UV-Vis (Absorption) Spectrometry (Chapters 13, 14)

Beer's Law:

$$A = \varepsilon bc = -\log T = -\log \frac{I}{I_0} = \log \frac{I_0}{I}$$

Absorbance is additive

$$A_{total} = A_1 + A_2 \ldots$$
$$= \varepsilon_1 b c_1 + \varepsilon_2 b c_2 \ldots$$

in a 2 component mixture

$$A_{\lambda 1} = \varepsilon_{1,\lambda 1}\ b\ c_1 + \varepsilon_{2,\lambda 1}\ b\ c_2$$
$$A_{\lambda 2} = \varepsilon_{1,\lambda 2}\ b\ c_1 + \varepsilon_{2,\lambda 2}\ b\ c_2$$

Limitations of Beer's Law (pp 303-311):

(1) Chemical effects - analyte associates, dissociates or reacts to give molecule with different ε

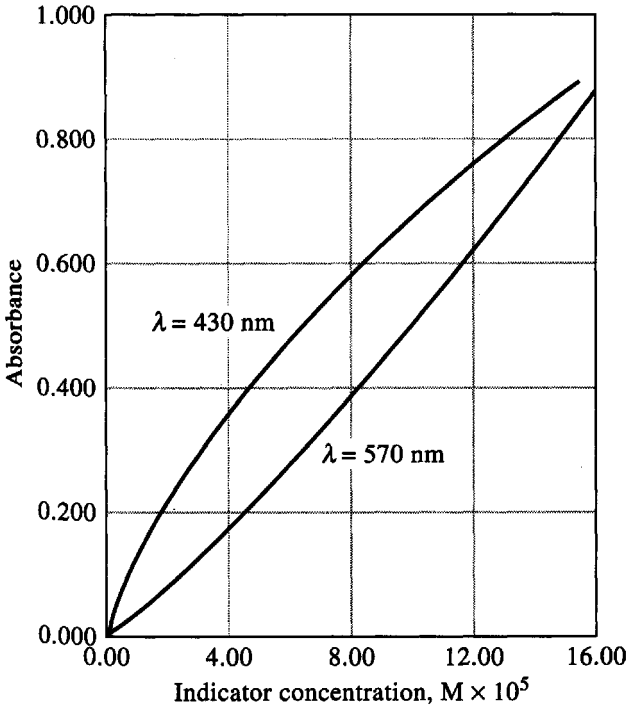


Fig 13-3

(2) Physical effects - stray light, polychromatic radiation or noise

$$A_{\lambda_1} = -\log T_{\lambda_1} = \varepsilon_{\lambda_1} bc$$

$$= \log \left(\frac{I_0}{I} \right)_{\lambda_1}$$

$$I_{\lambda_1} = I_{0\,\lambda_1} 10^{-\varepsilon_{\lambda_1} bc}$$

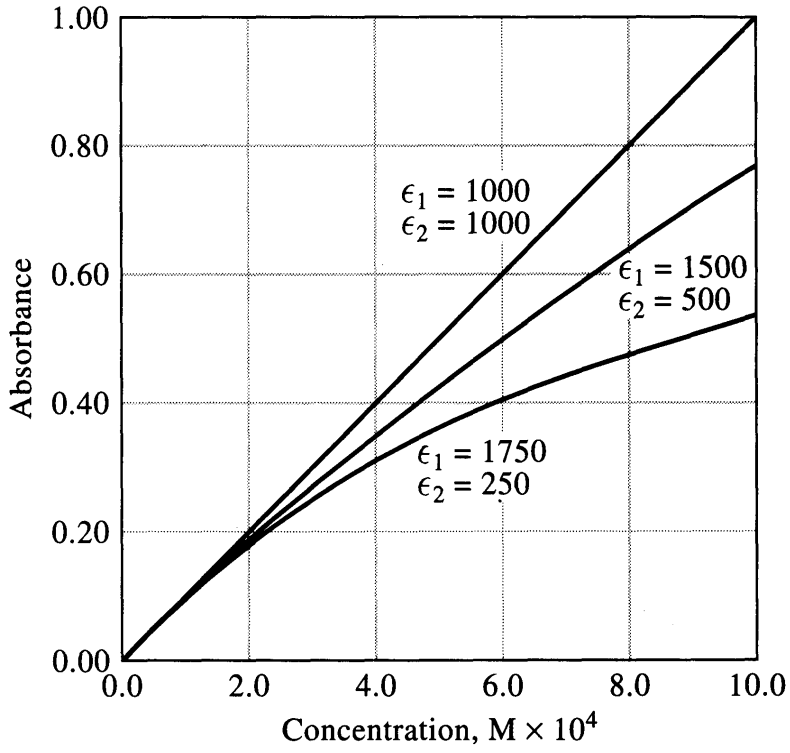
$$I_{\lambda_2} = I_{0\,\lambda_2} 10^{-\varepsilon_{\lambda_2} bc}$$

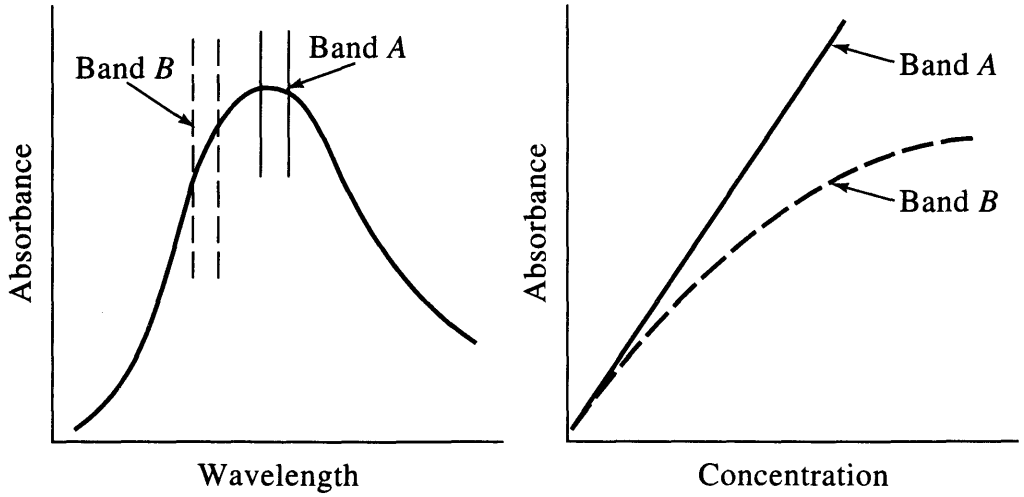
$$A_{\bar{\lambda}} = \left(\frac{I_{0\,\lambda_1} + I_{0\,\lambda_2}}{I_{\lambda_1} + I_{\lambda_2}} \right)$$

$$= \left(\frac{I_{0\,\lambda_1} + I_{0\,\lambda_2}}{I_{0\,\lambda_1} 10^{-\varepsilon_{\lambda_1} bc} + I_{0\,\lambda_2} 10^{-\varepsilon_{\lambda_2} bc}} \right)$$

$$A_{\bar{\lambda}} = \log\left(I_{0\,\lambda_1} + I_{0\,\lambda_2} \right) - \log\left(I_{0\,\lambda_1} 10^{-\varepsilon_{\lambda_1} bc} + I_{0\,\lambda_2} 10^{-\varepsilon_{\lambda_2} bc} \right)$$

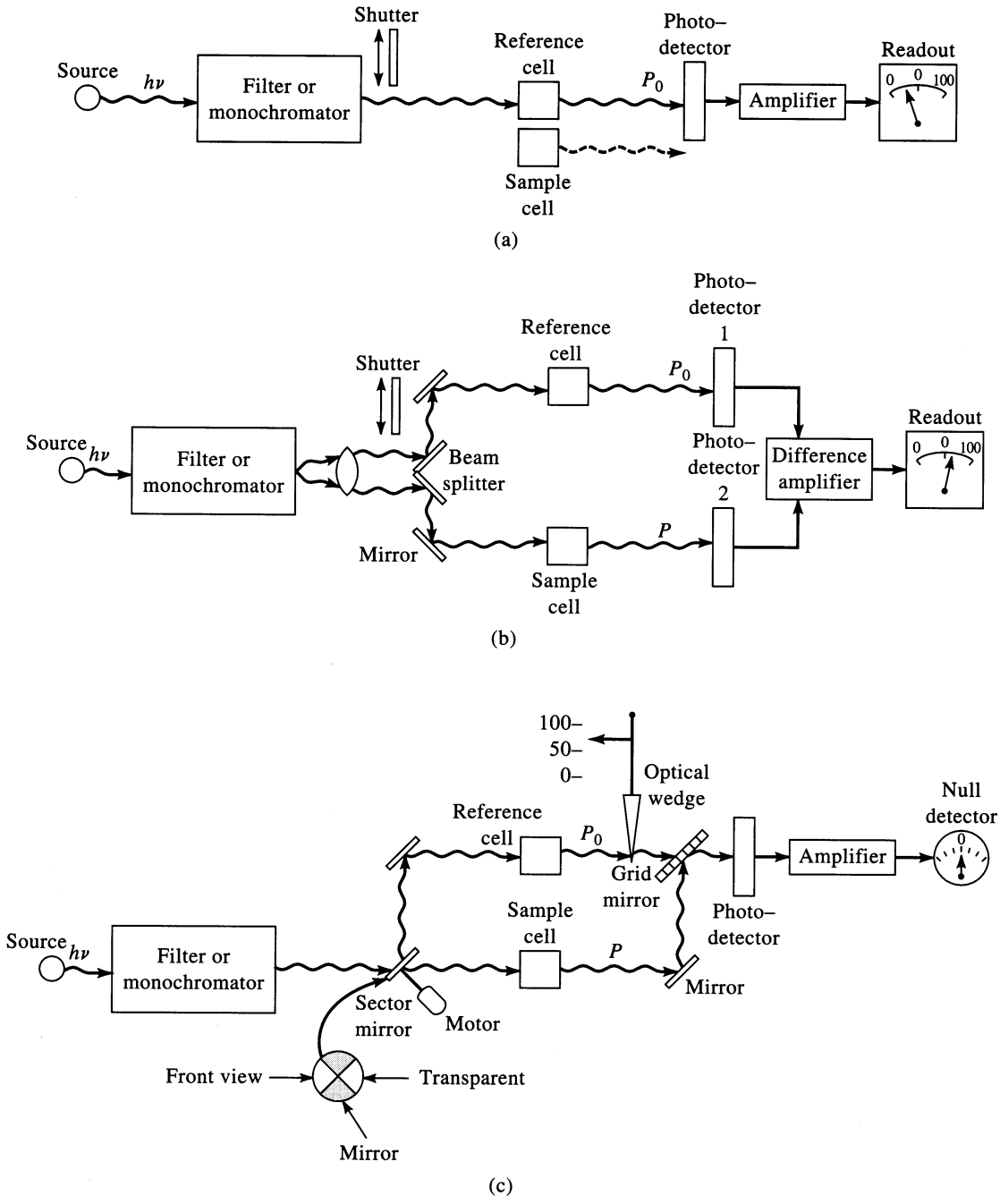
→ non-linear calibration curve (Fig 13-4, 13-5)





Typical UV-Vis Spectrophotometers:

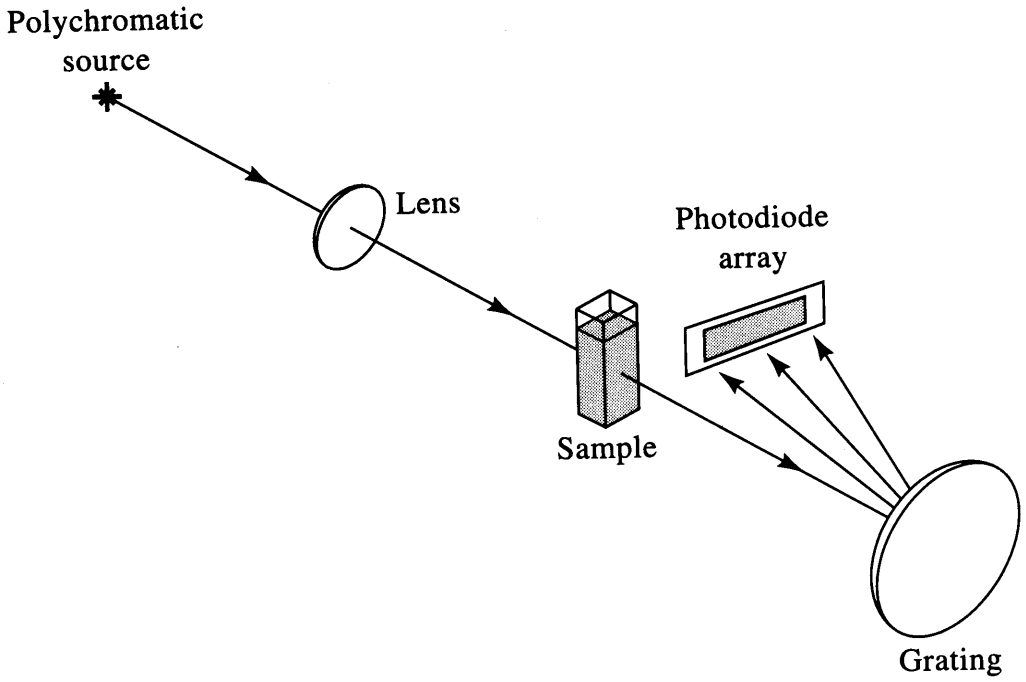
(Fig 13-12) includes λ selection



(a) single beam (SB) (b) double-beam (DB)-in-space (c) double-beam-in-time

Multichannel Spectrophotometer

No monochromator, but disperses transmitted light and measures "all wavelengths at once" (Fig 13-13)



No scanning - simple and fast

More expensive

Limited resolution

Applications of UV-Vis Spectrometry:

$$M + h\upsilon \xrightarrow{\text{excitation}} M^* \xrightarrow{\text{relaxation}} M + h\upsilon \text{ / heat}$$

How probable?

ε ranges 0 to ~100,000 L/mol·cm

"forbidden" "allowed"

electronic transition

Which electrons get excited?

In UV-Vis, photon provides enough energy to move outer valence (bonding) electrons

Organic molecules

$\psi_\sigma = \psi_{s_A} + \psi_{s_B}$ Bonding σ molecular orbital

$\psi_{\sigma^*} = \psi_{s_A} - \psi_{s_B}$ Antibonding σ^* molecular orbital

$\psi_\pi = \psi_{p_A} + \psi_{p_B}$ Bonding π molecular orbital

$\psi_{\pi^*} = \psi_{p_A} - \psi_{p_B}$ Antibonding π^* molecular orbital

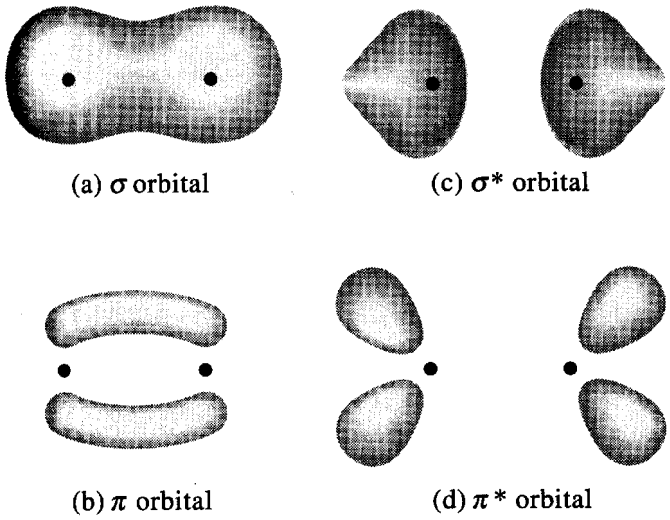


Fig 14-1

σ, π (bonding) and n (non-bonding) electrons

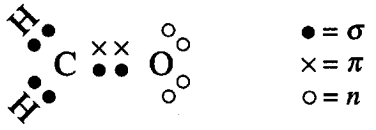


Fig 14-2

Arrange in terms of **energy**:

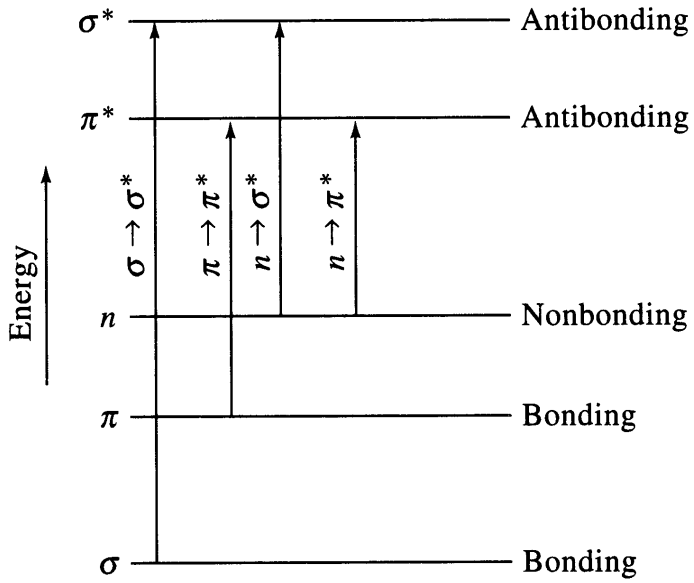


Fig 14-3

σ → σ* ΔE large (λ<150 nm) ε=10-10,000 L/mol·cm

n → σ* (halogens, N, O, S) ΔE smaller (λ=150-250 nm) ε=200-2000 L/mol·cm

π → π* n → π* ΔE small (λ=200-700 nm) ε=10-10,000 L/mol·cm

Ideal for UV-Vis spectrometry of organic chromophore

- Red shift of λ_{max} with increasing **conjugation**

  $CH_2=CHCH_2CH_2CH=CH_2$ λ_{max} =185 nm

  $CH_2=CHCH=CH_2$ λ_{max} =217 nm

- Red shift of λ_{max} with **# of rings**

  Benzene λ_{max} =204 nm

  Naphthalene λ_{max} =286 nm

- Blurred with **solvent**

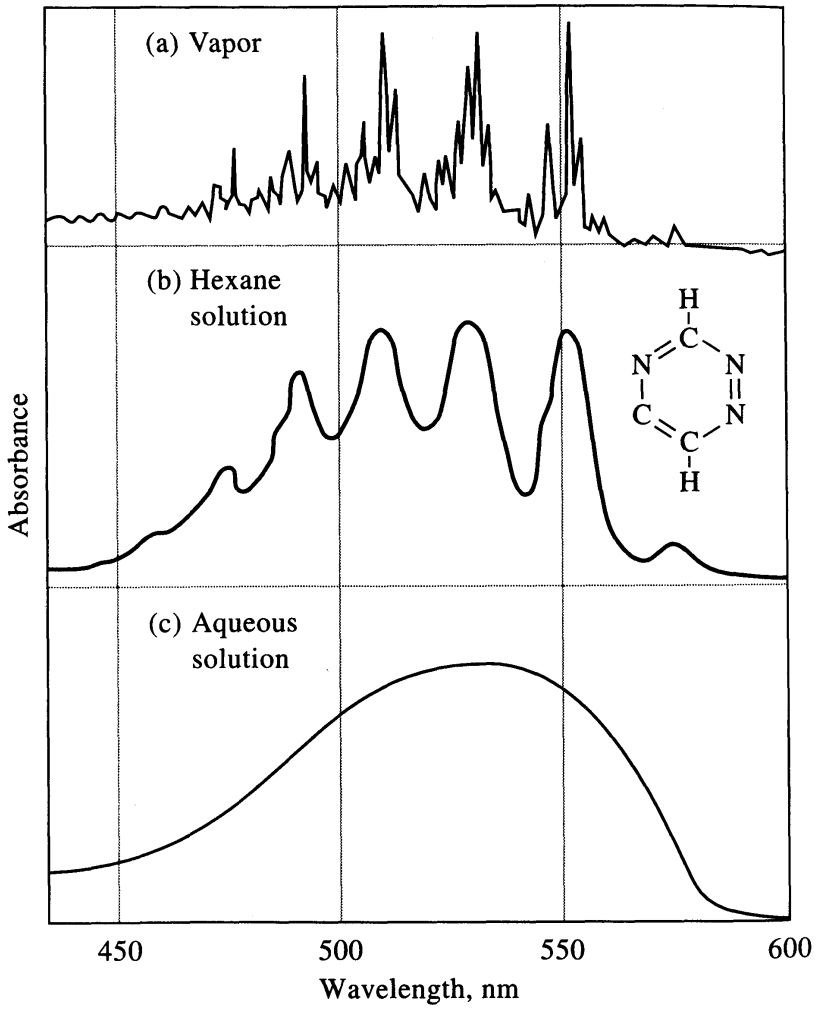
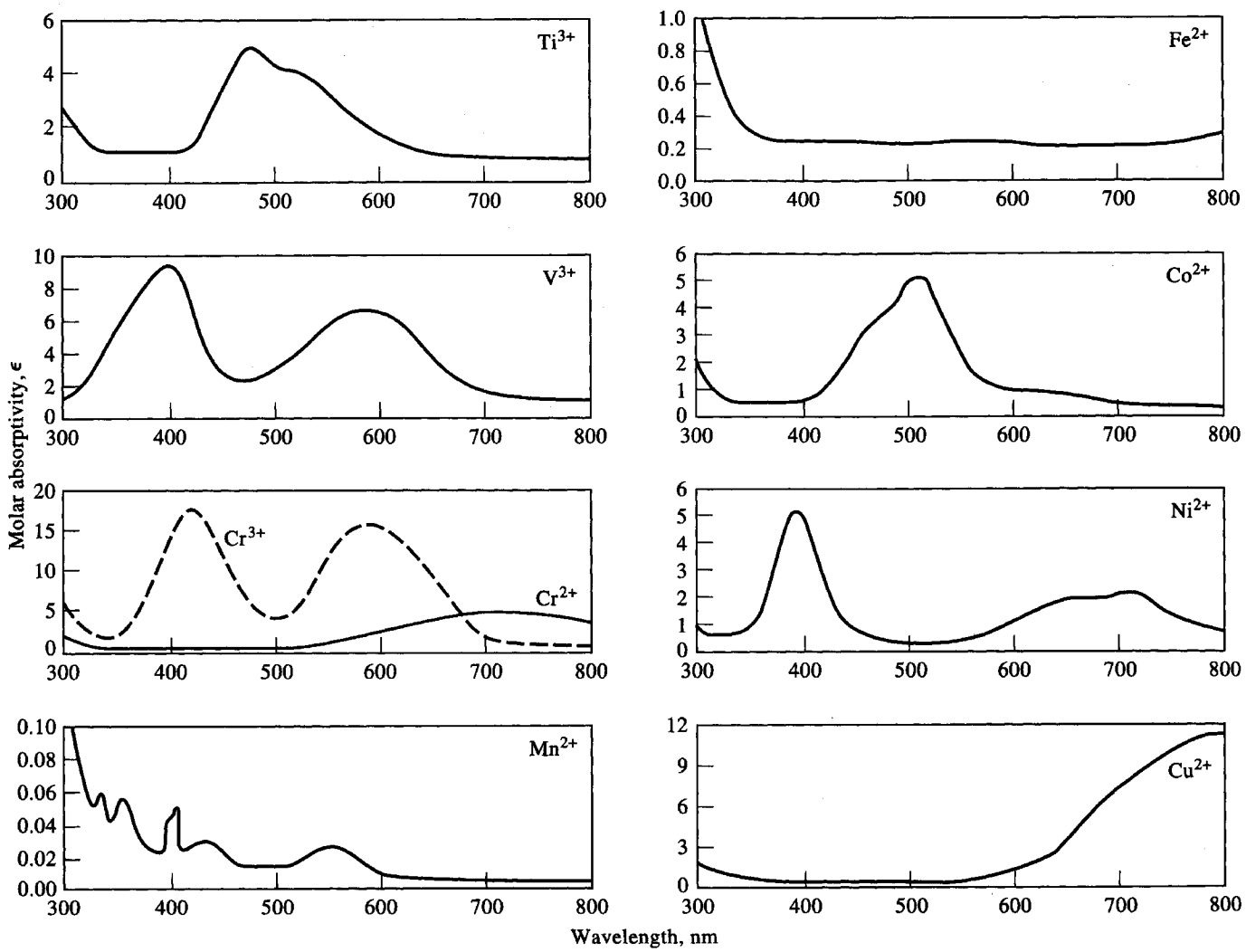


Fig 14-5

Inorganic Ions

Most transition metal ions are colored (absorb in UV-vis) due to d → d electronic transitions (Fig 14-7)

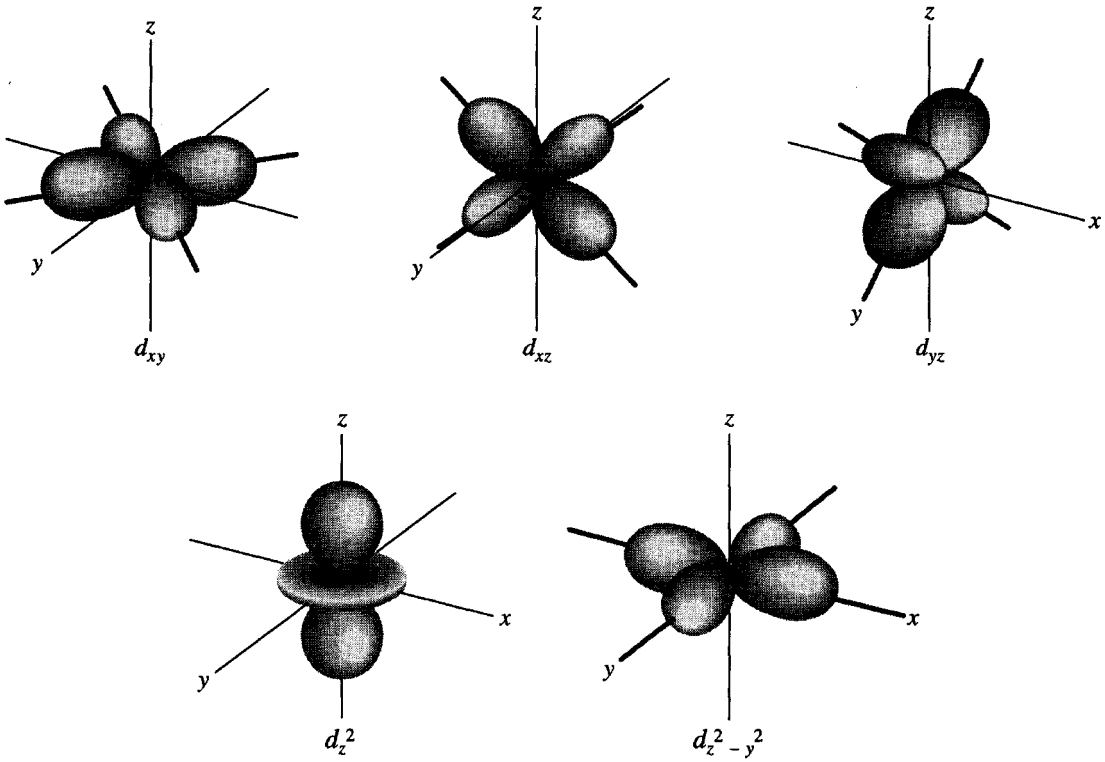


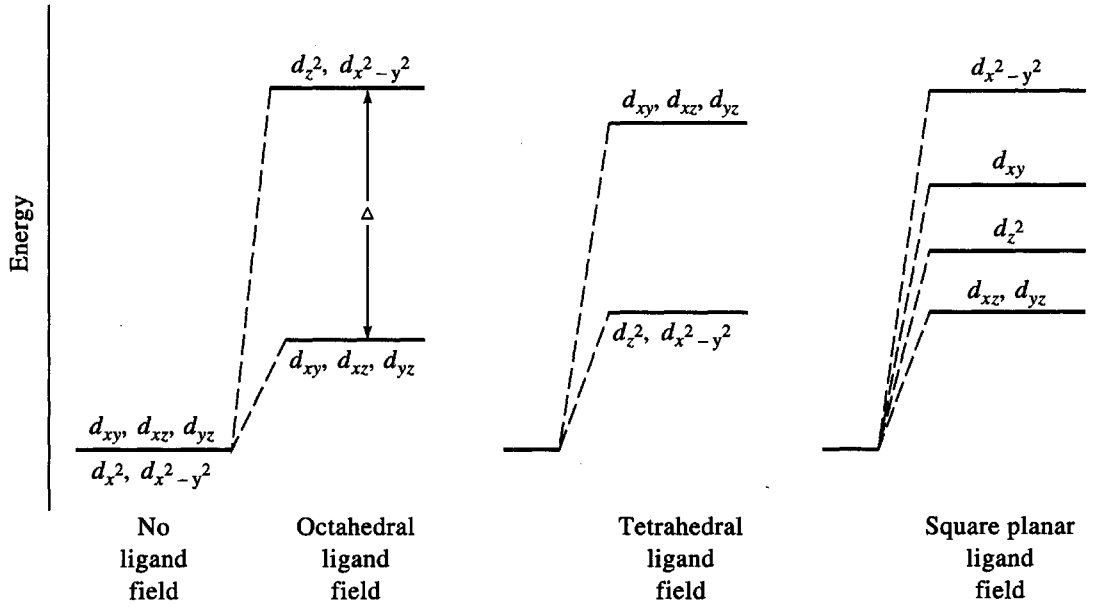
Remember:

- Solution absorbs red appears blue-green
- Solution absorbs blue-green appears red

Ligands cause different interactions with d electrons (Fig 14-8, 14-9)

- ligand field splitting





Ligand Field Strengths:

	λ_{max} for complex (nm)				
	Increasing Ligand Field Strength →				
	$6Cl^-$	$6H_20$	$6NH_3$	3en	$6CN^-$
Cr(III)	736	573	462	456	380

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < SCN^- < NH_3 < en < NO_2^- < CN^-$

vis UV

"Spectrochemical Series"

Solvent Effects:

(i) Solvent transparency in UV (Table 14-6)

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

[a]For 1-cm cells.

(ii) Polar solvents "blur" vibrational features more than nonpolar

(iii) Polar solvents more likely to shift absorption maxima

Shifts of λ_{max} with solvent polarity

$n \rightarrow \pi^*$ hypsochromic/blue shift

$\pi \rightarrow \pi^*$ bathochromic/red shift

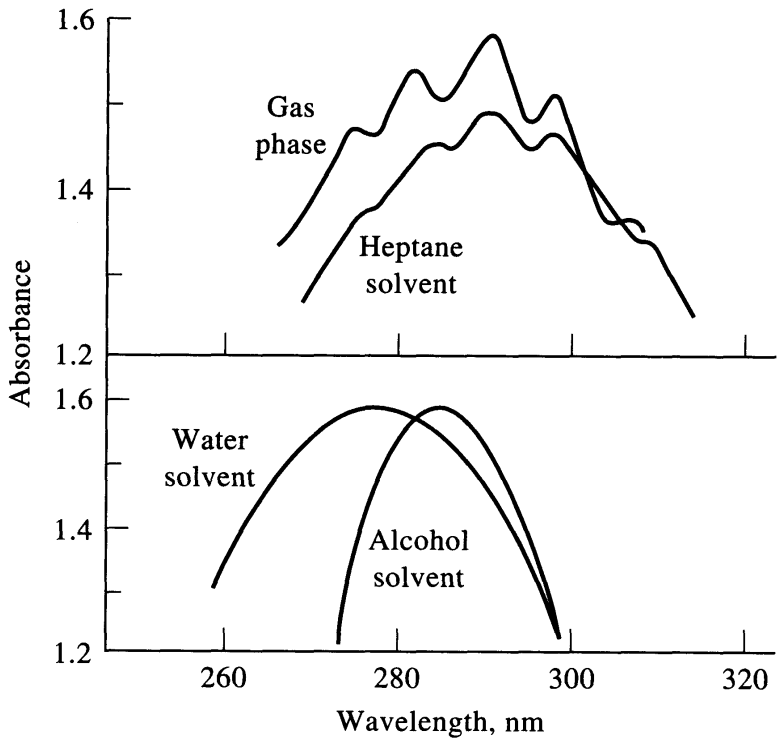


Fig 14-12

Solvent effects mean UV-Vis **not reliable for qualitative** but **excellent for quatitative** analysis.