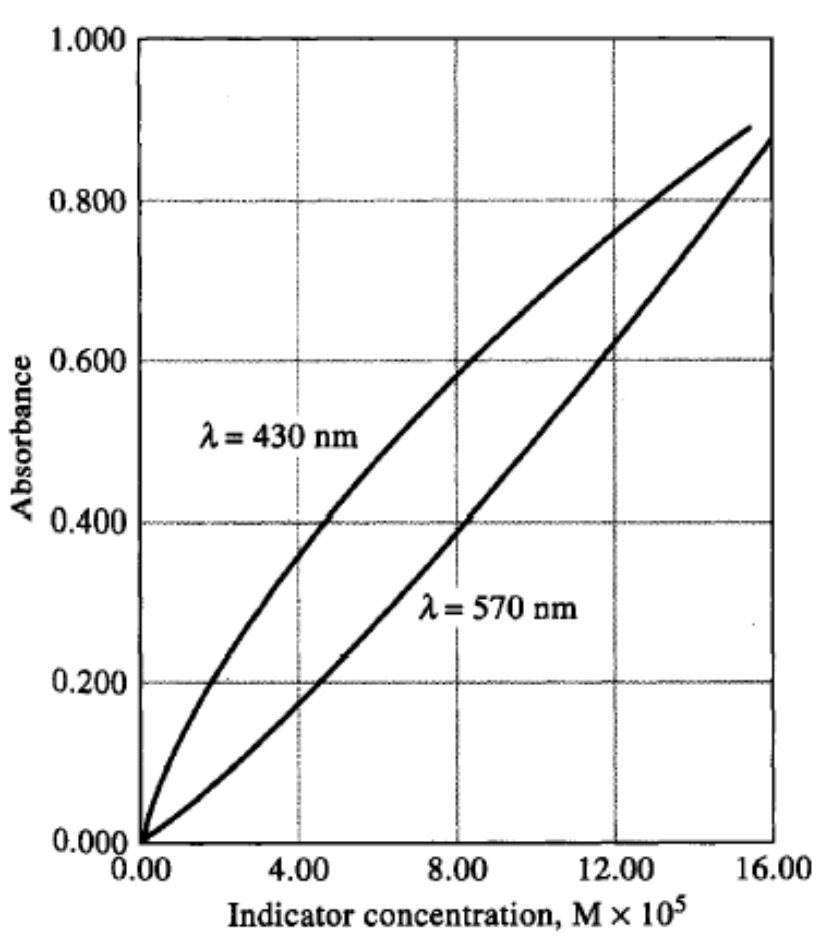
- **Area S can be described by volume and length**
  - **$S=V/b$ (cm^2)**
  - **Substitute for S**
  - **n/V = concentration**
  - **Substitute concentration and collect constant into single term ε**

$$\log\frac{P_o}{P}=\frac{anb}{2.303V}$$

- **Beer's law can be applied to mixtures**
  - **$A_{tot}=\Sigma A_x$**

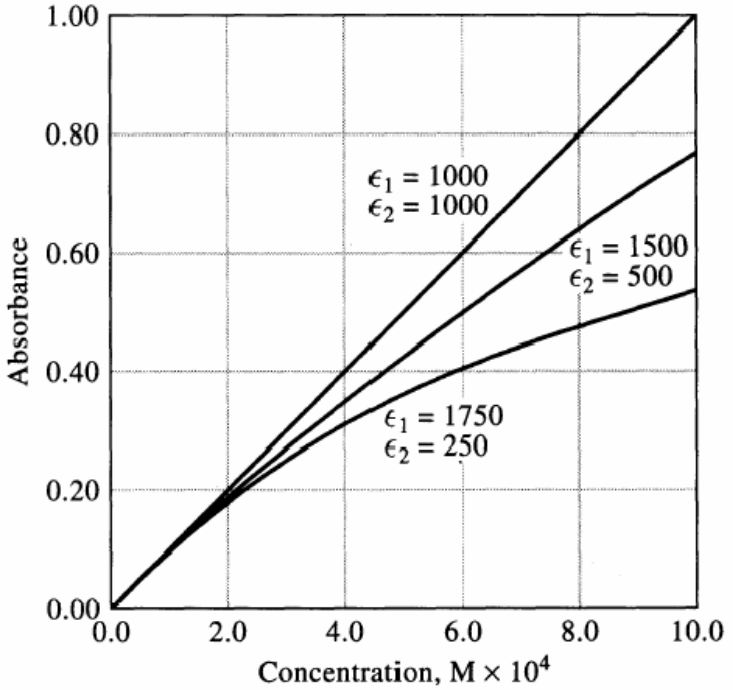
Beer's Law Limitations

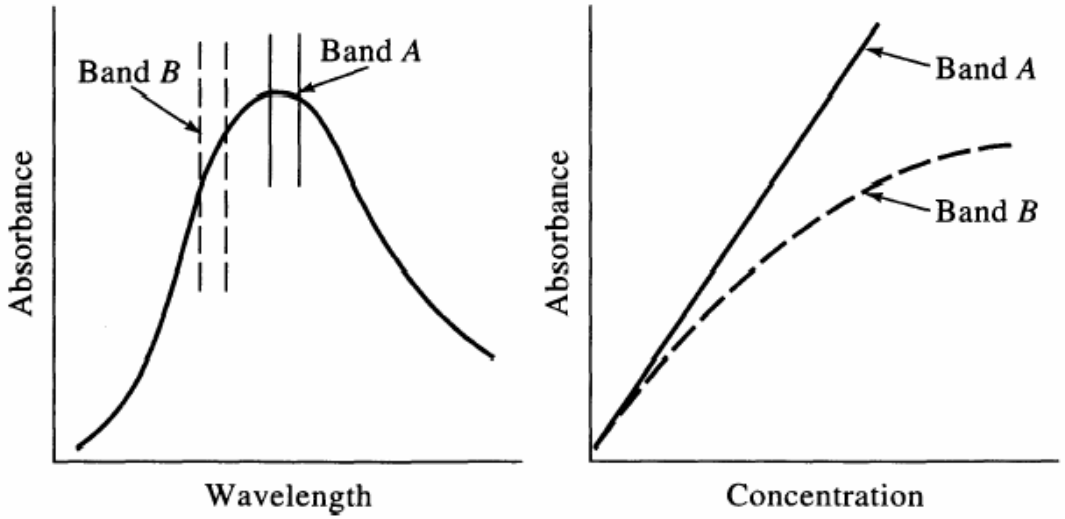
- **Equilibrium shift**
  - **pH indicators**
    - → **Need to consider speciation**
    - → **Weak acid equilibrium**



Beer's Law Limitation

- **Polychromatic Light**
  - **More than one wavelength**





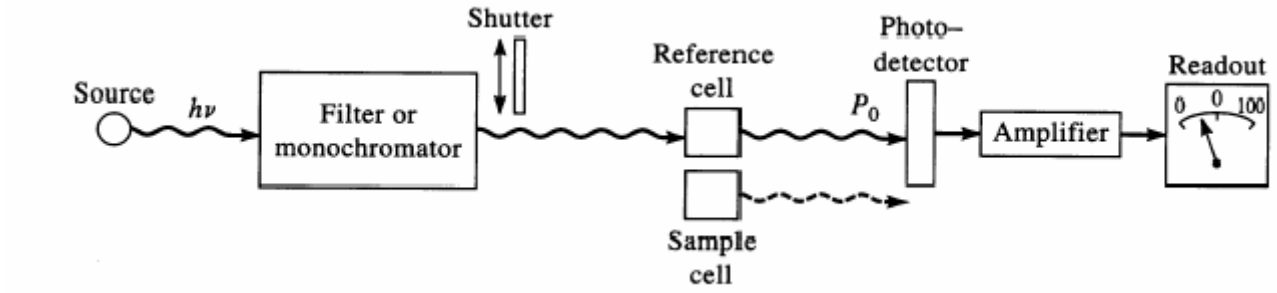
Noise

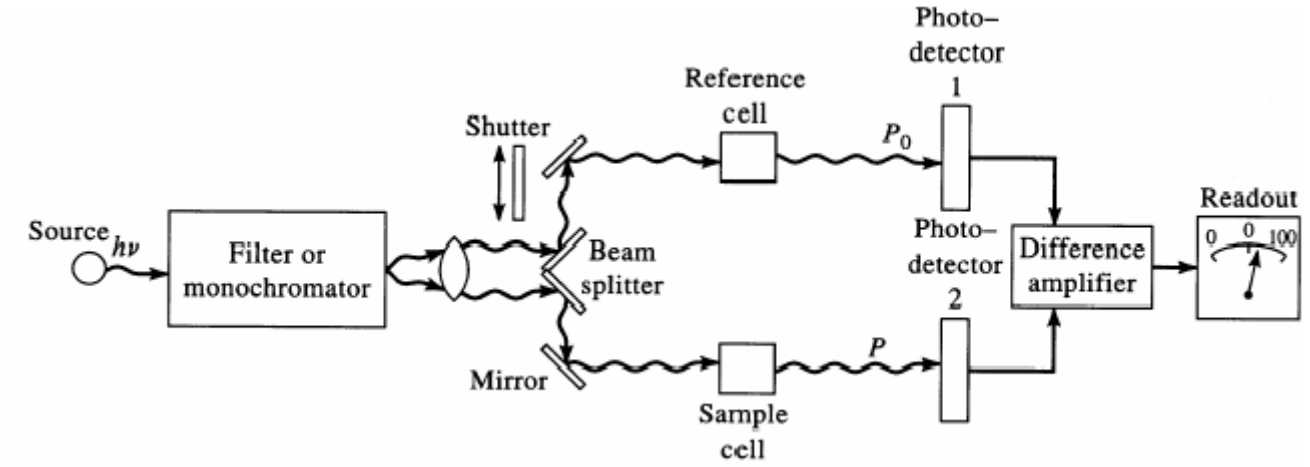
- Limited readout resolution
- Dark current and electronic noise
- Photon detector shot noise
- Cell position uncertainty
  - Changing samples
- Flicker

Instrumentation

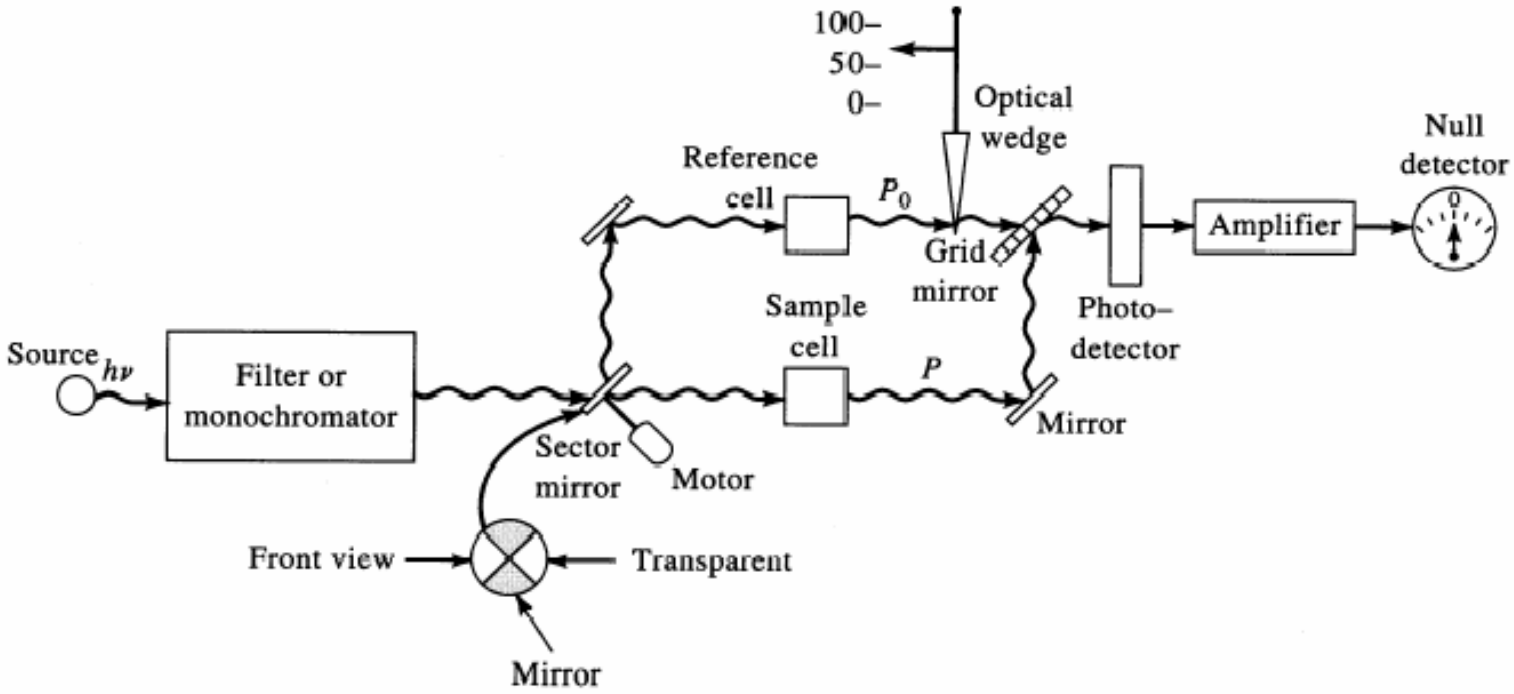
- **Light source**
  - **Deuterium and hydrogen lamps**
  - **W filament lamp**
  - **Xe arc lamps**
- **Sample containers**
  - **Cuvettes**
    - → **Plastic**
    - → **Glass**
    - → **Quartz**

Spectrometers





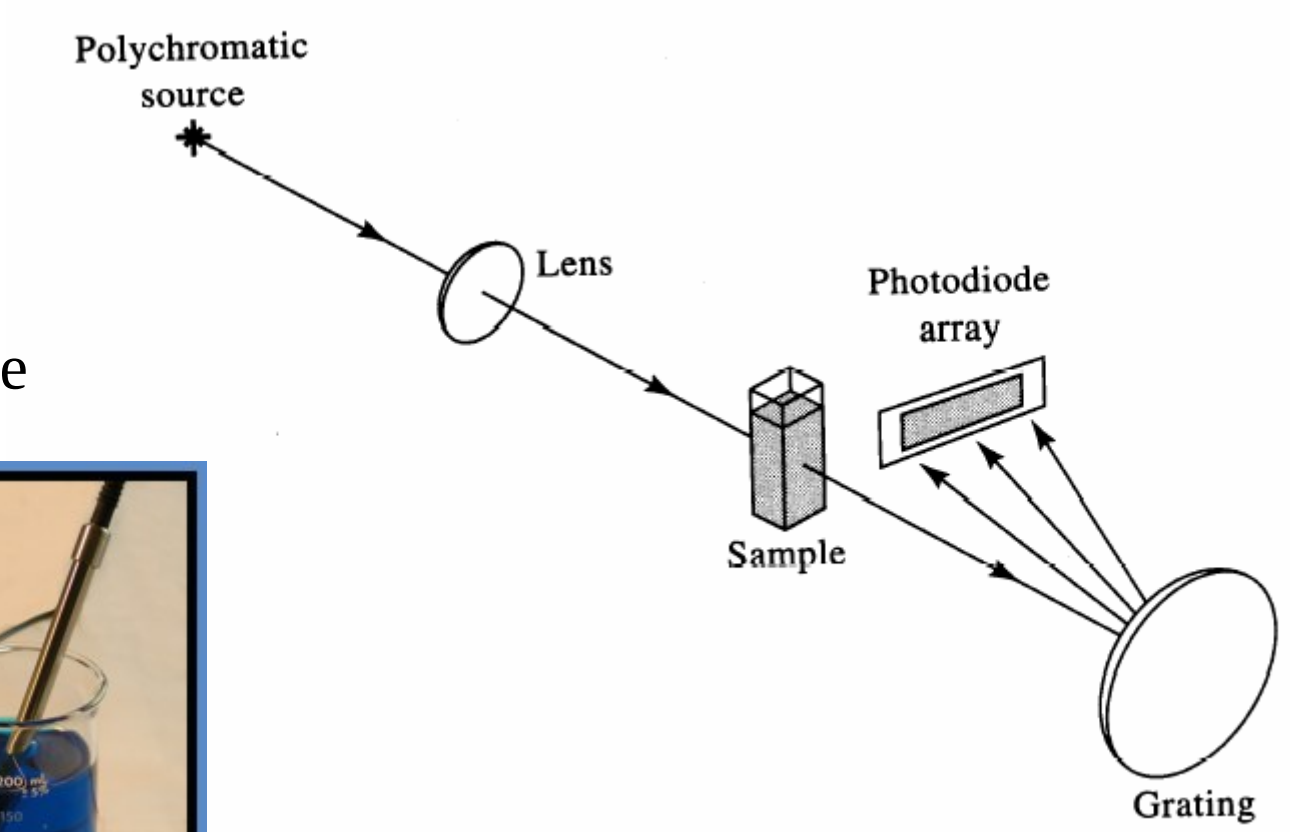
Spectrometer



Time separated double beam

Spectrometer

Dip probe



Multichannel photodiode array

Application of UV-Visible Spectroscopy

- **Identification of inorganic and organic species**
- **Widely used method**

- **Magnitude of molar absorptivities**
- **Absorbing species**
- **methods**

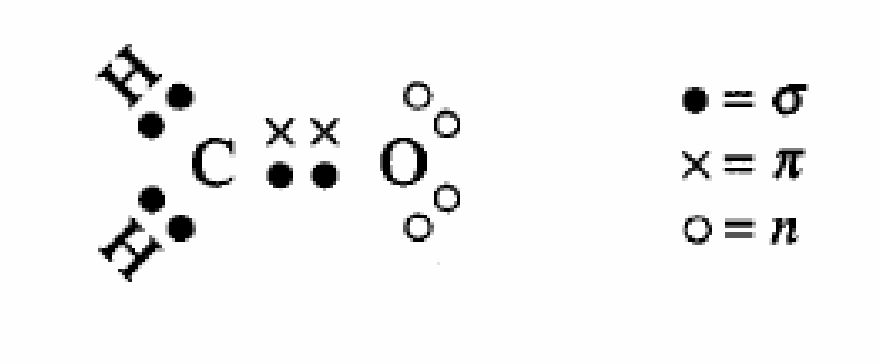
Molar Absorptivties

- **Range from 0 to 1E5**
  - **ε=8.7E19PA**
    - → **P=transition probability**
    - → **A=target cross section (cm^2)**
      - * **Allowed transitions 0.1>P>1**
        - **ε range 1E4 to 1E5**
      - * **Forbidden transition 0.01**
- **Absorbing species**
  - **M+γ->M***
    - → **M^* has a short lifetime (nanoseconds)**
    - → **Relaxation processes**
      - * **Heat**
      - * **Photo emission**
        - **Fluorescence or phosphorescence**

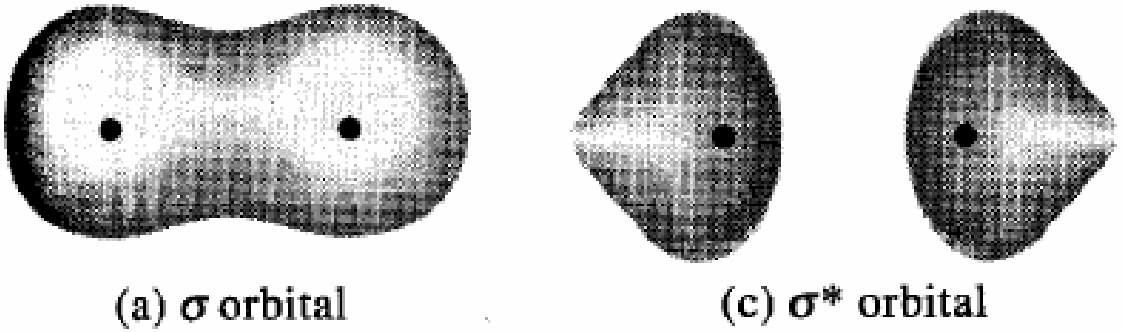
Absorbing species

- **Electronic transitions**
  - **π, σ, and n electrons**
  - **d and f electrons**
  - **Charge transfer reactions**

π, σ, and n (non-bonding) electrons

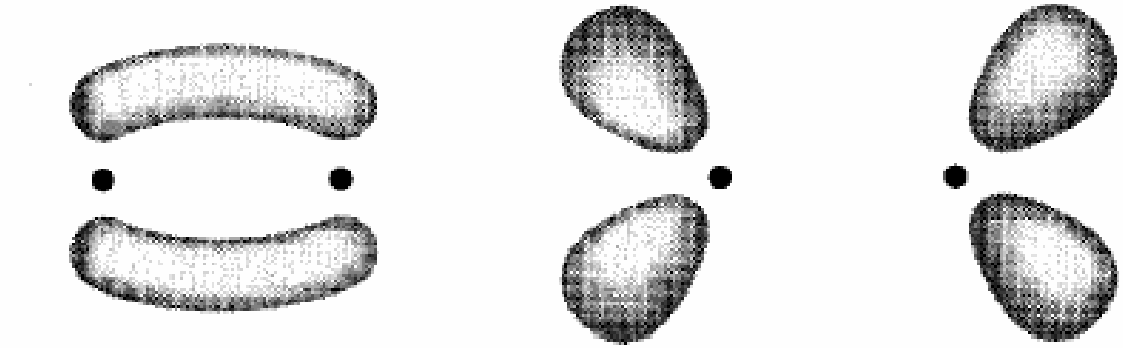


Sigma and Pi orbitals



(a) σ orbital

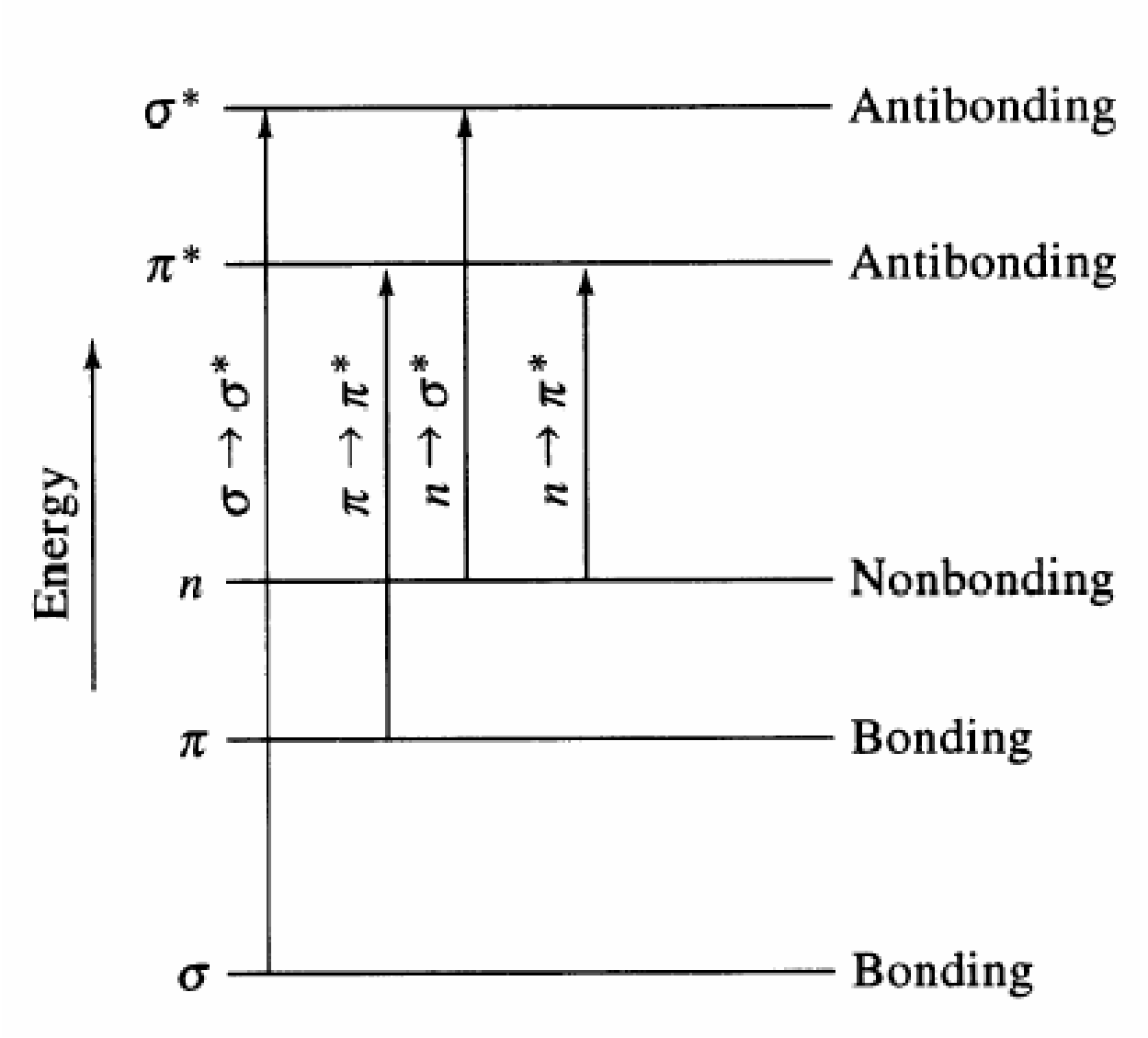
(c) σ^* orbital



(b) π orbital

(d) π^* orbital

Electron transitions



Transitions

- σ–>σ*
  - UV photon required, high energy
    - → Methane at 125 nm
    - → Ethane at 135 nm
- n-> σ*
  - Saturated compounds with unshared e^-
    - → Absorption between 150 nm to 250 nm
    - → ε between 100 and 3000 L cm^{-1} mol^{-1}
    - → Shifts to shorter wavelengths with polar solvents
      - * Minimum accessibility
  - Halogens, N, O, S

Transitions

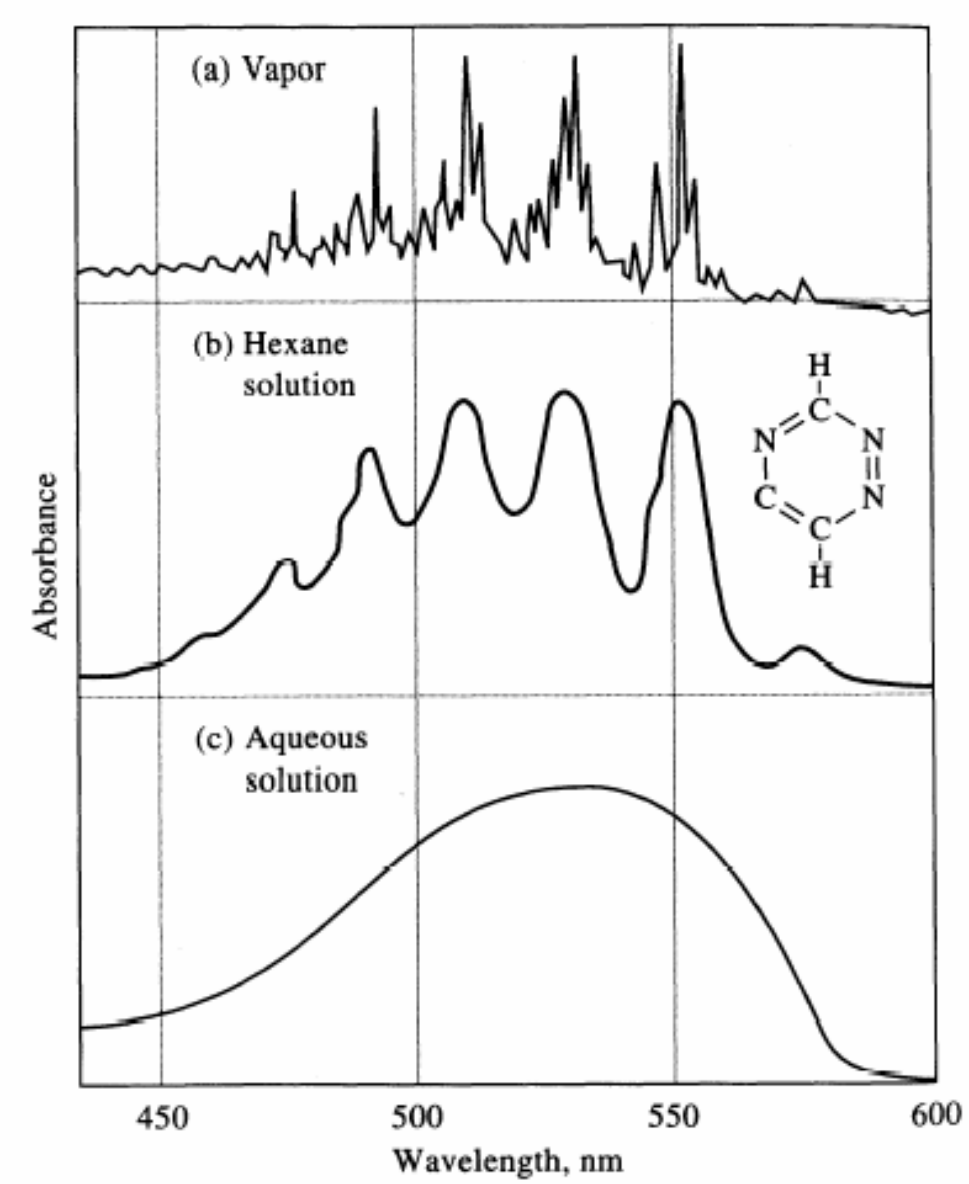
- **n->π*, π–>π***
  - **Organic compounds, wavelengths 200 to 700 nm**
  - **Requires unsaturated groups**

    →n->π* low ε (10 to 100)

    *** Shorter wavelengths**

    →π–>π* higher ε (1000 to 10000)

Solvent effects

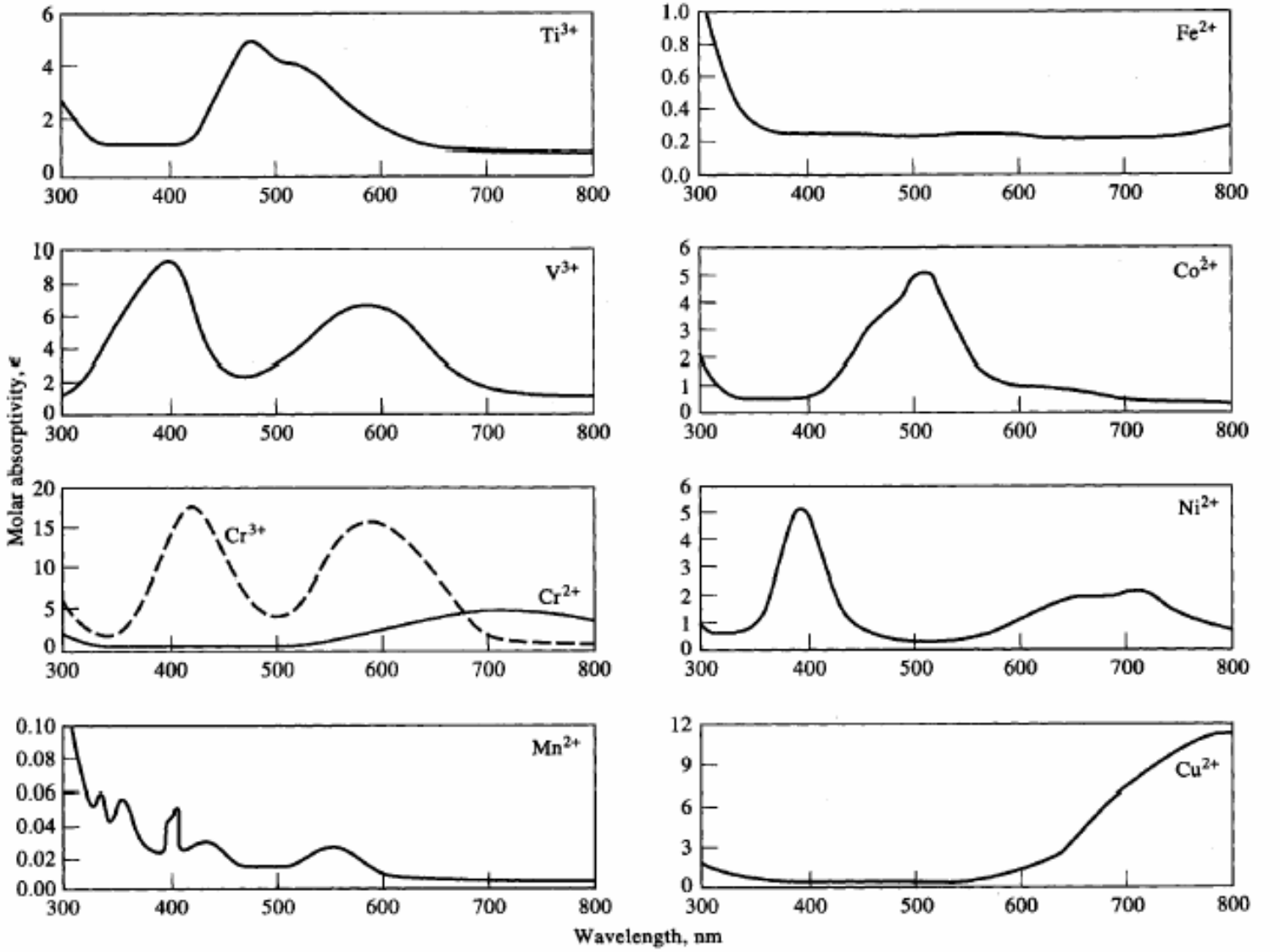


Transitions

- **d-d**
  - **3d and 4d 1st and 2nd transitions series**
  - **Broad transitions**

    →Impacted by solution

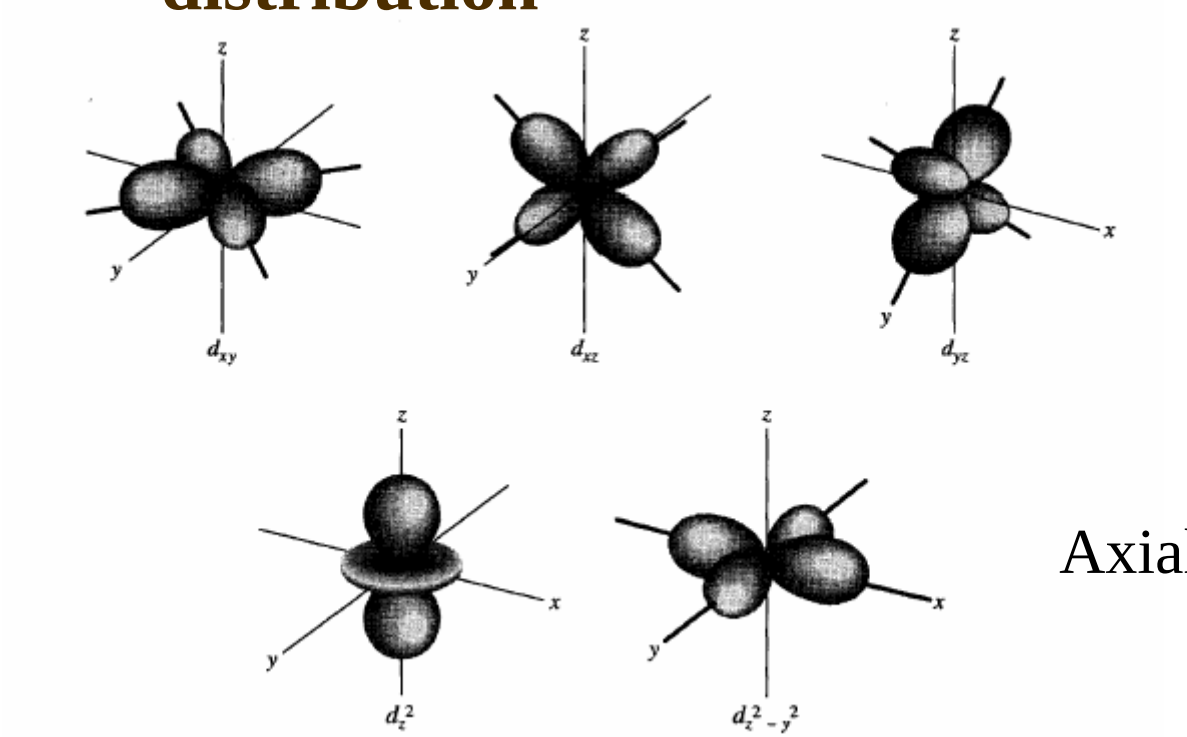
Transitions



D transitions

- **Partially occupied d orbitals**
  - **Transitions from lower to higher energy levels**

→Splitting of levels due to spatial distribution

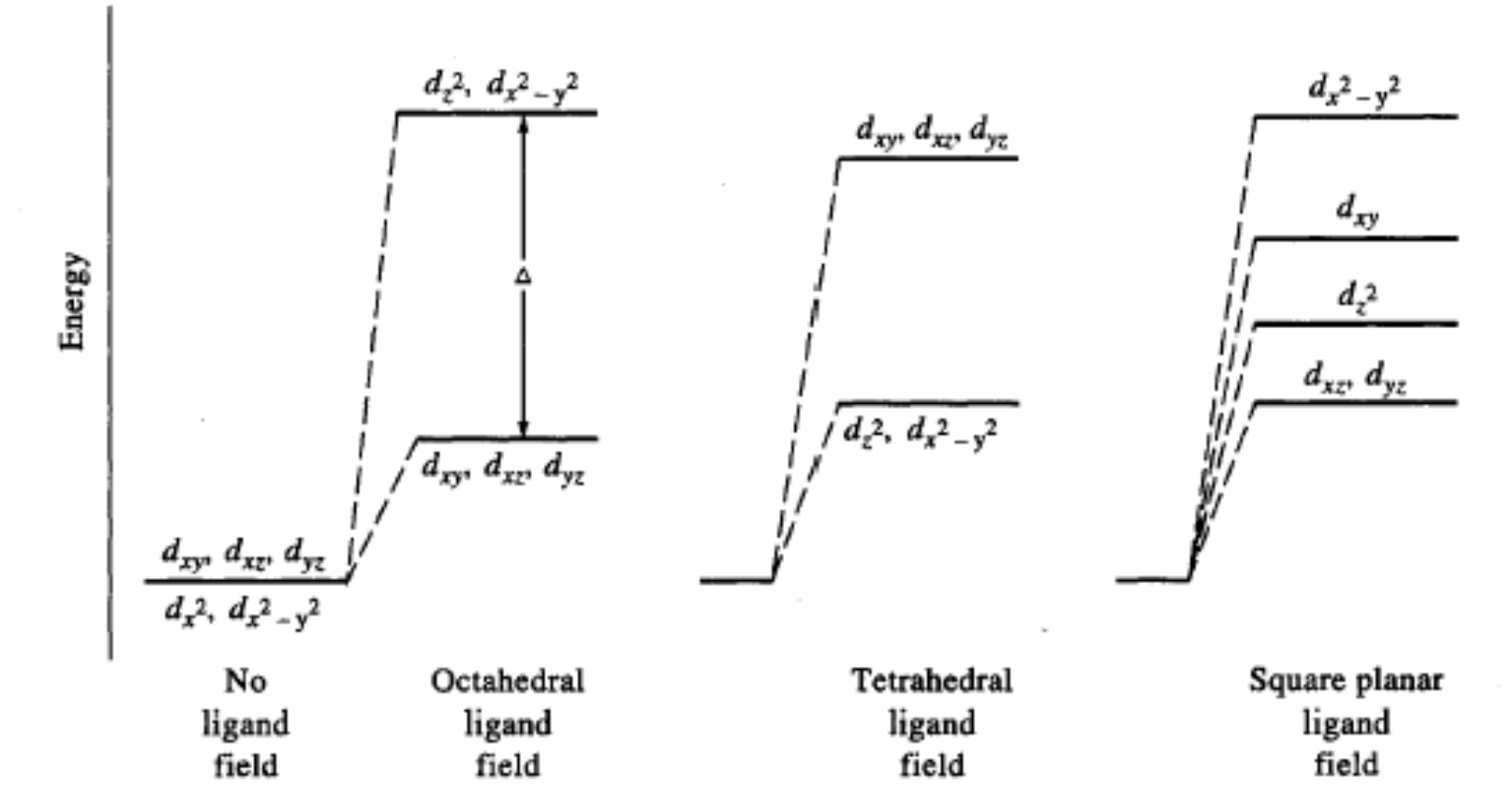


similar

Axial direction

D transitions

- **Binding ligands on axis have greater effect on axial orbitals**



D transitions

- **Δ value dependent upon ligand field strength**
  - <Br-<Cl-<F-<OH-<C2O42-~H2O<SCN-<NH3<en<NO2-<CN^-
  - **Δ increases with increasing field strength**
- **f-f**
  - **4f and 5f (lanthanides and actinides)**
  - **Sharper transitions**

Actinide transitions

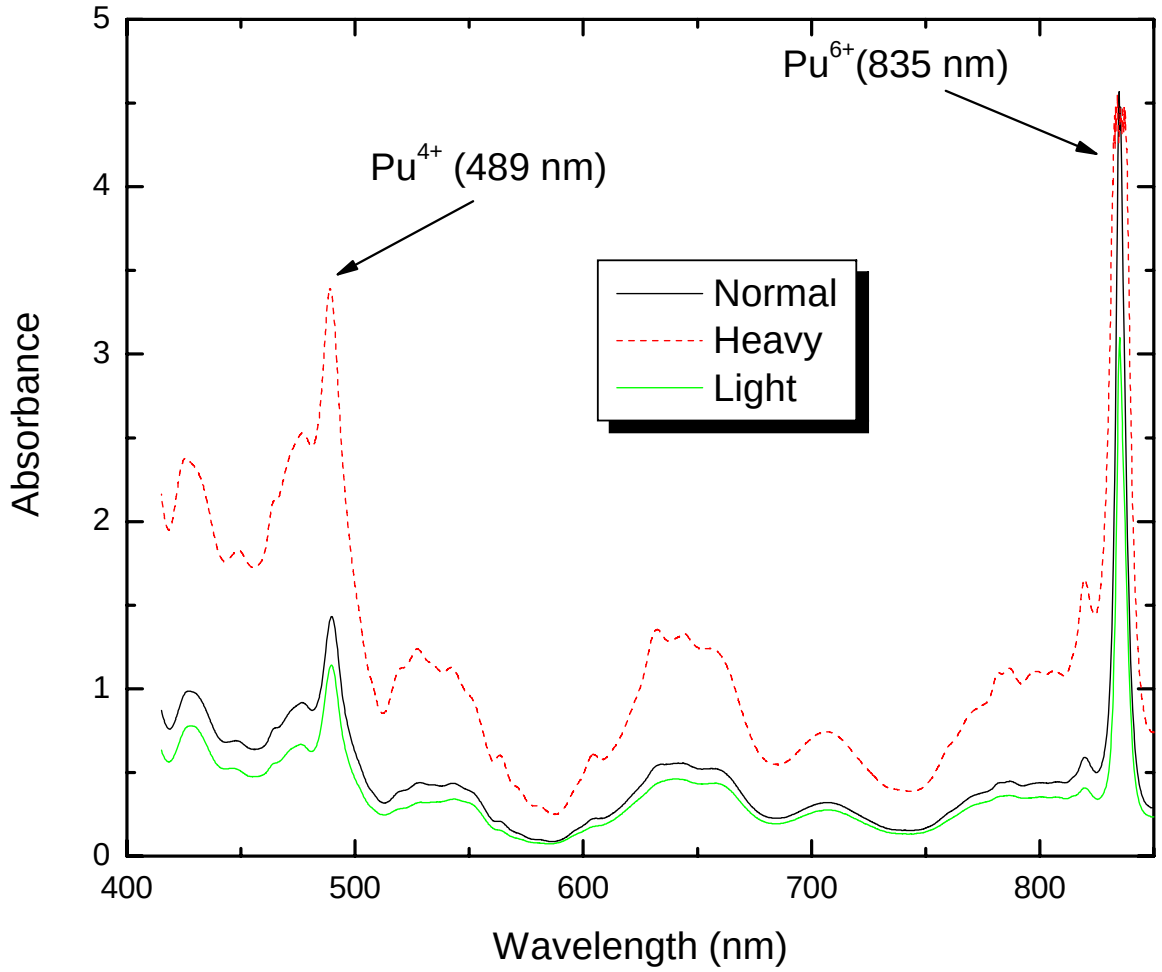


Figure 2: UV-vis spectra of organic phases for 13M HNO_3 system

Charge-transfer Transitions

- **Electron donor and acceptor characteristics**
  - **Absorption involves e^- transitions from donor to acceptor**

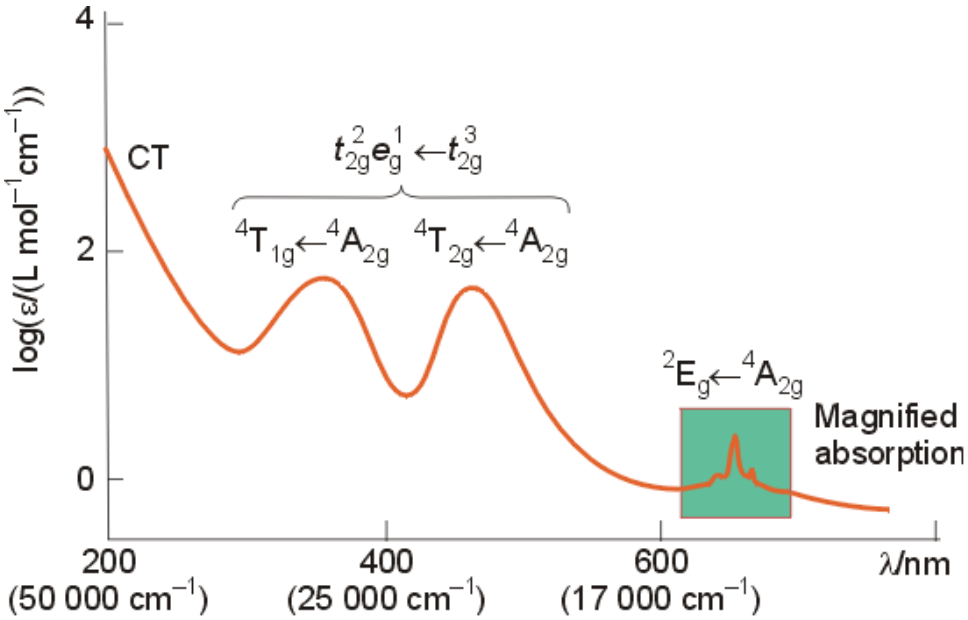
    →SCN to Fe(III)

    *** Fe(II) and neutral SCN**
  - **Metal is acceptor**

    →Reduced metals can be exception

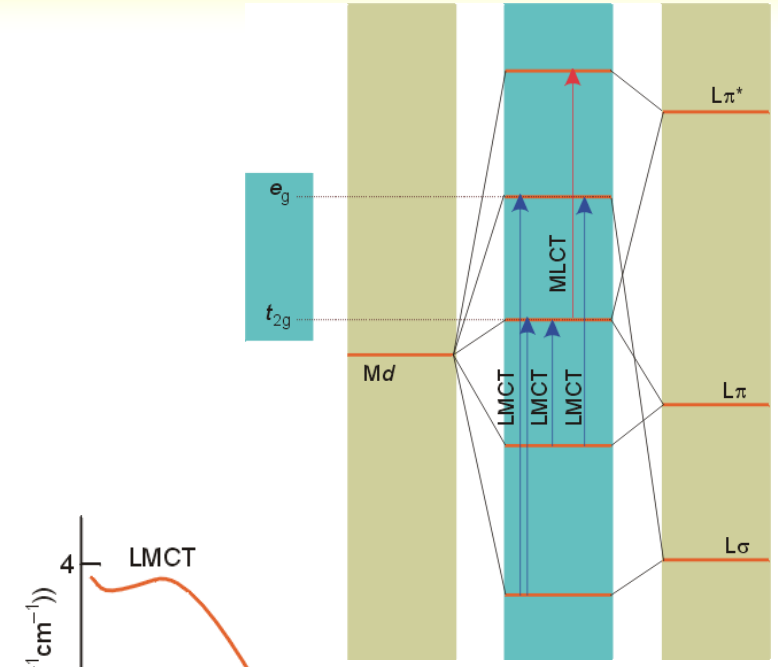
Electronic Spectra

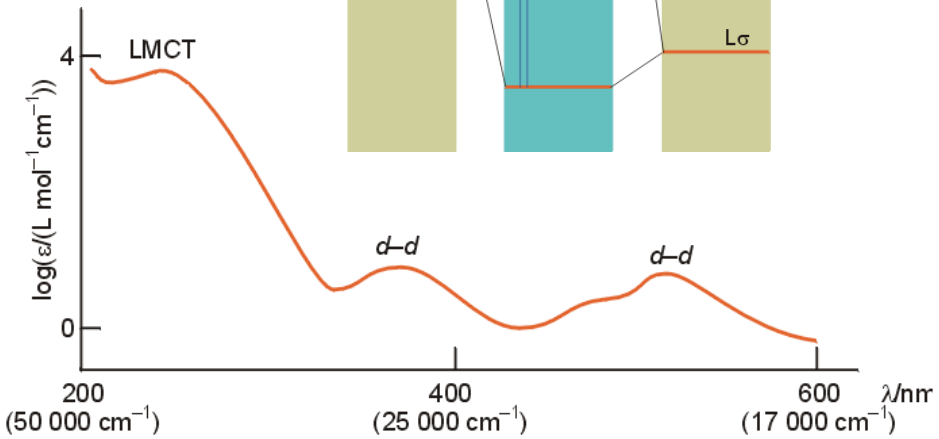
- $Cr(NH_3)_6^{3+}$
  - d^3
  - Weak low energy transition
    - → Spin forbidden
  - 2 stronger transitions
    - → Spin allowed
      - * t_{2g} and e_g transitions
        - Lower energy to higher energy
  - CT at higher energy
    - → Ligand to metal transition



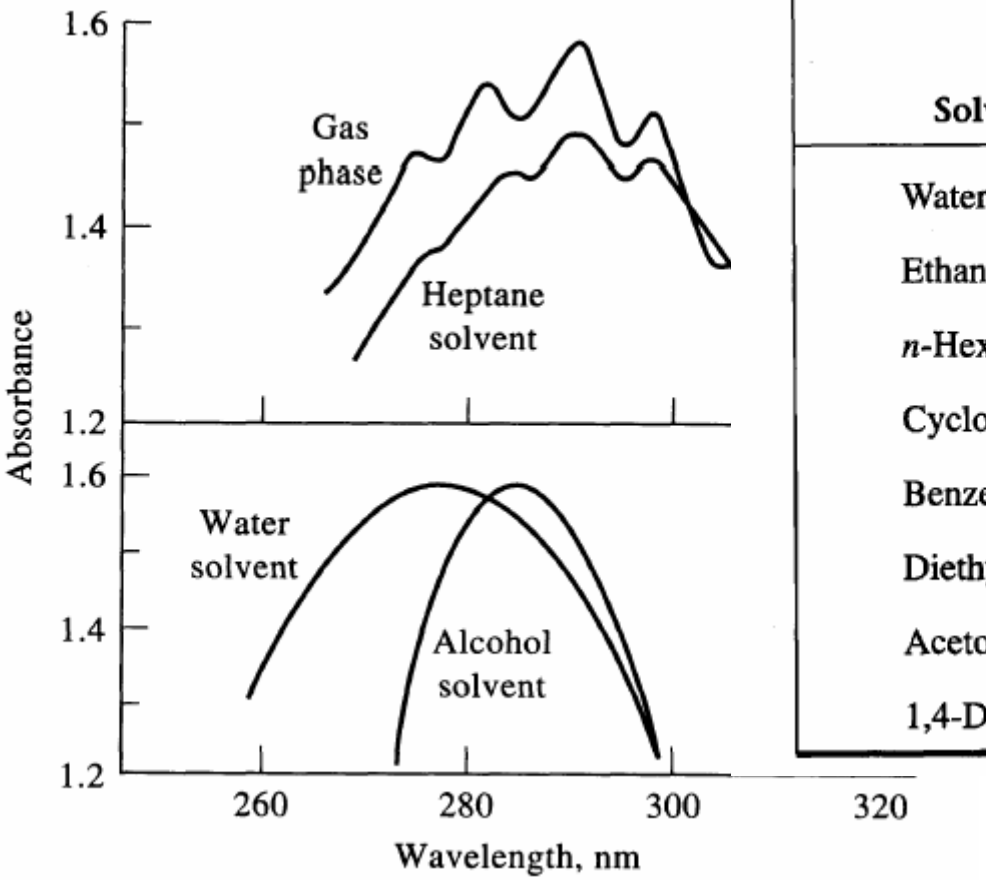
Charge transfer bands

- High energy absorbance
  - Energy greater than d-d transition
    - → Electron moves between orbitals
      - * Metal to ligand
      - * Ligand to metal
    - → Sensitive to solvent
- LMCT
  - High oxidation state metal ion
  - Lone pair ligand donor
- MLCT
  - Low lying pi, aromatic
  - Low oxidation state metal
    - → High d orbital energy





Solvent effect



Solvent	Approximate[a] Transparency Minimum (nm)
Water	190
Ethanol	210
n-Hexane	195
Cyclohexane	210
Benzene	280
Diethyl ether	210
Acetone	330
1,4-Dioxane	220

Methods

- **Titration**
  - **Change of absorbance with solution variation**

    →pH, ligand, metal
- **Photoacoustic effect**
  - **Emission of sound**