

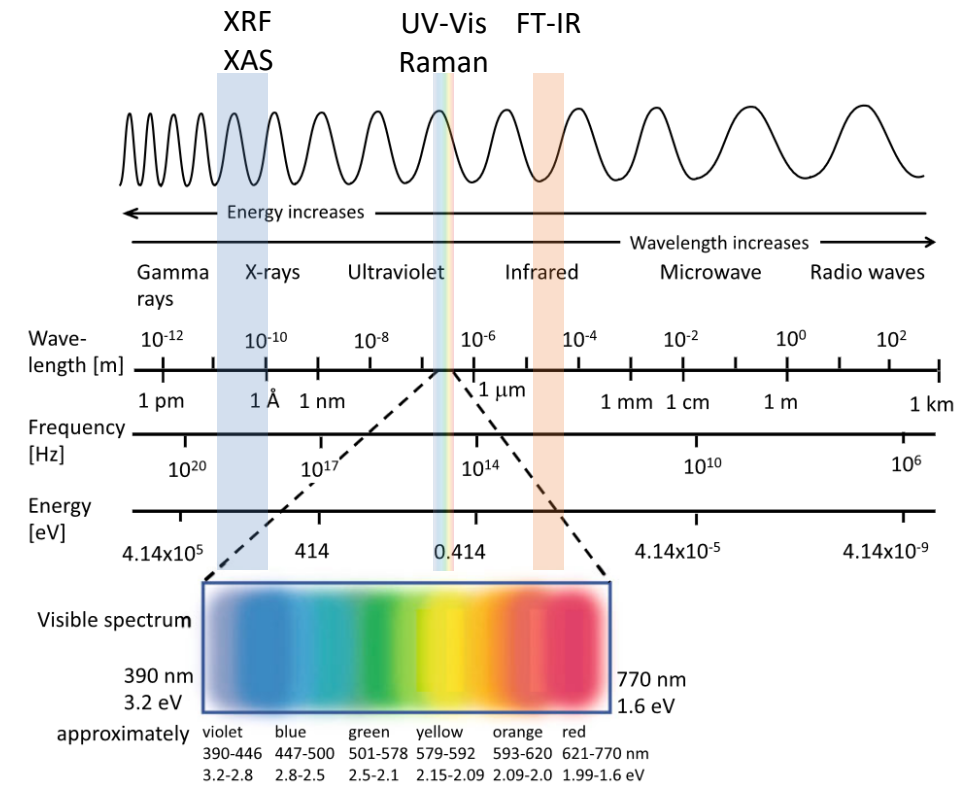
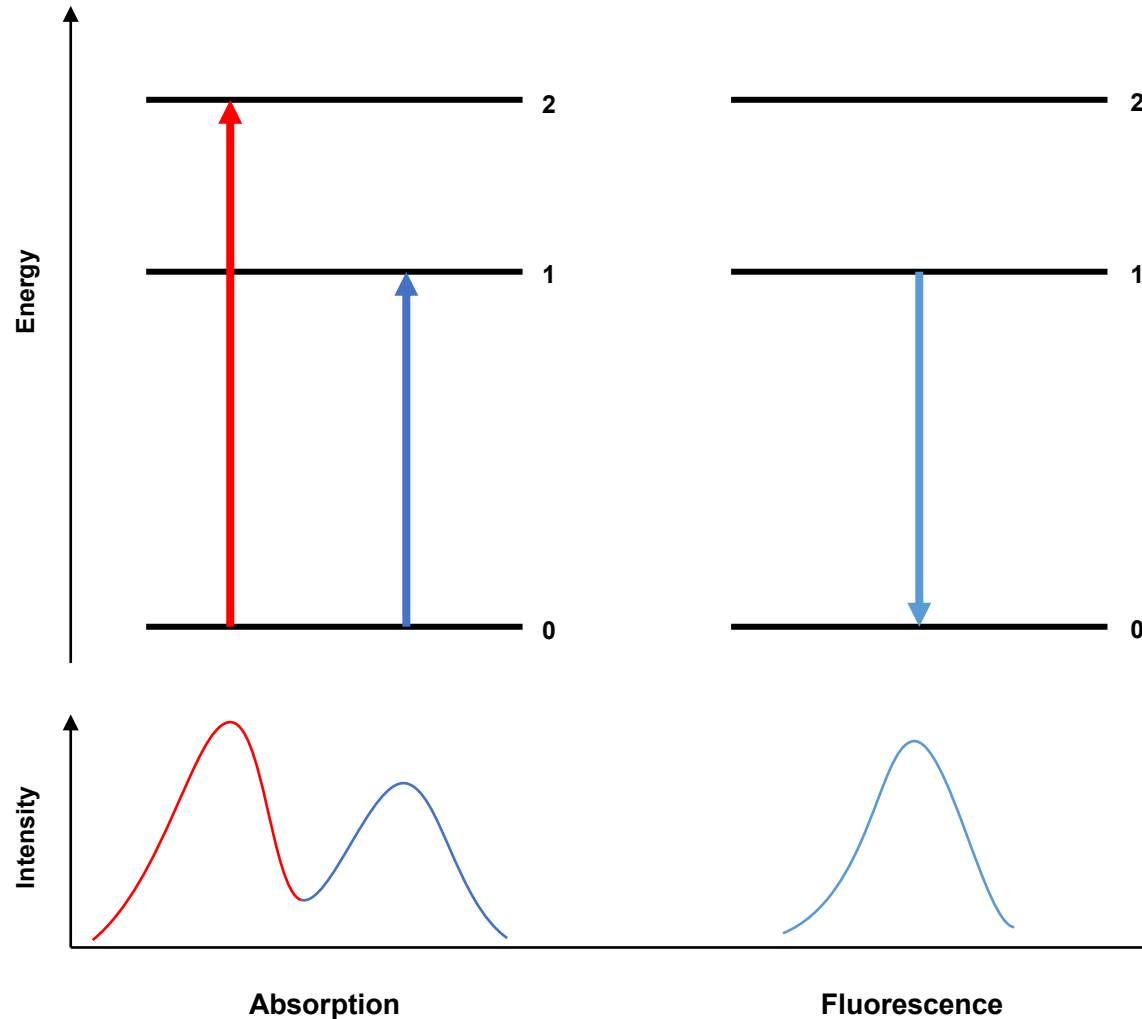
Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

Lecturer: **Paolo Dolcet**

Basics of spectroscopy



UV-Vis, ICP-OES, XRF, XPS: electronic levels

FTIR and Raman: vibrational levels

Each transition is a «fingerprint» of a specific species

Basics of spectroscopy

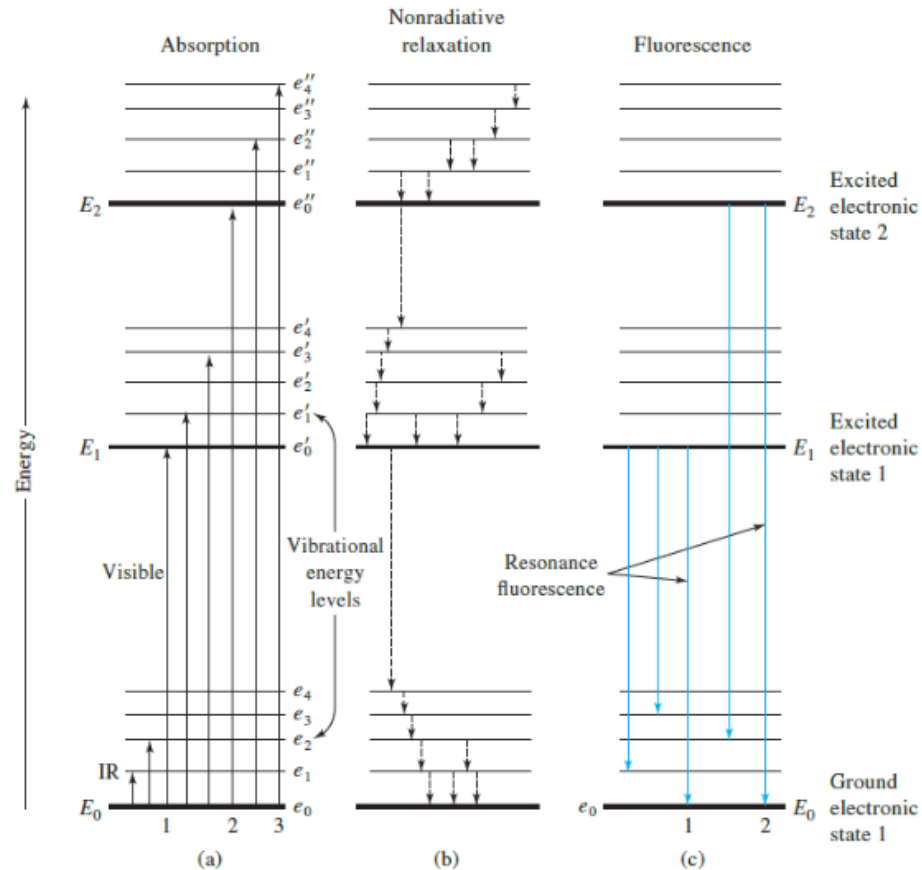


FIGURE 6-24 Partial energy-level diagrams for a fluorescent organic molecule.

Jablonski diagram

- Absorption can occur if $E_{\text{photon}} = \Delta E_{\text{states}}$
- Energy transfer from radiation to atoms/ions/molecules
- Absorption can occur if spin-allowed
- For atoms and monatomic ions: only electronic states involved $\rightarrow E = E_{\text{electronic}}$
- For molecules and polyatomic ions: $\rightarrow E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$

Basics of spectroscopy

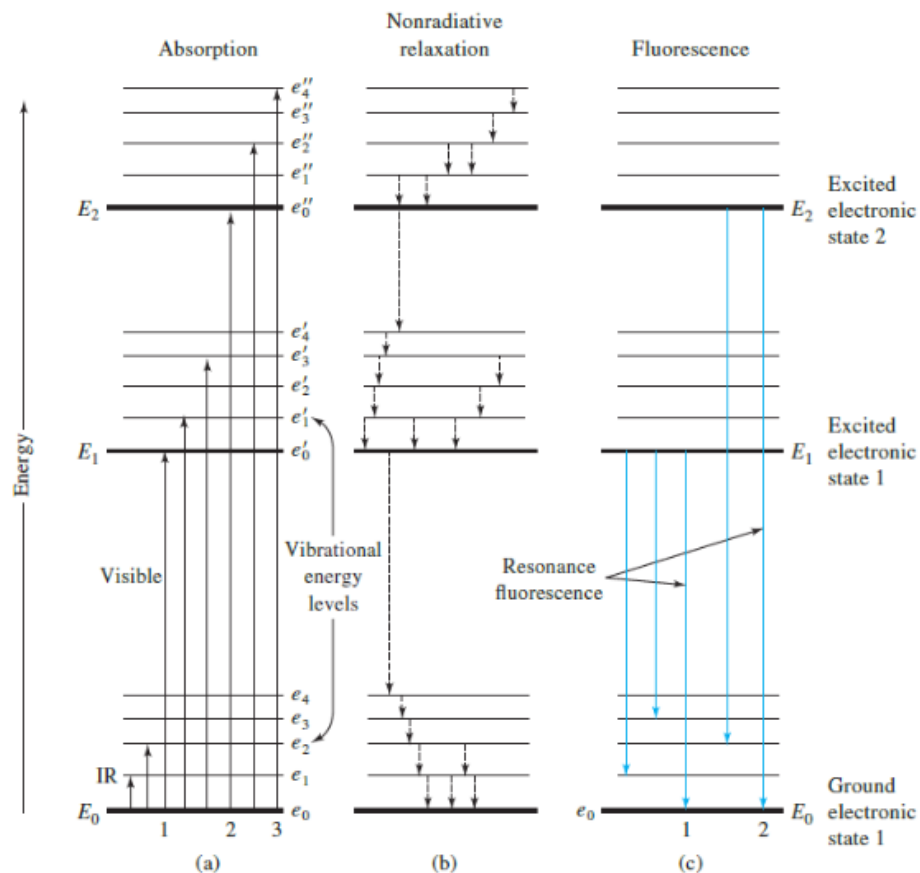


FIGURE 6-24 Partial energy-level diagrams for a fluorescent organic molecule.

- Electronic transitions frequencies

$$\nu_i = \frac{1}{h} (E_1 + e'_i - E_0)$$

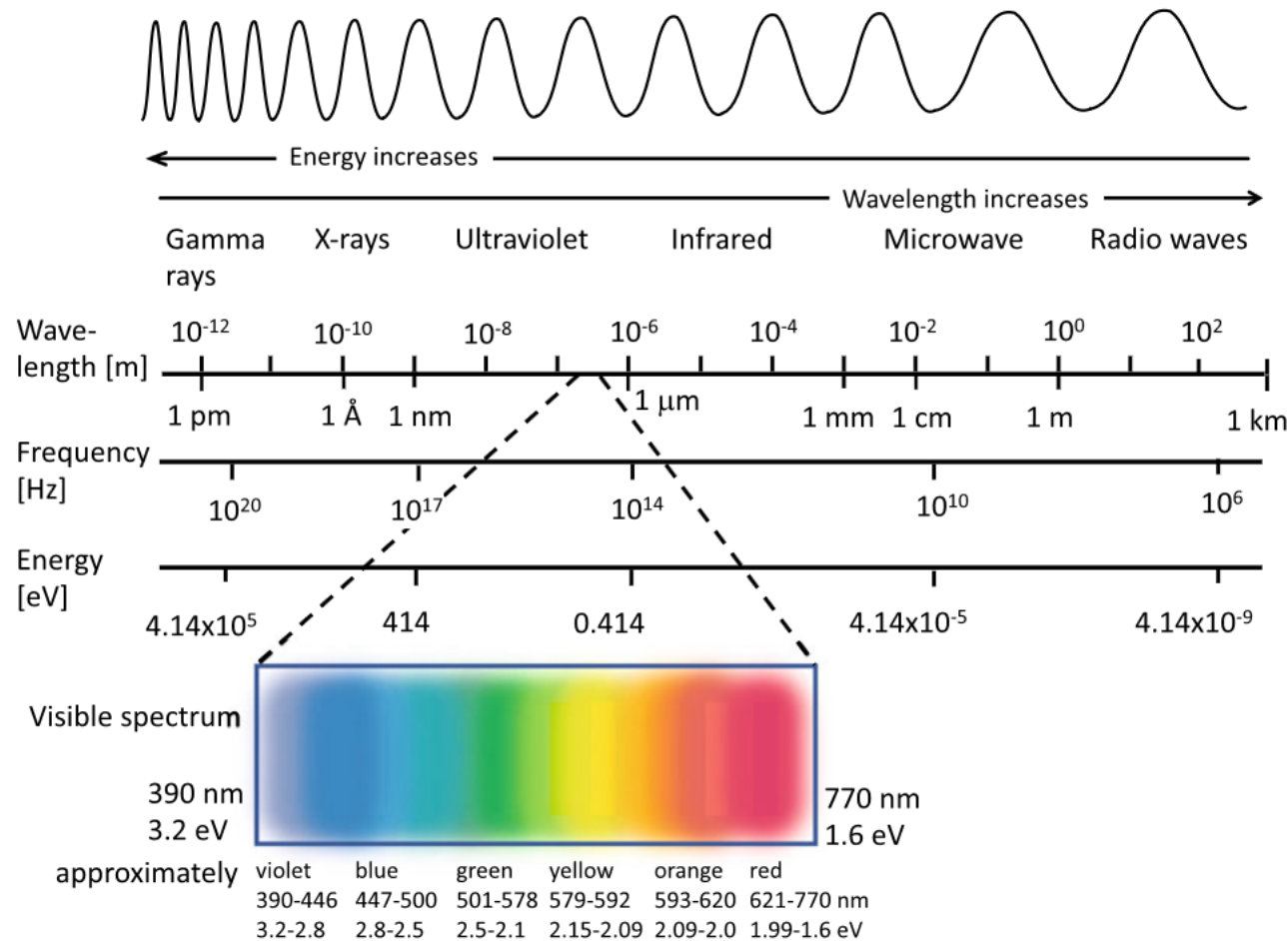
where $i=1, 2, 3, \dots n$

- Lifetime of excited state: 10^{-8} - 10^{-9} s
- Vibrational transitions frequencies (1st electronic state)

$$\nu_i = \frac{1}{h} (e_i - e_0)$$

where $i=1, 2, 3, \dots K$

UV-Vis molecular absorption spectrometry



Radiation: UV-Vis (190 -770 nm)

Basic working principle: comparison of radiation intensity before and after the sample

Pros:

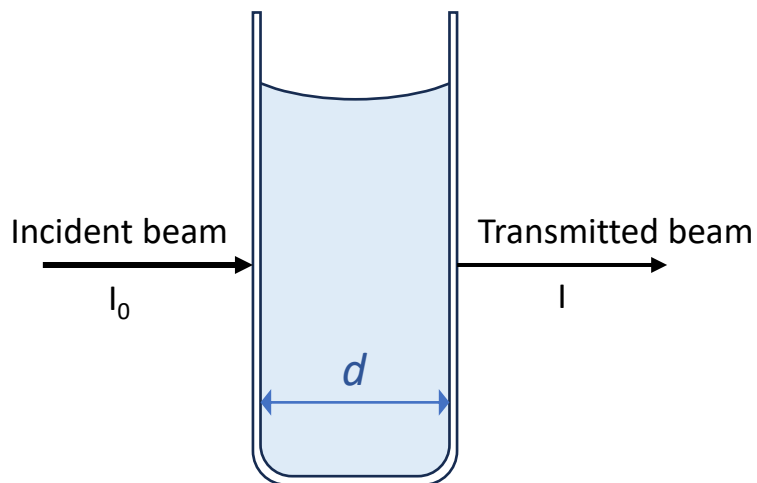
Simple & fast method

Cons:

Sample has to be liquid or gaseous*

* For powders/solid reflectance mode is possible

UV-Vis molecular absorption spectrometry



ϵ = molar absorption coefficient [$\text{cm}^{-1} \text{M}^{-1}$]
 C = molar concentration [M]

- Transmittance $T = \frac{I}{I_0}$
- Absorbance $A = -\log T = -\log \frac{I}{I_0}$
- Absorbance is the commonly adopted unit

Lambert-Beer's Law

$$A = \epsilon d C$$

$$A_{tot} = \sum_{i=1}^N A_i = d \sum_{i=1}^N \epsilon_i C_i$$

For mixtures of
N components

Lambert-Beer's law

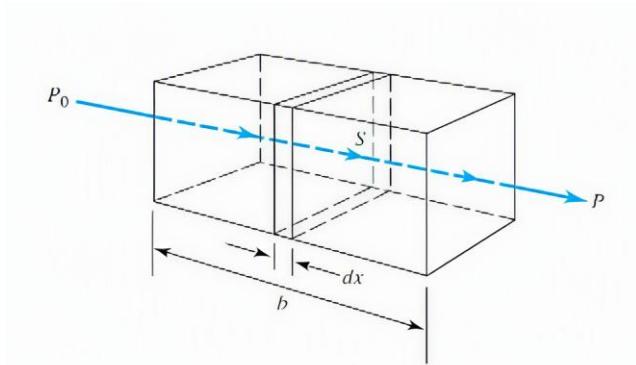


FIGURE 13-2 Radiation of initial radiant power P_0 is attenuated to transmitted power P by a solution containing c moles per liter of absorbing solution with a path length of b centimeters.

S	Area
dS	Area occupied by absorbing particles
a	Cross-section of a single molecule
dn	Number or absorbing particles

1. Probability of absorption

$$-\frac{dP_x}{P_x} = \frac{dS}{S}$$

2. Effective area of irradiated particles

$$dS = a \, dn$$

3. Integration over path length

$$-\int_{P_0}^P \frac{dP_x}{P_x} = \int_0^b \frac{a \, dn}{S}$$

4. Natural logarithm

$$-\ln \frac{P}{P_0} = \frac{an}{S}$$

5. Base-10 logarithm

$$\log \frac{P_0}{P} = \frac{an}{2.303S}$$

6. Converting area

$$S = \frac{V}{b}$$

7. Substituting area

$$\log \frac{P_0}{P} = \frac{anb}{2.303V}$$

8. Converting particle to mol

$$\text{moles} = \frac{n \text{ particles}}{6.022 \times 10^{23} \text{ particles/mol}}$$

9. Expressing concentration

$$c = \frac{n \times 1000}{6.022 \times 10^{23} V} \text{ mol/L}$$

10. Substituting n

$$\log \frac{P_0}{P} = \frac{6.022 \times 10^{23} abc}{2.303 \times 1000}$$

- 11.



Molar absorption coefficient ϵ



- Also known as molar absorptivity
- Units: $\text{cm}^{-1} \cdot \text{M}^{-1}$ or $\text{cm}^{-1} \cdot \text{L} \cdot \text{mol}^{-1}$
- Typical ranges:
 - Very low absorption, $\epsilon < 100$
 - Forbidden transitions
 - Very pale or light solutions
 - Weak to moderate, $100 < \epsilon < 1000$
 - Weakly absorbing species
 - Moderate to strong, $1000 < \epsilon < 10000$
 - Standard transitions
 - Very strong, $10000 < \epsilon < 100000+$
 - Intensely colored compounds



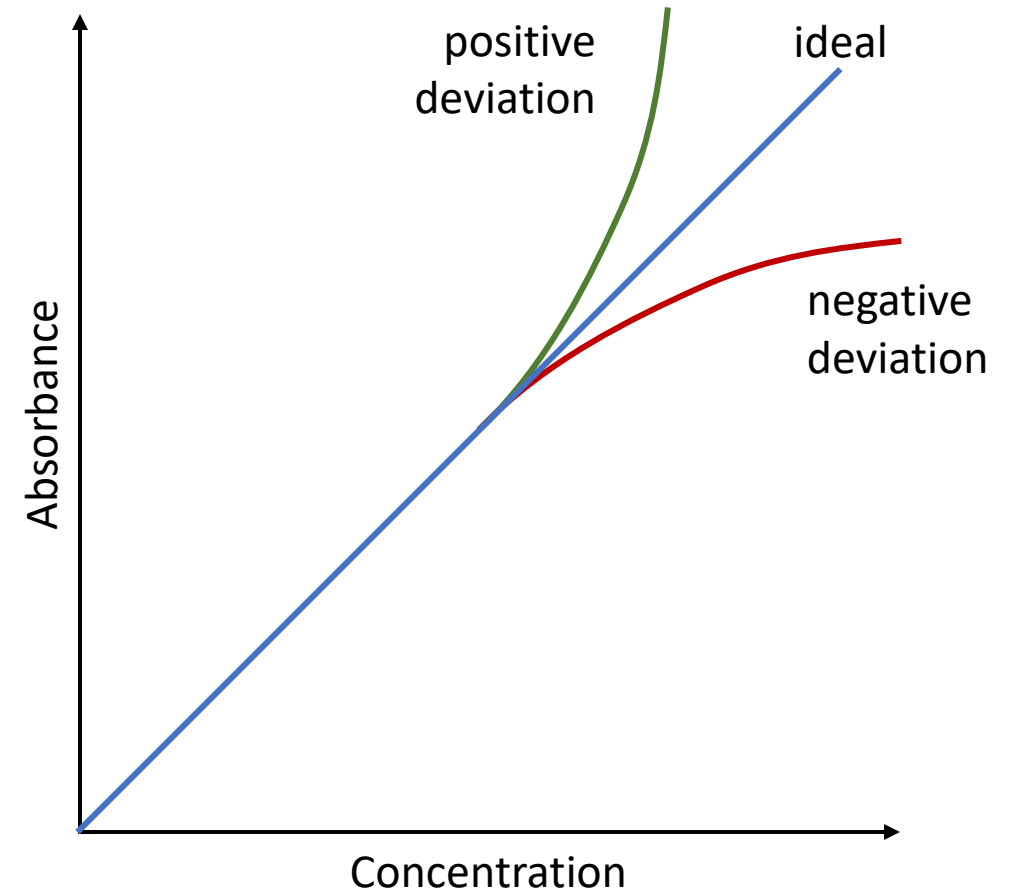
Lambert-Beer's law



- Lambert-Beer's Law

$$A = \epsilon dC$$

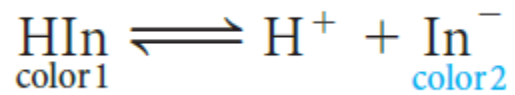
- Strictly speaking, L-B law valid for $C \leq 10 \text{ mM}$
→ Ideal range: 0.2-0.8 Units of absorption (U.A.)
- High C: increased molecular interactions → change in ϵ
- Chemical equilibria can modify apparent ϵ
- Instrumental deviation can also cause deviations



Lambert-Beer's law



Chemical deviations

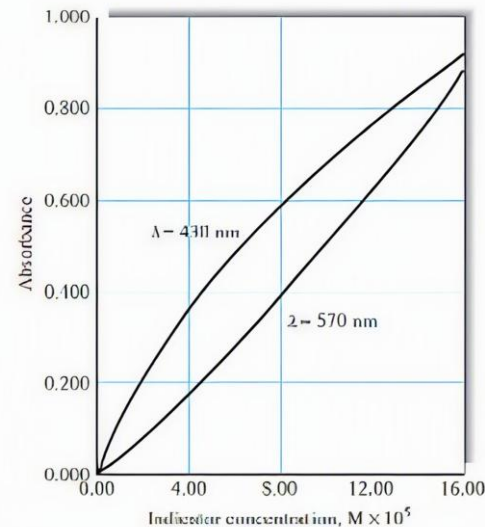


	ϵ_{430}	ϵ_{570}
HIn	6.30×10^2	7.12×10^3
In ⁻	2.06×10^4	9.61×10^2

pH-dependent nonlinearity

Positive deviations at 430 nm

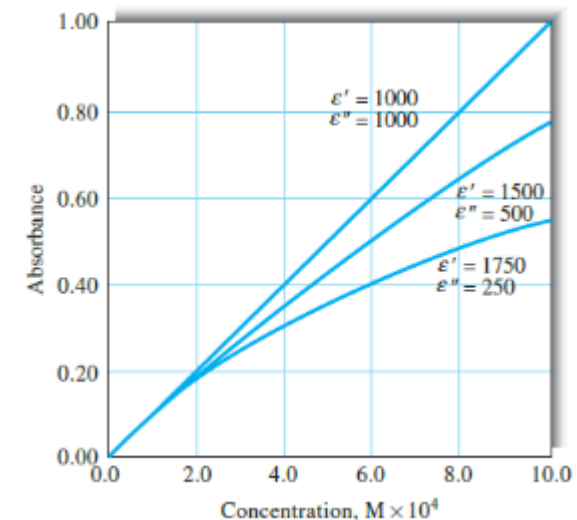
Negative deviations at 570 nm



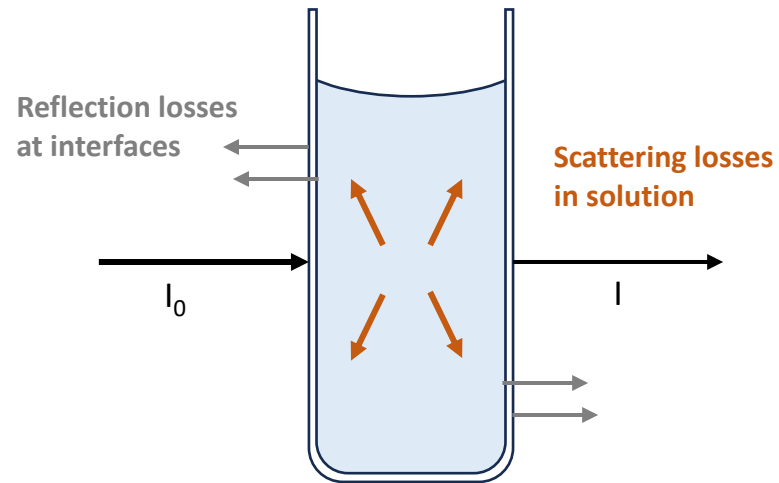
Instrumental deviations

- The incident wavelength is never truly monochromatic
- If we have λ' and $\lambda'' \rightarrow A'$ and A''

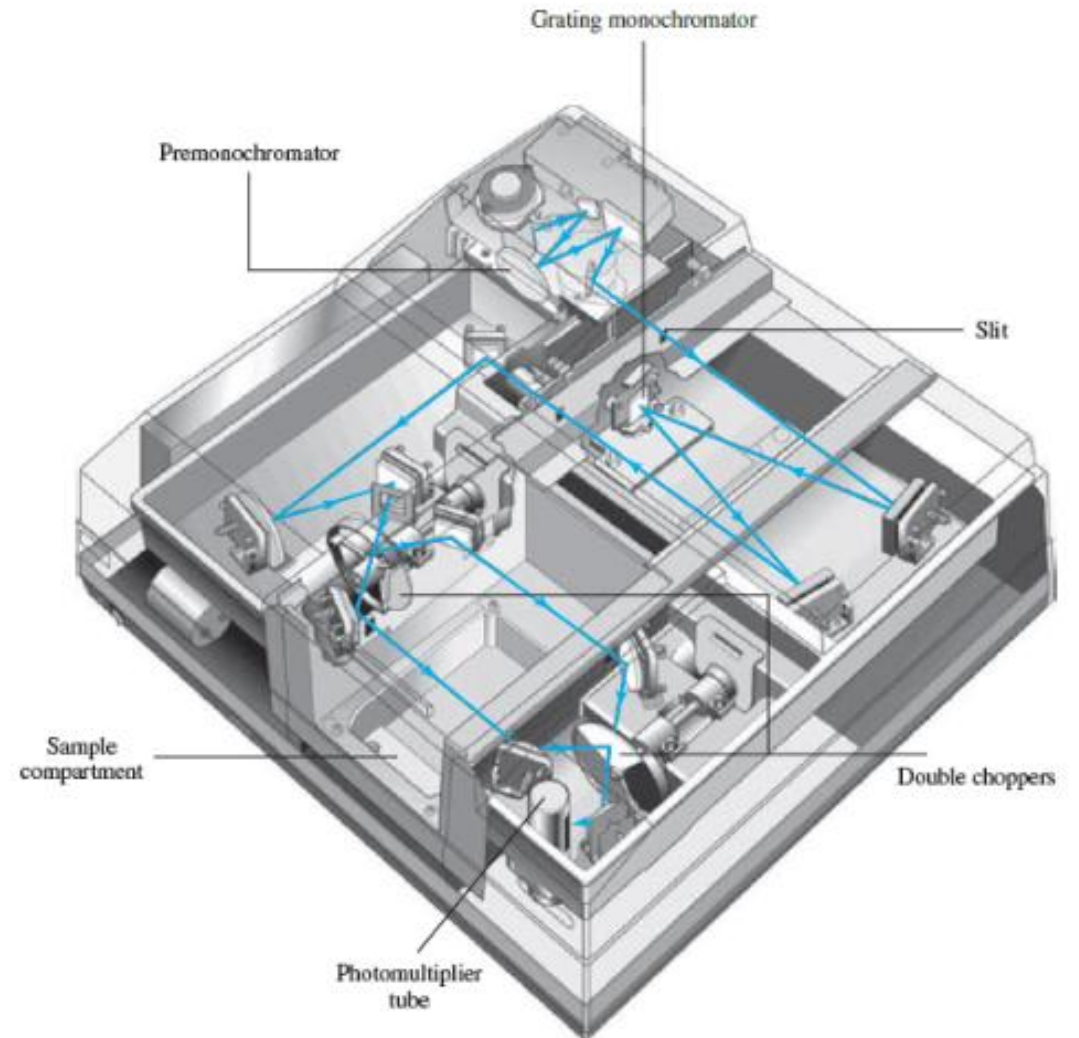
$$A_m = \log \frac{(I'_0 + I''_0)}{(I'_0 \times 10^{-\epsilon' dC} + I''_0 \times 10^{-\epsilon'' dC})}$$



UV-Vis molecular absorption spectrometry



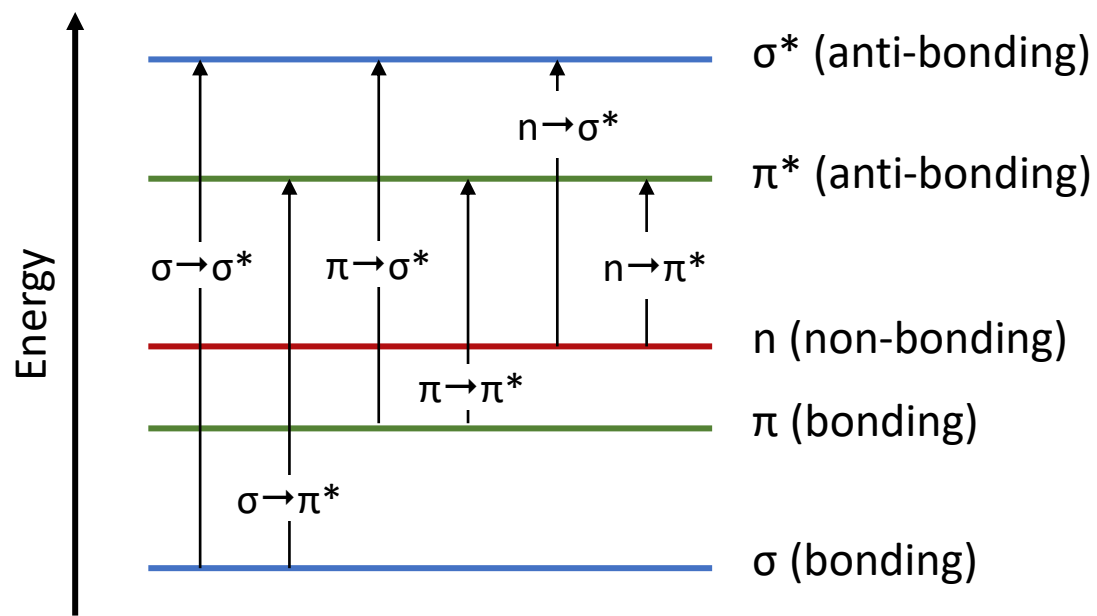
Scratches and etching of the cuvettes can cause artifact to the UV-Vis spectrum.
One well-accepted method is to use lens paper wet by ultra-pure methanol for cleaning the cuvette.



Effect of the solvent



- UV-vis radiation excites the outermost electrons → information on the bonding nature



Chromophores: organic



- **Chromophore:** molecule (or part of it) capable of absorbing light

TABLE 14-1 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	$\lambda_{\max}$, nm	$\epsilon_{\max}$	Transition Type
Alkene	$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$\text{C}_5\text{H}_{11}\text{CH}\equiv\text{C}-\text{CH}_3$	<i>n</i> -Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	—
			225	160	—
Carbonyl	CH_3CCH_3 	<i>n</i> -Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$\text{CH}_3\text{CH}=\text{O}$ 	<i>n</i> -Hexane	180	large	$n \rightarrow \sigma^*$
Carboxyl	CH_3COOH 	Ethanol	293	12	$n \rightarrow \pi^*$
			204	41	$n \rightarrow \pi^*$
Amido	CH_3CNH_2 	Water	214	60	$n \rightarrow \pi^*$
Azo	$\text{CH}_3\text{N}=\text{NCH}_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	$\text{C}_4\text{H}_9\text{NO}$	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$\text{C}_2\text{H}_5\text{ONO}_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Most organic compounds do not absorb wavelengths > 180 nm

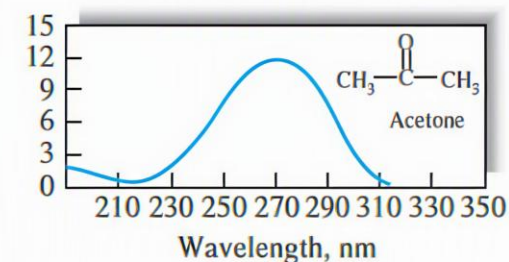
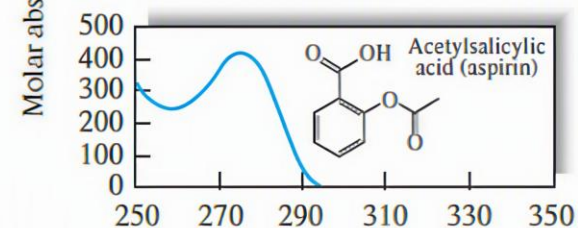
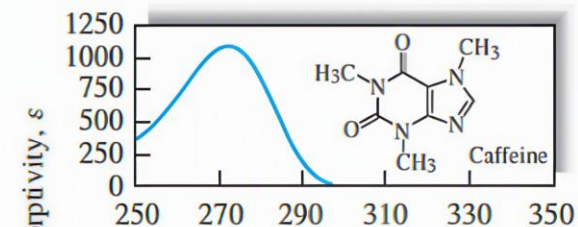
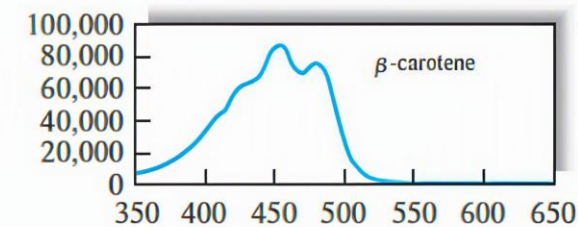
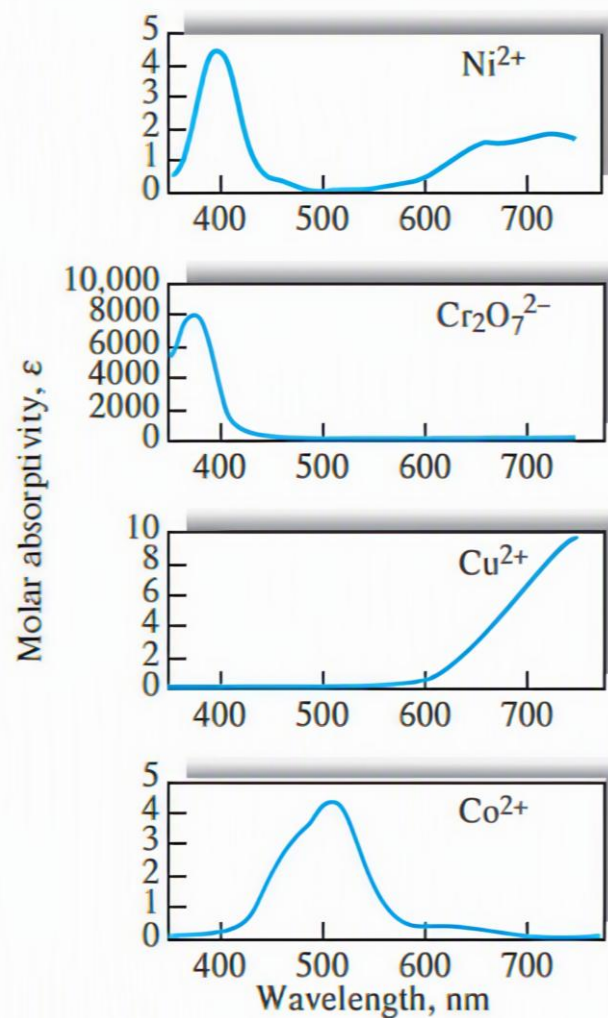


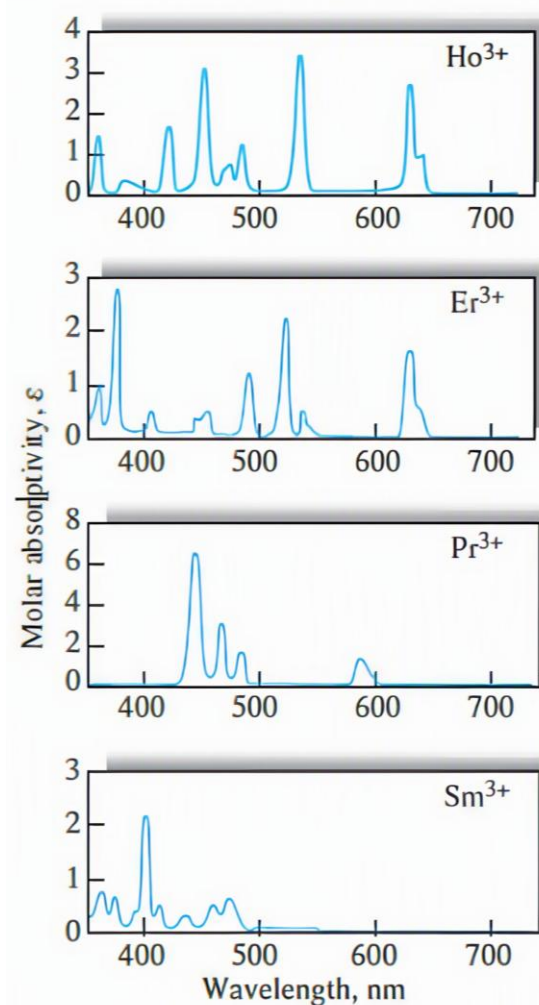
FIGURE 14-2 Absorption spectra for typical organic compounds.

Chromophores: inorganic

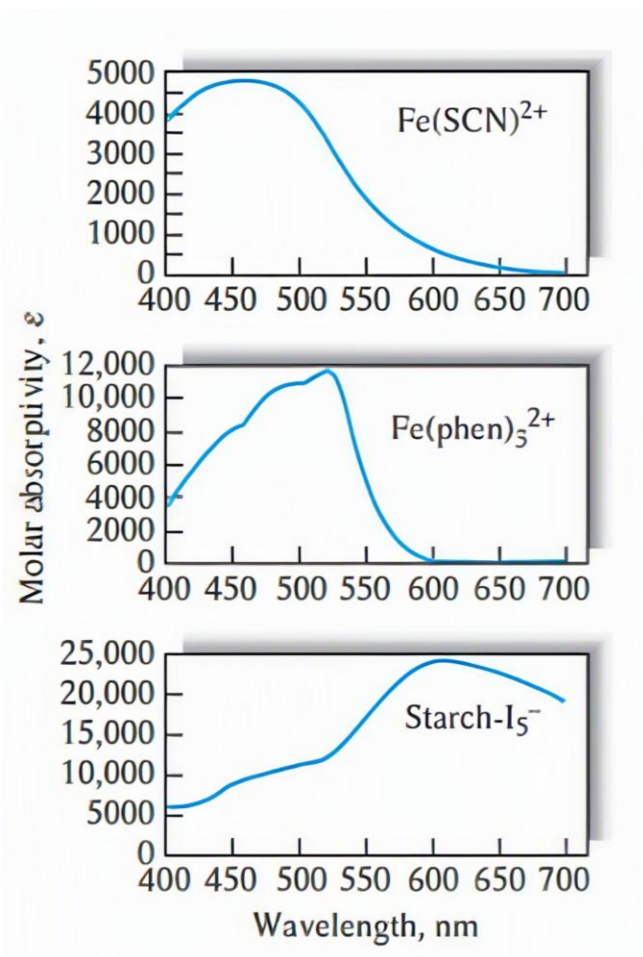


For transition metals,
d orbitals are involved in
the bonding

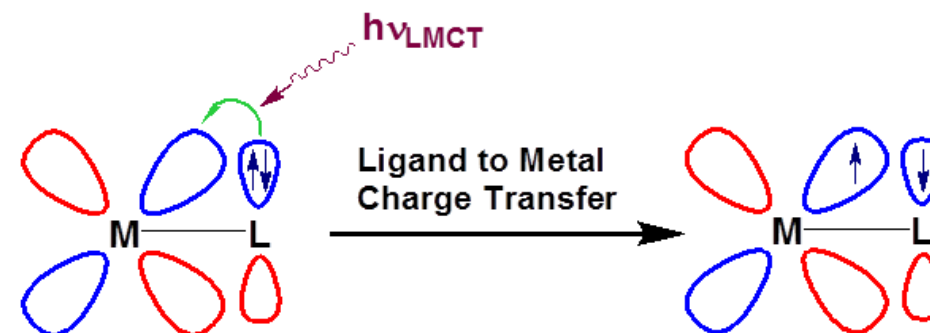
For lanthanides,
f orbitals are screened by
orbitals with higher *n* →
not affected by the ligands



Charge-transfer complexes



- **Charge-transfer complex:**
 e^- -donor group bound to e^- -acceptor group



- Metals usually are acceptors (Lewis acids)
- In this case, the excited e^- lies in an atomic orbital

Quantitative analysis



- L-B law allows for **quantitative analyses**
- Wide applicability to both organic and inorganic systems
- Typical detection limits: $10^{-4} - 10^{-5}$ M; Moderate – high selectivity, good accuracy
- For quantification, the absorbance maximum is selected (max SNR)
- Beware of **matrix effect**: other reagents (e.g., sulfates, fosfates) can partially quench the colored product → add *standard* with known concentration

For **non-absorbing** species:

Add an analyte that reacting with non-absorbing species creates a colored product.

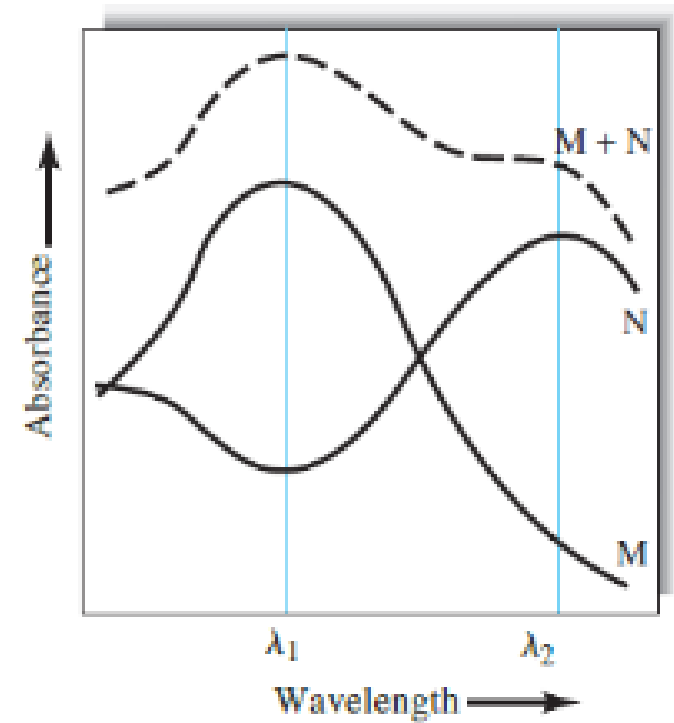
The reaction should reach completion to be able to correlate measured absorbance to analyte concentration.

E.g. *Thiocyanate* for Fe^{3+} , Co^{2+} , Mo^{5+} ; H_2O_2 for Ti^{4+} , V^{5+} , Cr^{6+} ; I^- for Bi^{3+} and Pd^{2+}

Quantitative analysis (mixtures)



- For quantitative analysis of mixtures, wavelengths must be properly selected
- E.g., for a mixture of M and N, need to choose λ_1 and λ_2 so that $\epsilon_{M1} \gg \epsilon_{N1}$ and $\epsilon_{N2} \gg \epsilon_{M2}$



$$A_1 = \epsilon_{M1}bc_M + \epsilon_{N1}bc_N$$

$$A_2 = \epsilon_{M2}bc_M + \epsilon_{N2}bc_N$$

Spectrophotometric titrations



- Exploiting L-B law, titrations are possible (L-B law **must be fulfilled!**)

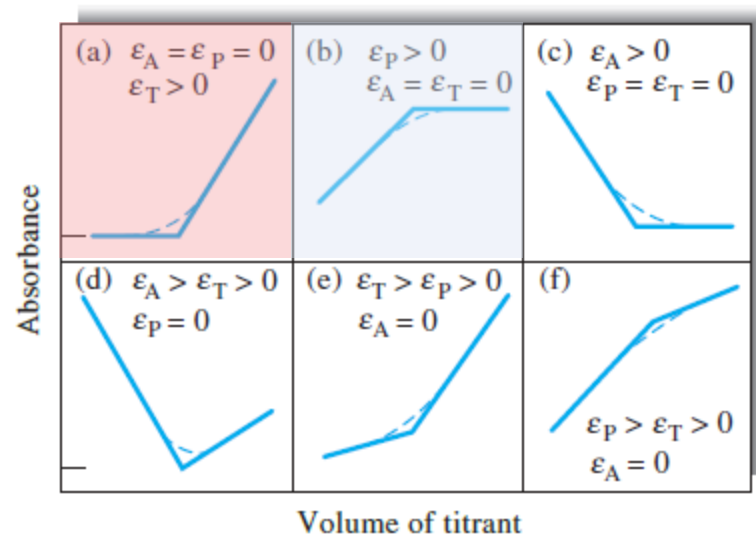
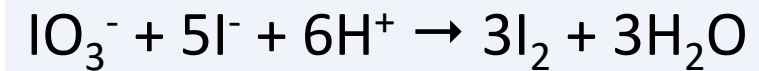


FIGURE 14-12 Typical photometric titration curves. Molar absorptivities of the analyte, the product, and the titrant are given by ϵ_A , ϵ_P , ϵ_T , respectively. The dashed lines represent actual data, and the solid lines are extrapolated from the linear portions of the plots.

- Some examples:



Reaction kinetics



- Titrations = equilibrium state
- Dynamic conditions require transient methods



- E.g.
dissolution/leaching/catalyzed
reactions can be monitored

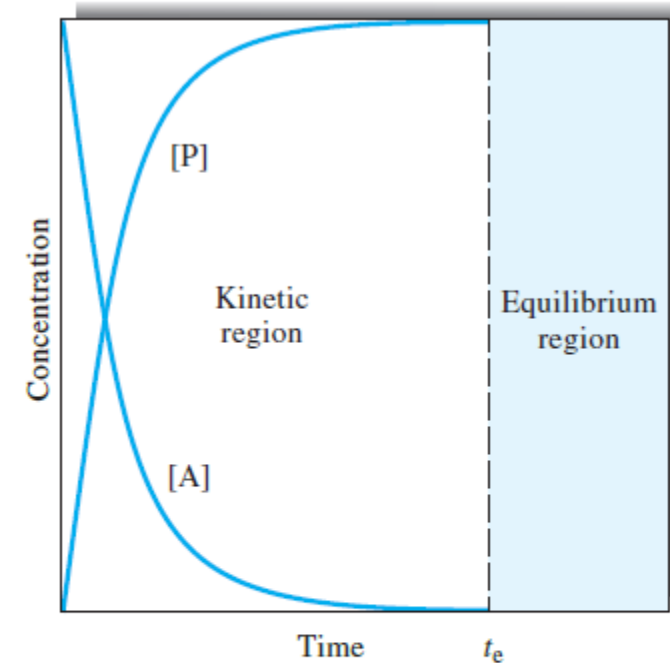
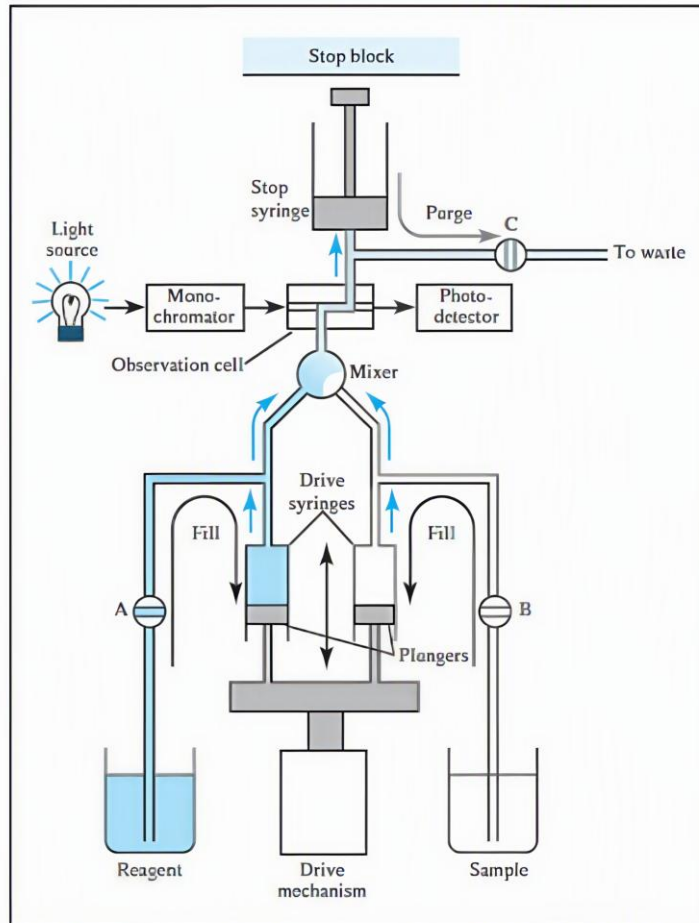


FIGURE 14-14 Change in concentration of analyte [A] and product [P] as a function of time. Until time t_e the analyte and product concentrations are continuously changing. This is the kinetic regime. In the equilibrium region, after t_e , the analyte and product concentrations are static.

How to monitor kinetics



- Temperature must be carefully controlled → it affects overall kinetics
- If reaction's half-time > 10 s, manual analysis is possible
- If reaction's half-time < 10 s, stopped-flow mixing (accuracy in ms range)

Photodegradation of pollutants

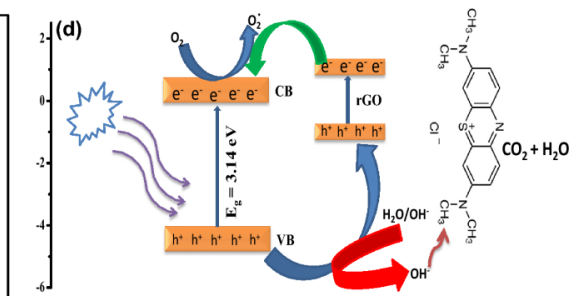
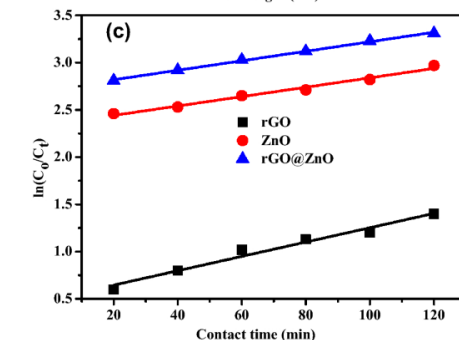
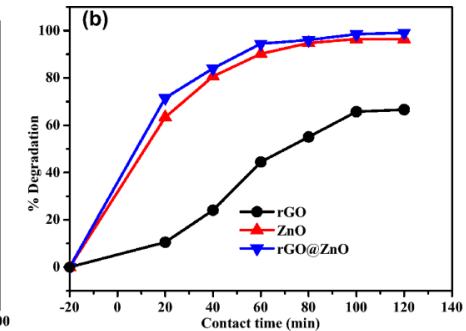
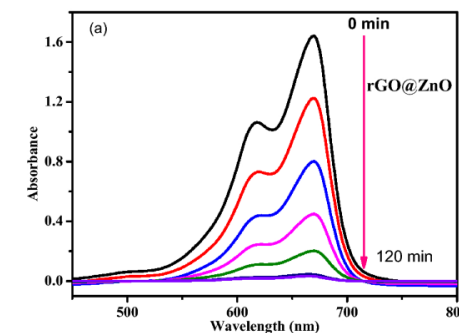
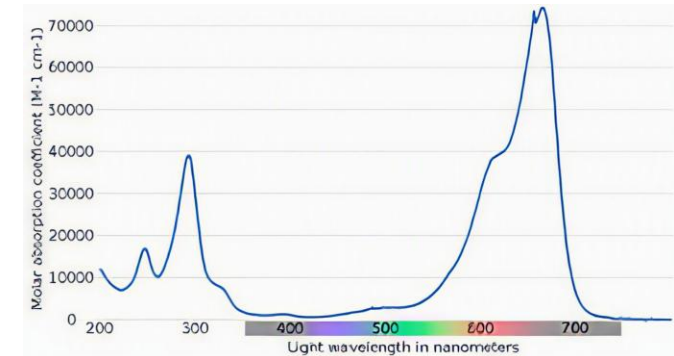


- Methylene blue is a dye used e.g., for testing freshness of milk or efficiency of filtration systems
- Can be photodegraded → rxn can be followed monitoring A at 665 nm

$$\frac{C_t}{C_0} = \frac{A_t}{A_0}$$

- For low [MB]:

$$-\frac{dC}{dt} = k_{app}C \Rightarrow \ln\left(\frac{A_0}{A_t}\right) = k_{app} \cdot t$$



https://en.wikipedia.org/wiki/Methylene_blue

<https://www.nature.com/articles/s41598-023-48826-7>

Wastewater treatment using waste cuprous oxide



- A circular and sustainable lab waste management
- Cu_2O catalyst prepared from undergraduate students' lab
- Biology lab produces waste rich in organic dyes
- Degradation of dyes by Cu_2O followed by UV-Vis

