INTRODUCTION TO SPECTROCHEMICAL METHODS

CEB 4032: ANALYTICAL CHEMISTRY
CFB3032: ANALYTICAL INSTRUMENTATION

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Chemical Engineering

Inspiring Potential·Generating Futures

Outline

- Electromagnetic Radiation
- Absorption Process
- Emission Process
- Qualitative Analysis
- Quantitative Analysis
- Analysis of Mixture
- Spectrometric Instrumentation

Learning Outcomes:

At the end of this chapter:

(1) Understand the properties of electromagnetic radiation, absorption and emission processes in spectrochemical methods.

(2) Make quantitative calculations, relating the amount of radiation absorbed to the concentration of an absorbing analyte.

(3) Describe the spectrometric instrumentation requires for making measurements.

INTRODUCTION

- Measurement based on light and other forms of electromagnetic radiation are widely used throughout analytical chemistry.

- The interactions of radiation and matter (absorption, emission and fluorescence) are the subject of the science call spectroscopy or spectrochemical method.

- Spectrochemical methods are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest.

- Can be classified according to the region of the electromagnetic spectrum involved in the measurement.

- Regions that have been commonly used: X-ray, ultraviolet (UV), visible, infrared (IR), microwave etc.

- Widely used tools for the elucidation of molecular structure as well as quantitative and qualitative determination of both inorganic and organic compounds.

- For example, the sample solution absorbs electromagnetic radiation from an appropriate source and the amount absorbed is related to the concentration of the analyte in the solution.

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- **Electromagnetic Radiation**
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Electromagnetic Radiation

- Electromagnetic radiation (EMR) → a form of radiant energy that is propagated as a transverse wave.

- General properties of EMR: i) wave and ii) particle (discrete of energy) properties.
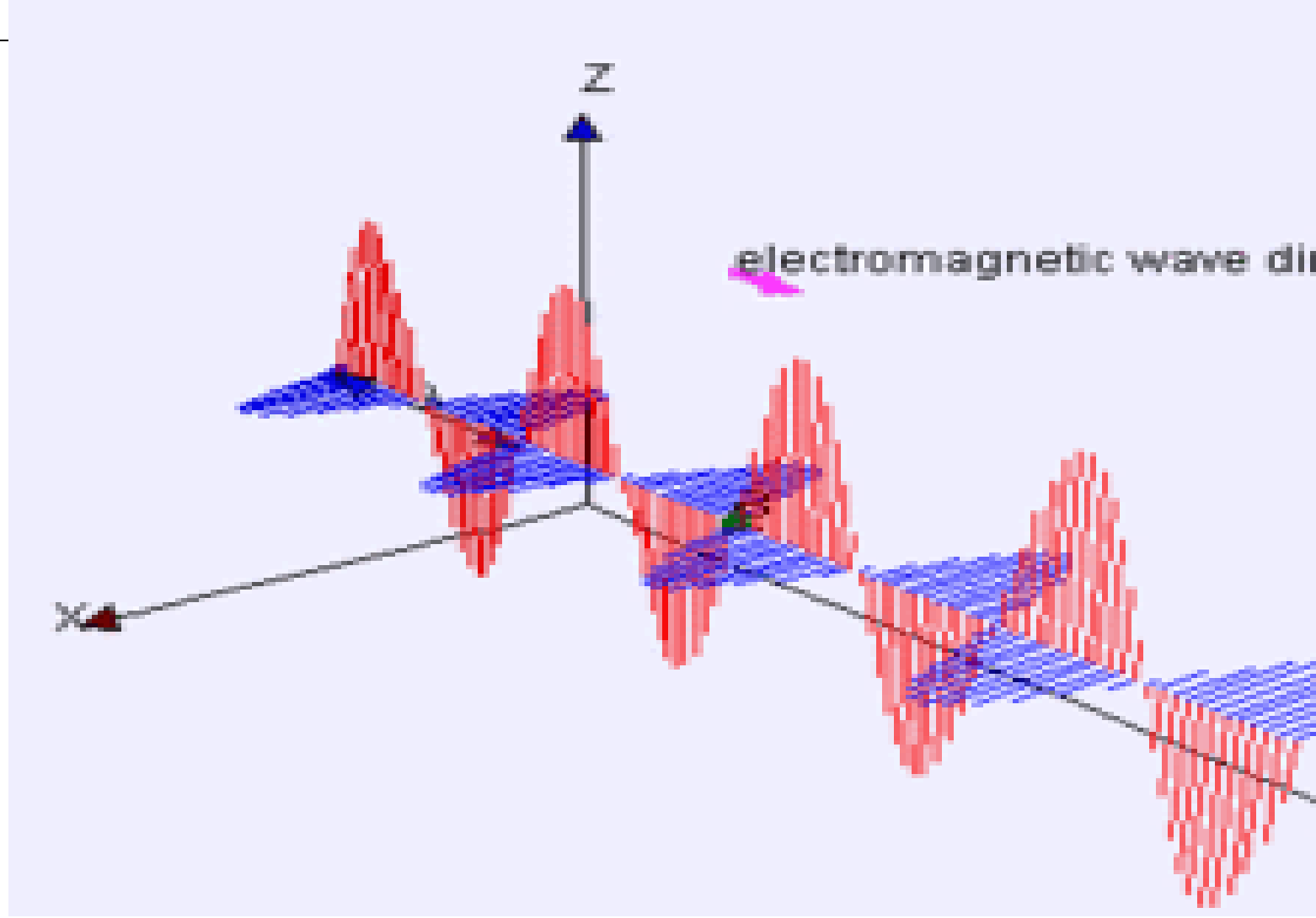
i) Characteristics of Wave
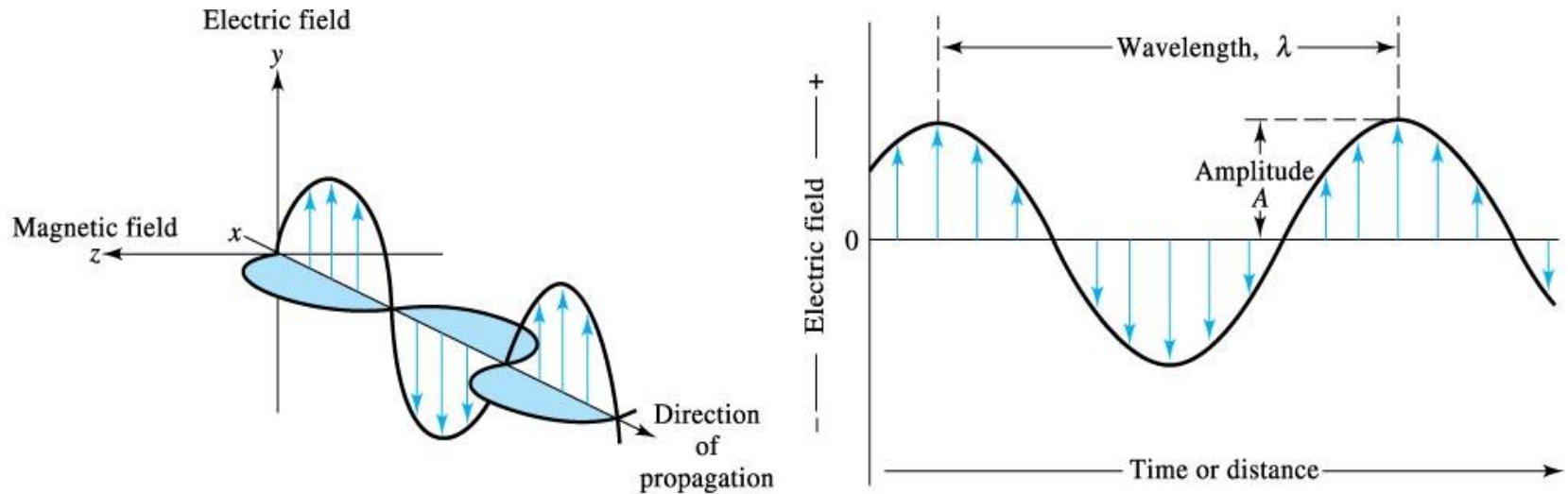
- **Amplitude (A):** Length of the electric vector at a maximum in the wave.

- **Period (p):** The time in seconds required for the passage successive maxima or minima through a fixed point in space.

- **Frequency (v):** The number of oscillations of the field that occur per second and is equal to $1/p$. (s^{-1} or Hz).

- **Wavelength (λ):** The linear distance between any two equivalent points on successive waves (successive maxima or minima). (Å, nm, etc.).

- **Velocity (*v*):** The relationship between the wavelength and frequency (the speed of light)

frequency, s^{-1} or Hz

$$V = v\lambda$$

velocity, cm/s   wavelength, cm

- In vacuum, the velocity of radiation is independent of wavelength and it at its maximum. The velocity, *c* has been determined to be 2.99792×10^8 m/s.

- The above equation can be written as :

$$c = v\lambda = 3.00 \times 10^{10} \text{ cm/s}$$

■ **<u>Wavenumber</u>** $(\bar{v})$**:** reciprocal of the wavelength (cm^{-1}).

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$$

ii) Characteristics of Particle

- When EMR is emitted or absorbed, a permanent transfer of energy from the emitting object or to the absorbing medium occurs.

- In this case, EMR is not a collection of wave but as a stream of discrete particle → photons (the energy of a unit of radiation).

- Each photon carries energy, *E*, which is given by:

$$E = h\nu$$

frequency, s^{-1} or Hz

Plank's constant = 6.626×10^{-34} J.s

- Energy is proportional to frequency, we can write:

$$E = h\nu = \frac{hc}{\lambda}$$

- The shorter the wavelength or the greater the frequency, the greater the energy.

Electromagnetic Spectrum

- encompasses an enormous range of wavelength and frequencies. Spectroscopic methods are classified according to the wavelengths or frequencies that are important for analytical purpose.
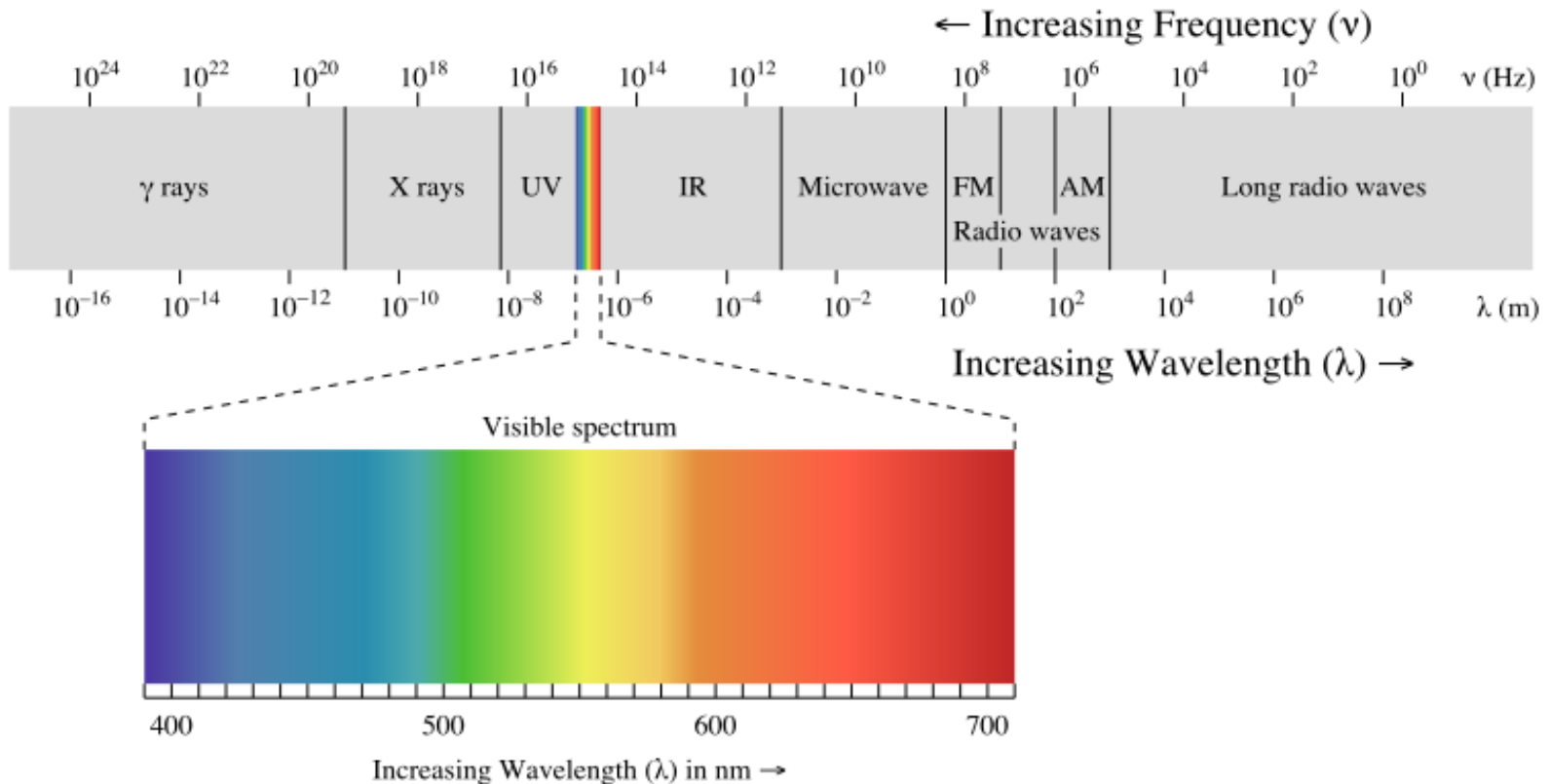
Common Spectroscopy Methods Based on EMR

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	–	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	–	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

1 Ǎ = 10^{-10} m = 10^{-8} cm
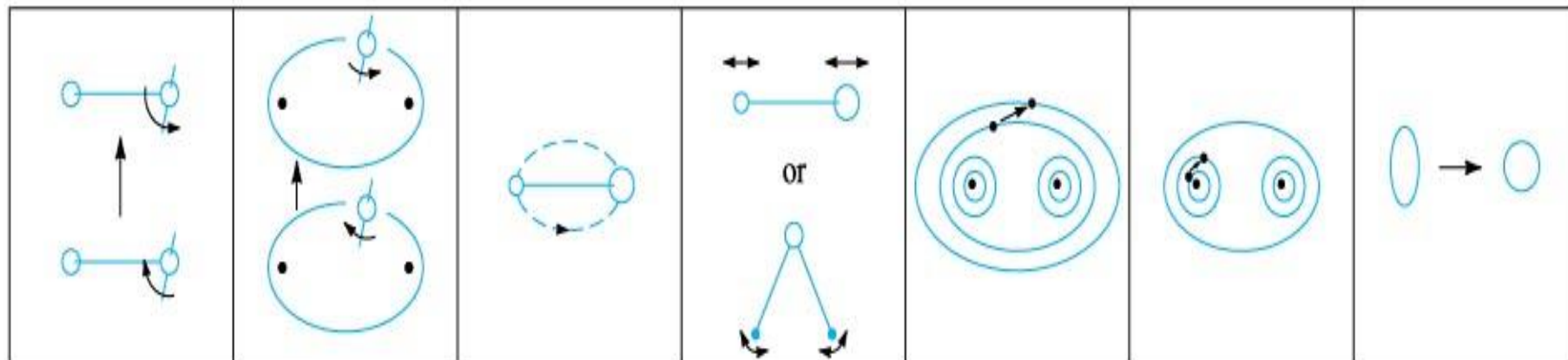1 nm = 10^{-9} m = 10^{-7} cm
1 μm = 10^{-6} m = 10^{-4} cm

Change of spin		Change of orientation	Change of configuration	Change of electron distribution		Change of nuclear configuration

Wavenumber, cm^{-1}

	10^{-2}	1	100	10^4	10^6	10^8

Wavelength

10 m	100 cm	1 cm	100 μm	1000 nm	10 nm	100 pm

Frequency, Hz

3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}	3×10^{18}

Energy, J/mol

10^{-3}	10^{-1}	10	10^3	10^5	10^7	10^9

Type of
spectroscopy:

NMR	ESR	Microwave	Infrared	Visible and ultraviolet	X-ray	g-ray

Example 1

In vacuum, what is the wavelength of light that has a frequency of 5.00 x 10^{14} Hz? Into what range of the light spectrum does it fall?

Solution

frequency, s⁻¹ or Hz

$$v = v\lambda$$

velocity, cm/s   wavelength, cm

$\lambda = c/v$ where $c = 3.00 \times 10^{8}$ m/s

$$\lambda = \frac{3.00 \times 10^{8} \text{m/s}}{5.00 \times 10^{14} \text{s}^{-1}} = \underline{6.00 \times 10^{-7} \text{ m} = 600 \text{ nm}}$$

So, the light is in the <u>visible region</u> on the spectrum

Example 2:

i) By how many kilojoules per mole is the energy of O_2 increased when it absorbs ultraviolet radiation with a wavelength of 147 nm?

ii) How much is the energy of CO_2 increased in kilojoules per mole when it absorbs infrared radiation with a wavenumber of 2300 cm^{-1}?

Solution for (i):

- $E = h\nu = \dfrac{hc}{\lambda}$, h = 6.626 x 10^{-34} J.s

$$E = (6.626 \times 10^{-34}\, \text{J.s}) \left[\frac{(3.00 \times 10^8\, \text{m/s})}{(147 nm)(\frac{10^{-9} m}{nm})} \right]$$

= 1.35 x 10^{-18} J/molecule

Convert to kJ/mol

1.35 x 10^{-18} J/molecule x 6.022 x 10^{23} molecules/mol)

= 814 kJ/mol

Solution for (ii):

For CO_2, the energy increase is

$$E = h\nu = \frac{hc}{\lambda} \quad \text{and} \quad \bar{\nu} = \frac{1}{\lambda}$$

Given : wavenumber, $1/\lambda = 2300 \text{ cm}^{-1}$

$E = (6.626 \times 10^{-34} \text{ J.s})(3.00 \times 10^8 \text{ m/s})(2300 \text{ cm}^{-1})(100 \text{ cm/m})$

$= 4.6 \times 10^{-20}$ J/molecule x 6.022×10^{23} molecules/mol

$= $ 28 kJ/mol

Exercise

Q1

Convert the wavelength 4000.0 Å into frequency (Hz) and into wavenumbers (cm^{-1}).

What is the energy in kJ/mol possessed by a radiation of wavenumber 1000.0 cm^{-1}?

Q3

Calculate the wavelength and energy in kJ/mol associated with a signal at 220.0 MHz.

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Absorption of Radiation

- When radiation passes through a sample (a layer of solid, liquid, or gas), certain frequencies may be selectively removed by absorption.

- a process in which electromagnetic energy is transferred to the atom, ions, or molecules composing the sample.

- Absorption promotes these particles excited from ground state (lower energy), to one or more higher energy states.

- The transition from one energy state to another, the frequency or the wavelength of the radiation is related to the energy difference between the states by the equation:

Energy of the photon

$$E_1 - E_o = h\nu = hc/\lambda$$

Energy of the higher state

Energy of the lower state

- For absorption of radiation to occur, the energy of the exciting photon must exactly match the energy difference between the ground state and excited state of the absorbing species.

- These energy differences are unique for each species, a study of the frequencies of absorbed radiation provides a means of characterizing the constituents of a samples of matter.
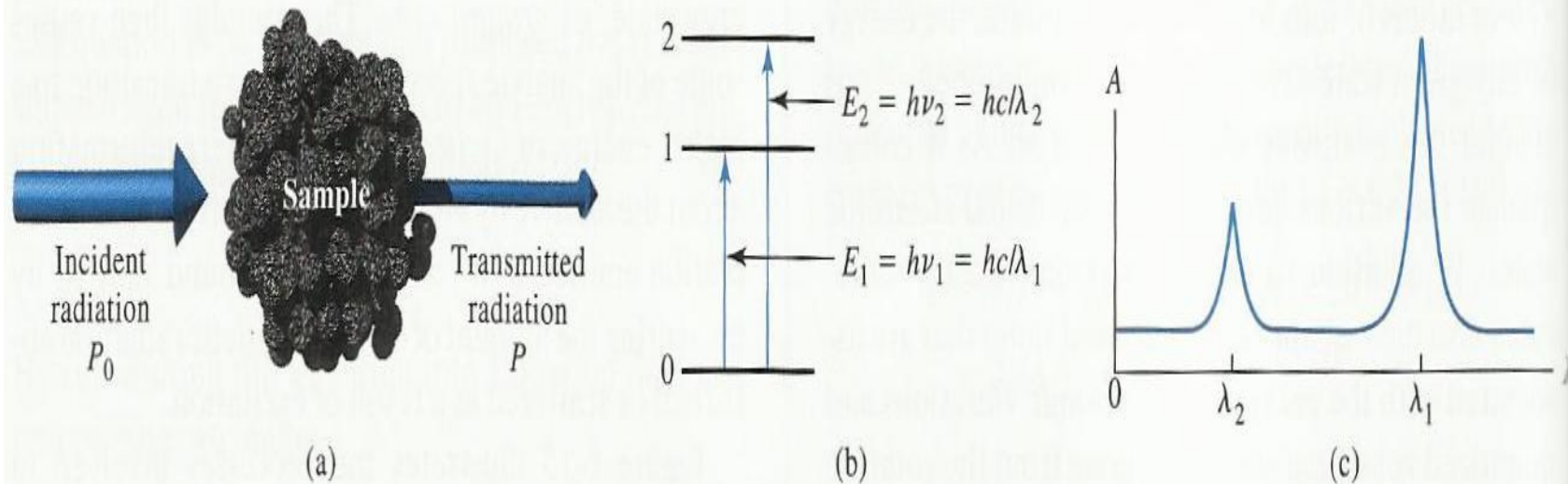

FIGURE 6-16 Absorption methods. Radiation of incident radiant power P_0 can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power P. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b). The resulting absorption spectrum is shown in (c).
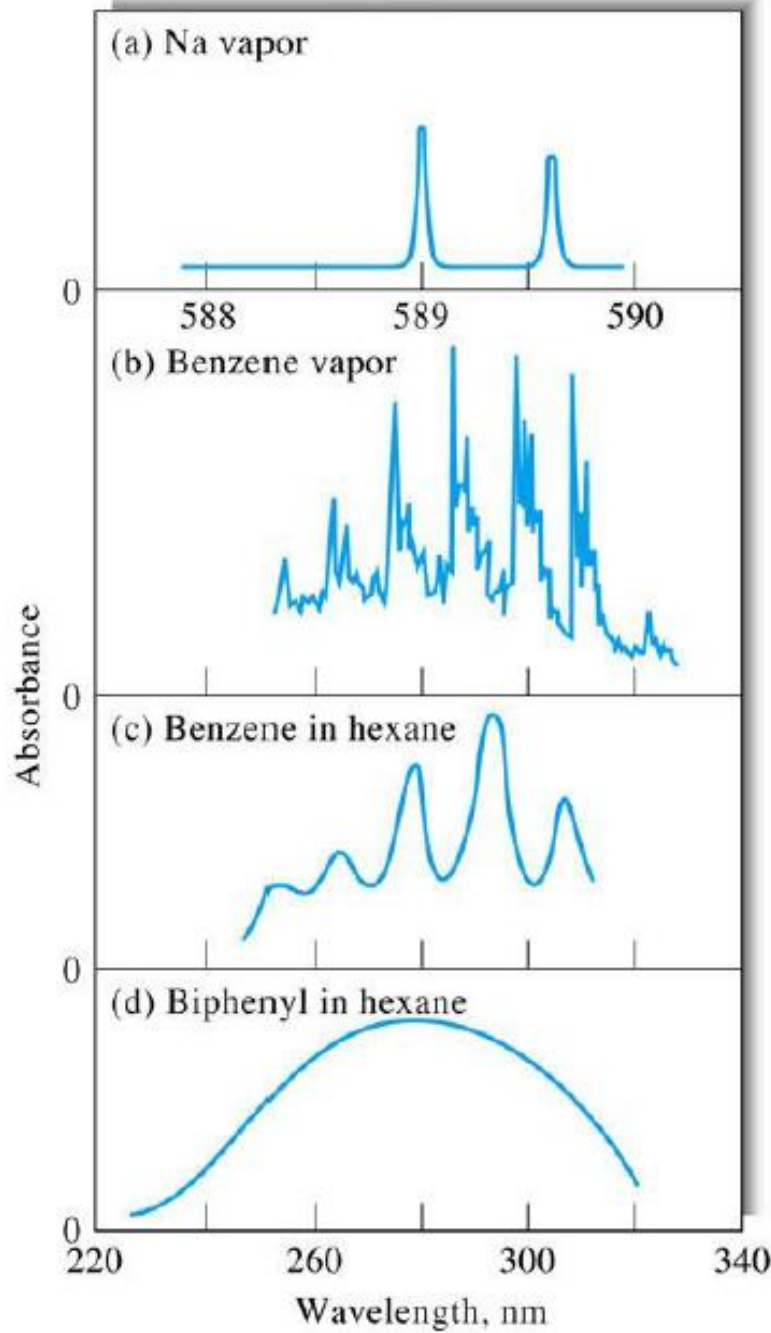
Examples of UV absorption spectra

Atomic Absorption

- The passage of radiation through a medium that consists of monoatomic particles results the absorption of a few well defined frequency.

- The relative simplicity of such spectra is due to the small number of possible energy states for the absorbing particles.

- Excitation occur by an electronic process in which one or more of the electrons of the atom are raised to a higher energy level.
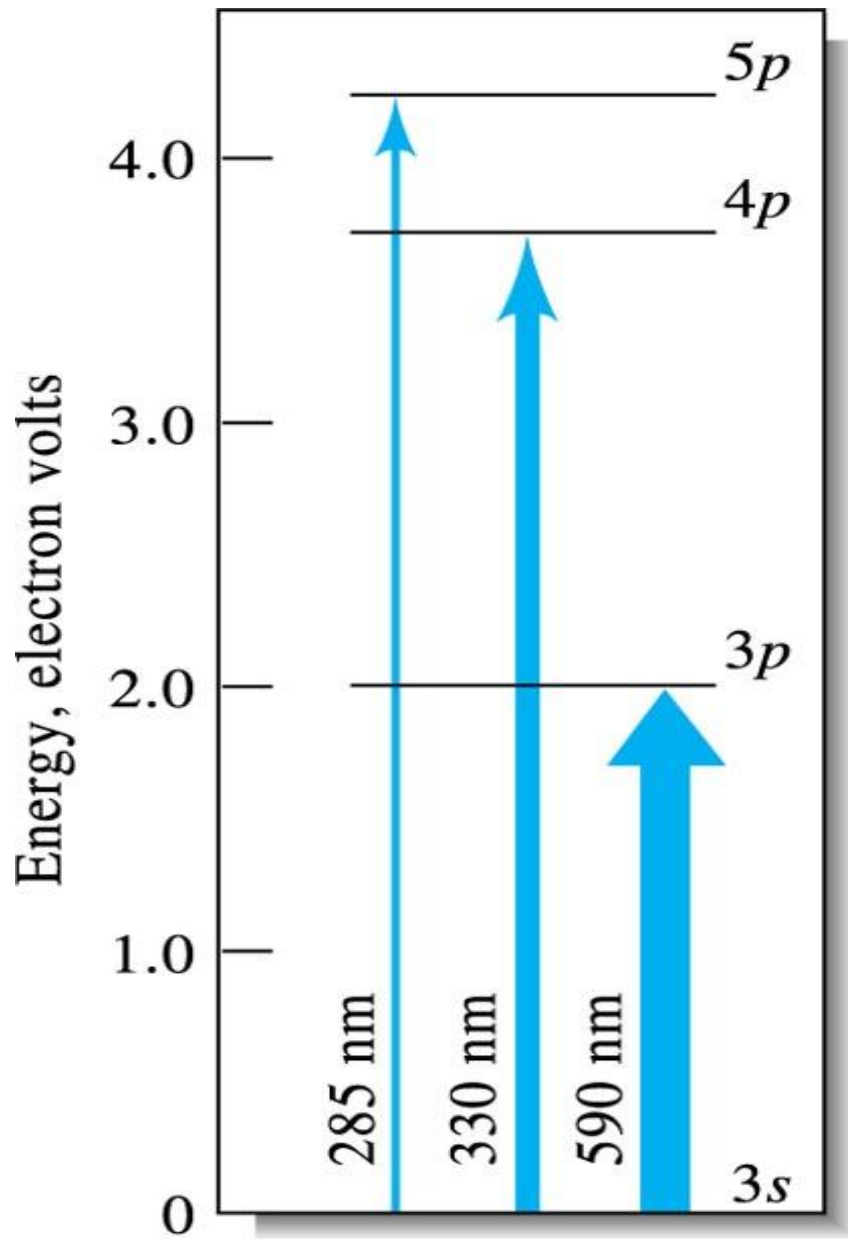
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Atomic Absorption

Molecular Absorption

- Absorption spectra for polyatomic molecules are considerably more complex than atomic spectra.

- Because the number of energy states of molecules is generally enormous when compared with the number of energy states for isolated atoms.

- The energy E associated with the bands of a molecule is made up of three components.

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

- $E_{electronic}$

  - energy produced when the electrons of the molecule raised to a higher energy level.

- $E_{vibrational}$

  - the total energy associated with the interatomic vibrations that are present in molecular species.
  - generally, a molecules has more vibrational energy level than it does electronic levels.

- $E_{rotational}$

  - is the energy caused by various rotational motions within a molecule.
  - the number of rotational states is much larger that the vibrational stages.

The relative energy levels are in the order:

electronic>vibrational>rotational

Rotational → very low energy (low wavelength, microwave or far-infrared region)

Vibrational →requires higher energies (near-infrared region)

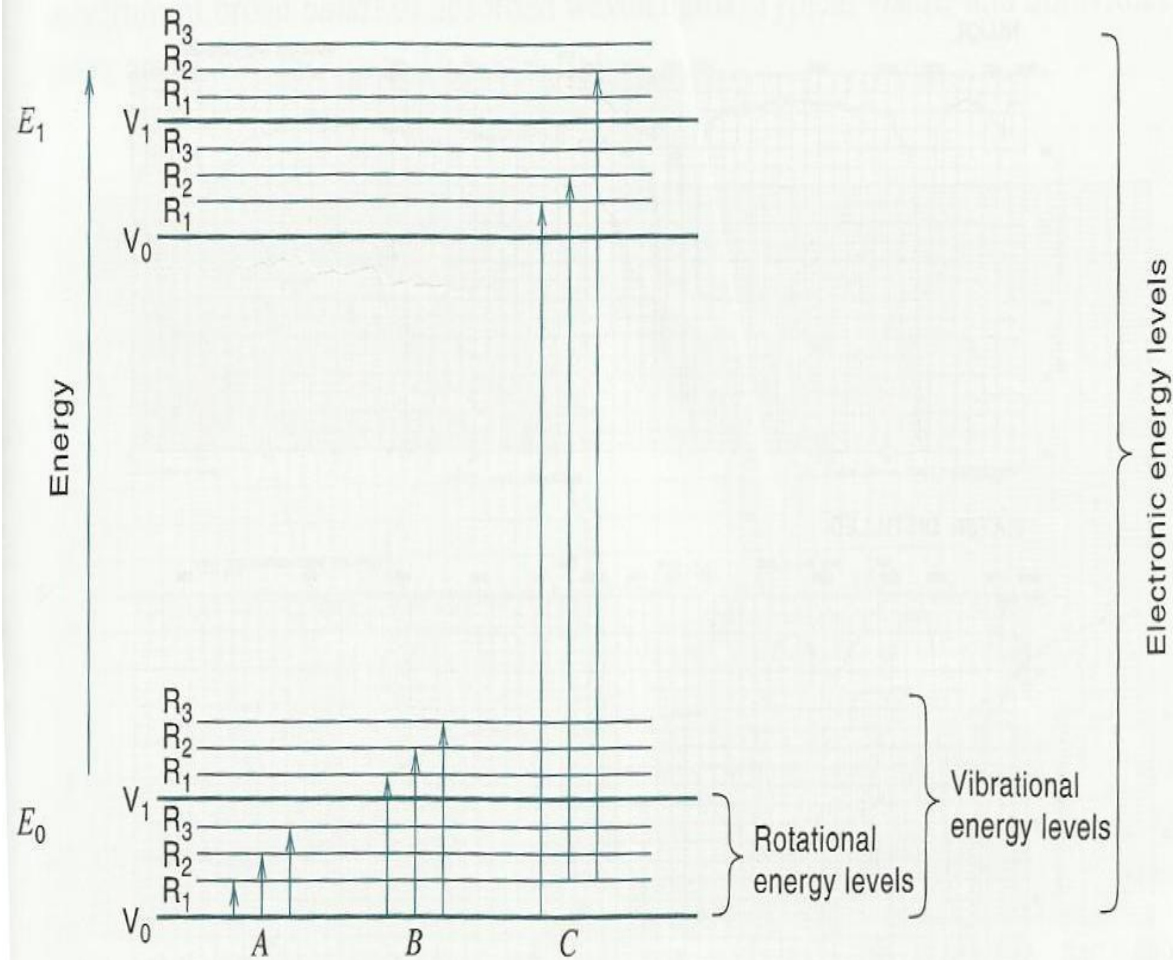Electronic → require still higher energies (visible and ultraviolet regions)
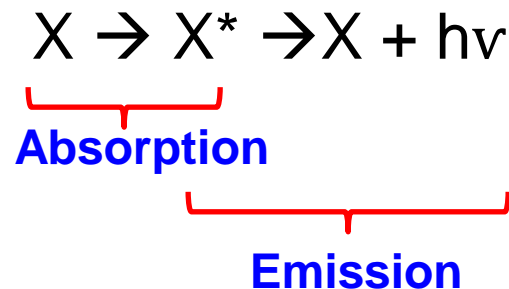
Energy Level Diagram

Fig. 16.3. Energy level diagram illustrating energy changes associated with absorption of electromagnetic radiation: A, pure rotational changes (far infrared); B, rotational–vibrational changes (near infrared); C, rotational–vibrational–electronic transitions (visible and ultraviolet). E_0 is electronic ground state and E_1 is first electronic excited state.
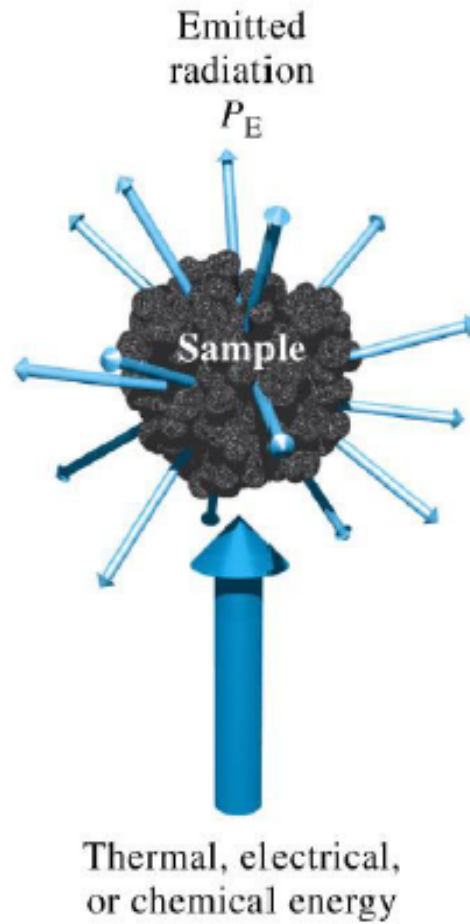
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Emission of Radiation

- Emission of radiation is occurred when excited particle (atoms, ions, or molecules) relax to lower energy levels by giving up their excess energy as photons.

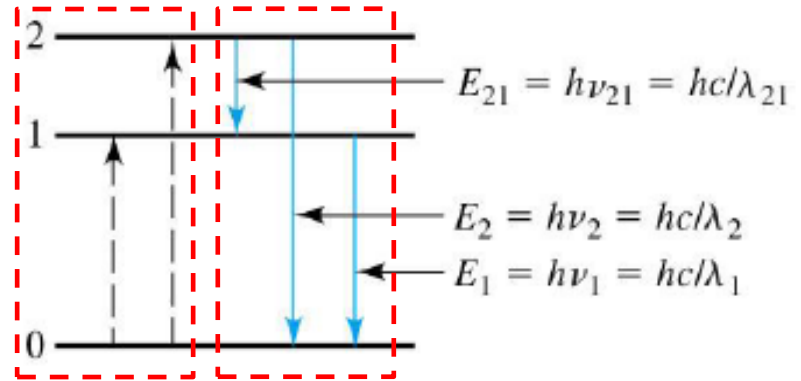- Radiation from an excited source is characterized by means of an emission spectrum.

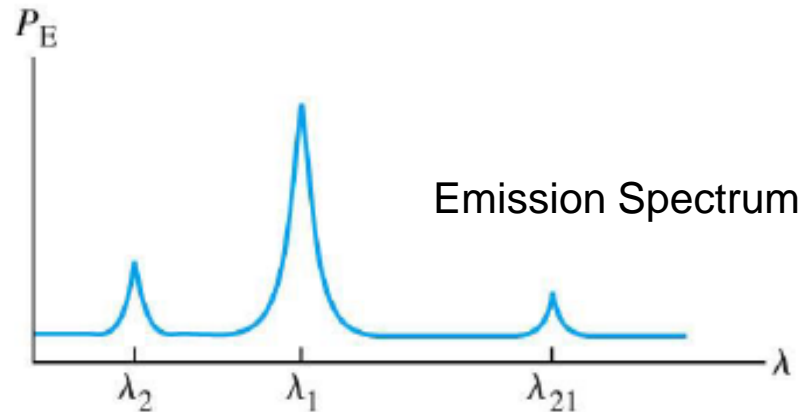$$X \rightarrow X^* \rightarrow X + h\nu$$

Absorption

Emission

Emission Process

Excitation

Emitted radiation P_E

$E_{21} = h\nu_{21} = hc/\lambda_{21}$

$E_2 = h\nu_2 = hc/\lambda_2$

$E_1 = h\nu_1 = hc/\lambda_1$

Emission (b)

Sample

Thermal, electrical, or chemical energy

(a)

P_E

Emission Spectrum

λ_2 λ_1 λ_{21} λ

(c)

Emission Spectrum

- Three type of emission spectra:

  1) Line spectrum
   - made up of a series of sharp, well-defined peaks caused by excitation of individual atoms.

  2) Band spectrum
     - consists of several groups of lines so closely spaced that they are not completely resolved.
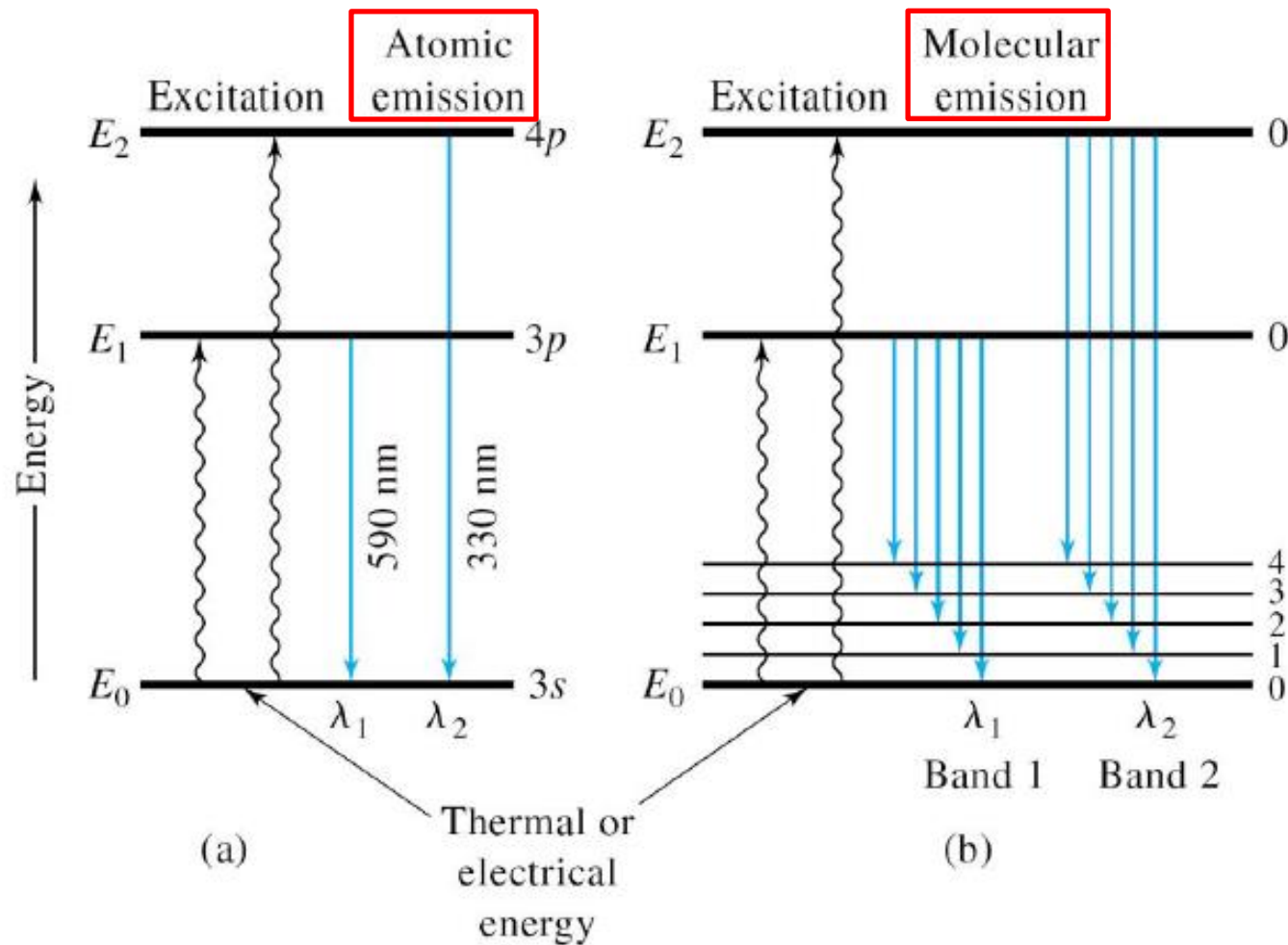
  3) Continuum spectrum
     - responsible for the increase in the background that is evident above about 350 nm. The line and band spectra are superimposed on this continuum.

Example Emission Spectrum
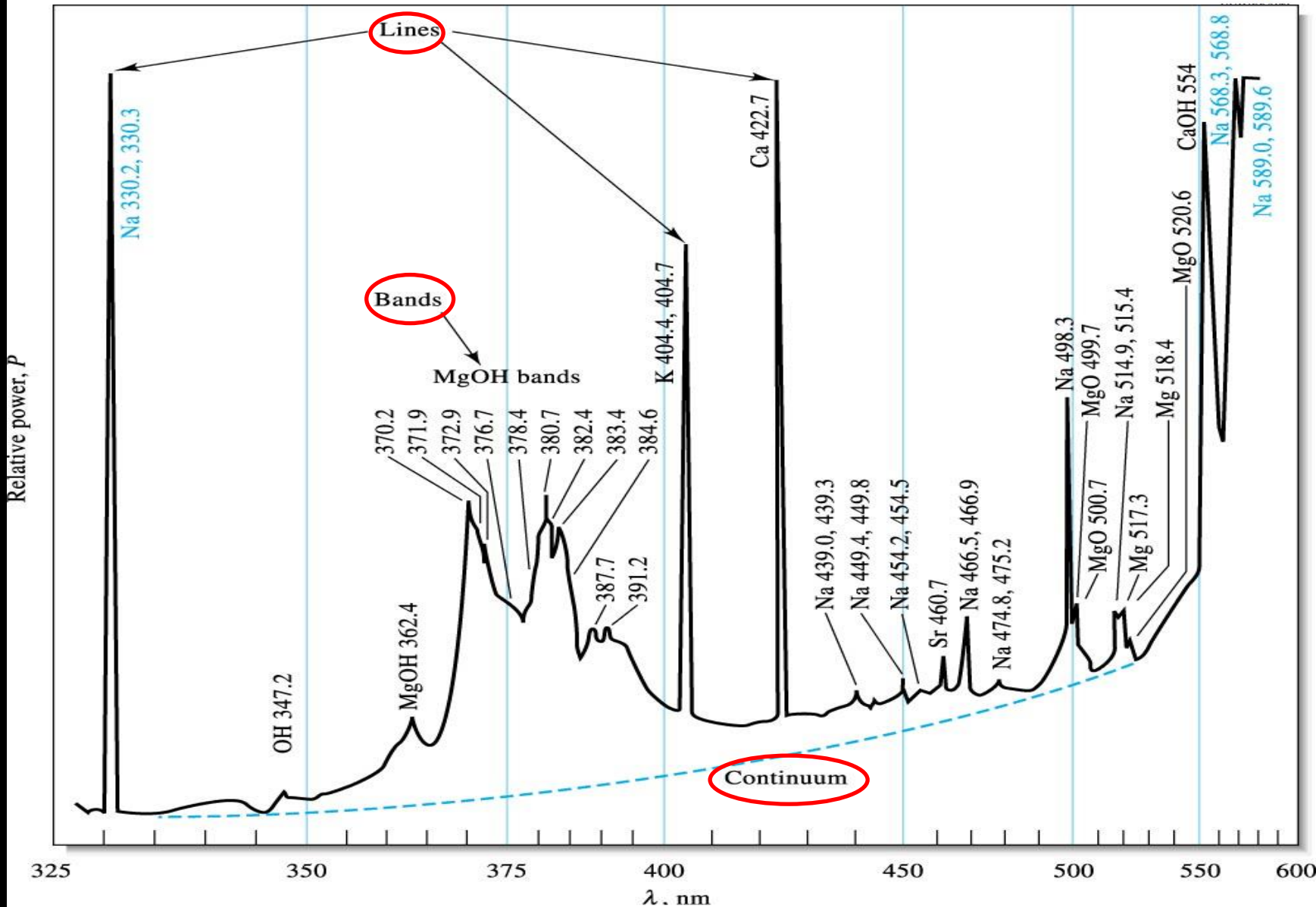
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Energy-level diagrams for

(a) a atom showing the source of a line spectrum and

(b) a simple molecule showing the source of a band spectrum

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- **Quantitative Analysis**

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# Qualitative Analysis

- Infrared spectroscopy is a very useful tool for obtaining qualitative information about molecules.

- The most important used of infrared spectroscopy is the identification and structure analysis.

Infrared Spectra

- The absorption peaks are much sharper than in the ultraviolet or visible regions → easier to identify.

- Each molecule will have a complete absorption spectrum unique to that molecule, and so a "fingerprint" of the molecule is obtained.

- Mixtures of absorbing compounds → exhibit the combined spectra of compounds.

Examples: IR spectrum of compound

Wavenumbers in cm^{-1}
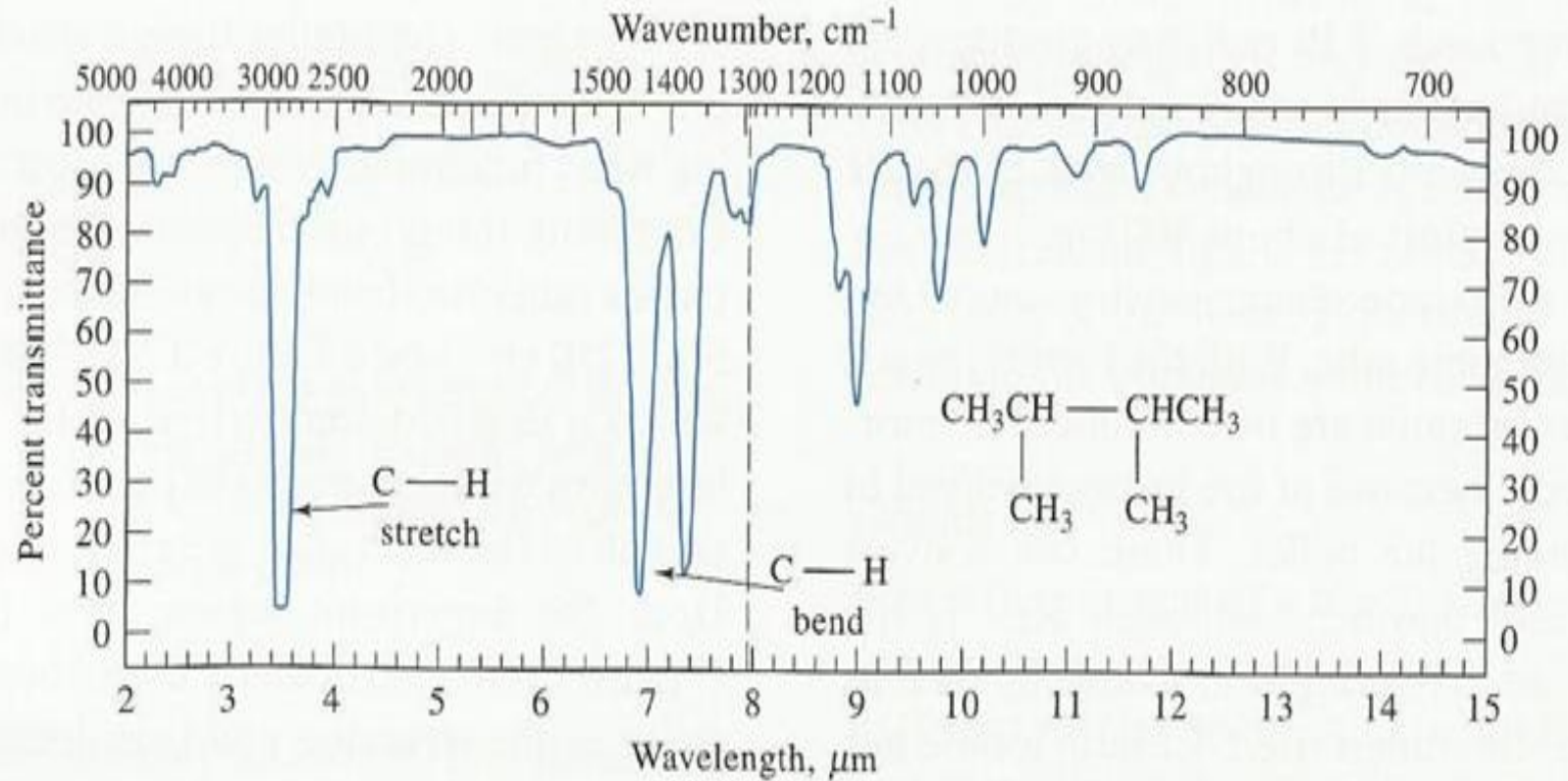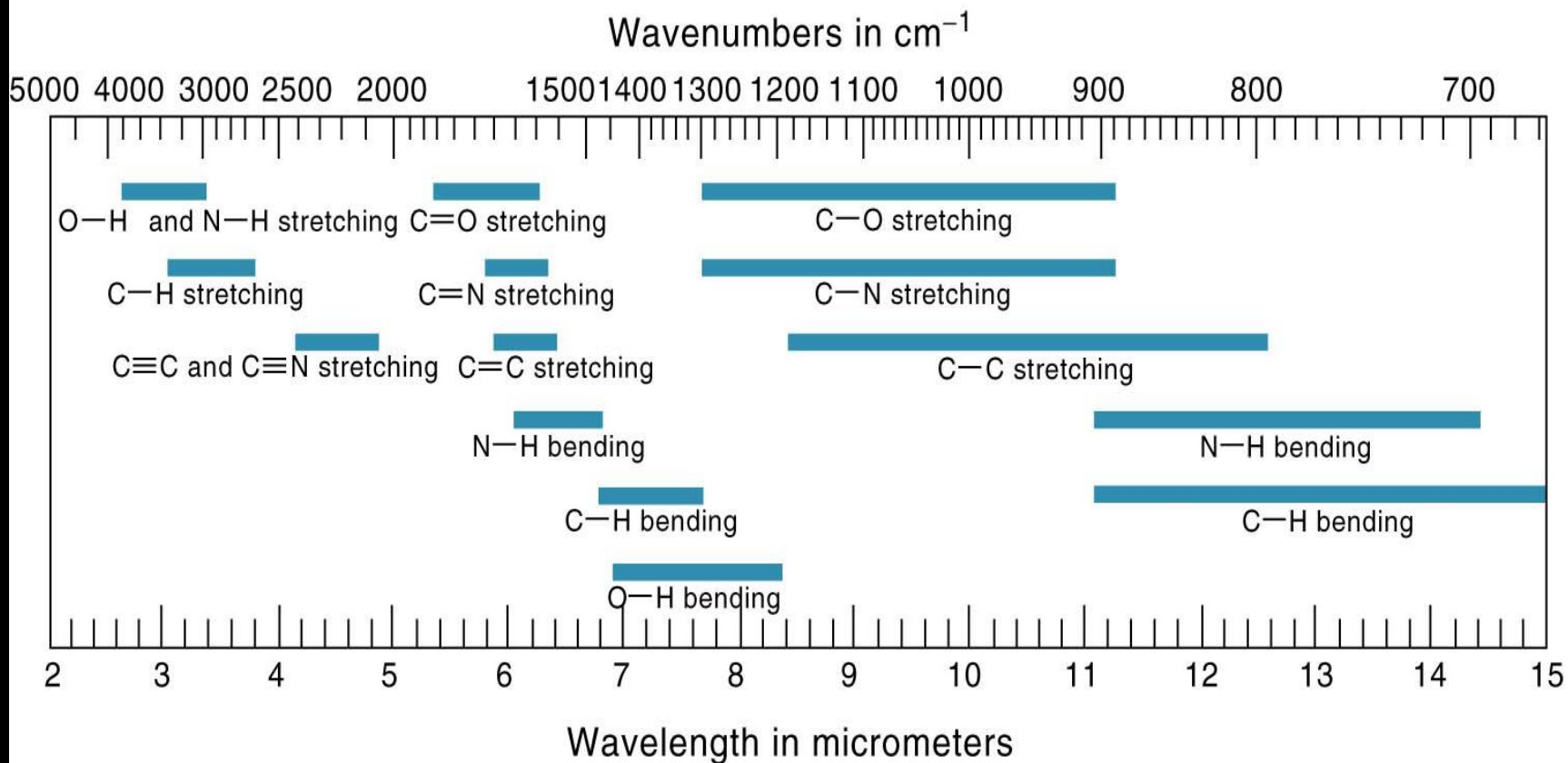
Simple correlations of group vibrations to regions of infrared absorption

Typical functional groups that can be identified include **alcohol, hydroxyl, ester carbonyl, olefin and aromatic unsaturated hydrocarbon group**.

Quantitative Analysis

- Quantitative absorption methods require two power measurement: one before a beam (incident radiation) has passed through the medium that contains the analyte (P_o) and the other after (P).

- Two terms, which are widely used in absorption spectrometry related to the ratio of P_o and P, are transmittance and absorbance.
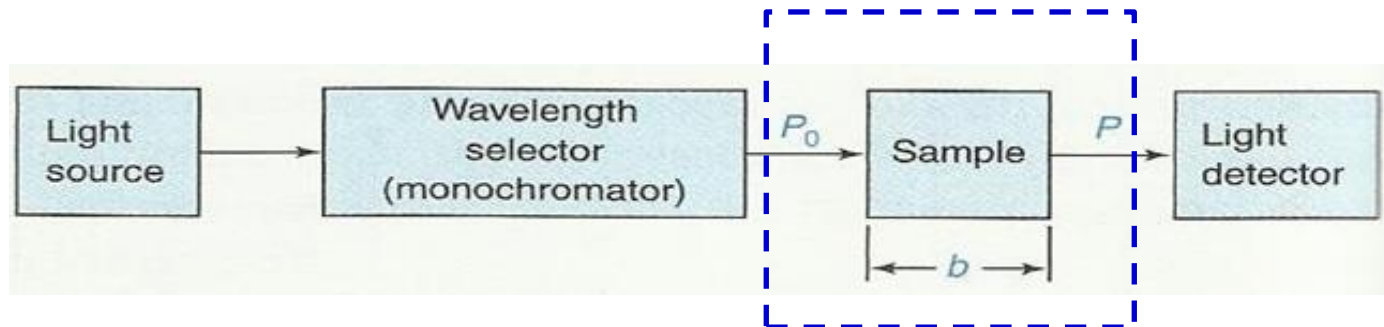
P<P_o (absorption depends on population and path length)

Transmittance

- The transmittance T of the medium is the fraction of incident radiation transmitted by the medium:

$$T = \frac{P}{P_o}$$

Transmittance is often expressed as a percentage or:

$$\%T = \frac{P}{P_o} \times 100\%$$

T has the range 0 to 1. The percent transmittance is simply 100T and ranges between 0 and 100%.
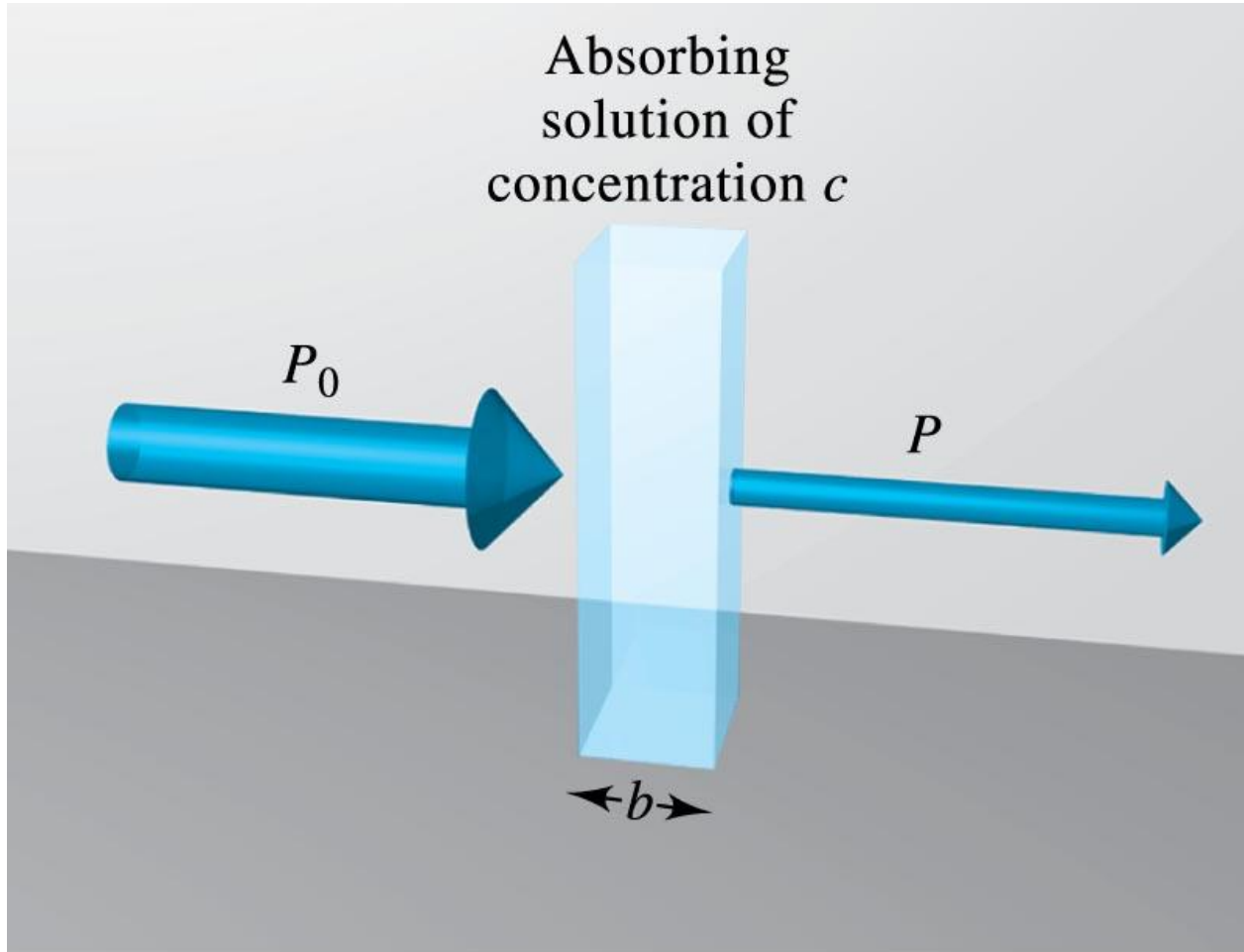
Absorbance

- The absorbance A of a medium is defined by the equation:

$$A = -\log T = \log (1/T) = \log (P_o/P)$$

- When no light is absorbed, $P=P_o$. If 90% of the light is absorbed, 10% is transmitted and $P/P_o = 0.1$, A = 1.
- If only 1% of the light is transmitted, A = 2.

P/P_o	%T	A
1	100	0
0.1	10	1
0.01	1	2

Absorbing solution of concentration c

P_0

P

$\leftarrow b \rightarrow$

$$T = \frac{P}{P_0}$$

$$A = \log \frac{P_0}{P}$$

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Beer's Law

- Basic for quantitative analyses by both atomic and molecular absorption measurement.

- For monochromatic radiation, absorbance is directly proportional to the path length b through the medium and the concentration c of the absorbing species.

$$A = abc$$

a is a proportionality constant called absorptivity.

b is commonly expressed in centimeters (cm) and

c is usually given in unit grams per liter (g L^{-1}).

Therefore, a has units of L $g^{-1}cm^{-1}$.

When the concentration expressed in moles per liter, the absorptivity is called molar absorptivity:

$$A = \varepsilon bc$$

c is in moles per liter (mol/L or M) and ε has the units L mol^{-1}cm^{-1}.

Example 3

Find the absorbance and transmittance of a 0.00240 M solution of a substance with a molar absorptivity of 313 M^{-1} cm^{-1} in a cell with a 2.00 cm path length.

Solution

A = εbc

   = (313 M^{-1} cm^{-1}) (2.00cm) (0.00240 M) = <u>1.50</u>

Transmittance:

$$A = -\log (T)$$
$$T = 10^{-A}$$
$$= 10^{-1.5}$$
$$\underline{= 0.0316}$$

3.16% of the incident light emerges from this solution.

Example 4

A sample in a 1.0 cm cell is determined with a spectrometer to transmit 80.0% light at a certain wavelength. If the absorptivity of this substance at this wavelength is 2.0, what is the concentration of the substance?

Solution

The percent transmittance is 80 %, and so T = 0.80.

$$A = -\log_{10}(T) = abc$$

$-\log (0.80) = 2.0 \text{ cm}^{-1}\text{g}^{-1}\text{L} \times 1.0 \text{ cm} \times c$

$0.097 = 2.0 \text{ g}^{-1}\text{L} \times c$

c = 0.097/2 = 0.048 g/L

Example 5

A solution containing 1.00 mg ion (as the thiocyanate complex) in 100.0 mL was observed to transmit 70.0% of the incident light compared to an appropriate blank.

(a) What is the absorbance of the solution at this wavelength?

(b) What fraction of light would be transmitted by a solution of iron four times as concentrated?

Solution

(a) The percent transmittance is 70%, and so T = 0.70:

$$A = -\log_{10}(T)$$
$$= -\log_{10}(0.7)$$
$$= 0.155$$

(b) $\qquad A = abc$, c = 0.001 g/0.1 L = 0.01 g/L

$$0.155 = ab \,(0.01 \text{ g/L})$$
$$ab = 15.5 \text{ L/g}$$

4 times concentrated, therefore,

$$A = 15.5 \text{ L/g} \,(4 \times 0.01 \text{ g/L}) = 0.620$$

$$0.620 = -\log_{10}(T), \text{ T} = 0.240$$

The absorbance of the new solution could have been calculated more directly:

$$\frac{A_1}{A_2} = \frac{abc_1}{abc_2} = \frac{c_1}{c_2}$$

$$A_2 = A_1 \times \frac{c_2}{c_1} = 0.155 \times \frac{4}{1} = 0.620$$

$0.620 = -\log_{10}(T)$, T= 0.240

Deviation from Beer's Law

- Beer's law states that absorbance is proportional to the concentration of the absorbing species.

- It applied to monochromatic radiation and it works very well for dilute solution ($\lesssim$ 0.01 M) of most substances.

- Deviations occur as the result of (1) chemical, and (2) instrumental factors.

- **Chemical deviations**

  → from Beer's law are caused by shifts in the position of a chemical or physical equilibrium involving the absorbing species.

- **Instrumental deviations**

  →Unsatisfactory performance of an instrument may be caused by fluctuations in the power-supply voltage, an unstable light source, or a non-linear response of the detector-amplifier system.

Exercise

Q1

Chloroaniline in a sample is determined as the amine picrate. A 0.0265 g sample is reacted with picric acid and diluted to 1.00 L. The solution exhibits an absorbance of 0.368 in a 1.00 cm cell. What is the % chloroaniline in the sample? (Given: MW of Chloroaniline = 127.6 g/mol, ϵ = 1.25 x 10^4 $cm^{-1}mol^{-1}$ L).

Q2

a. A 3.96×10^{-4} M solution of compound A exhibited an absorbance of 0.624 at 238 nm in a 1.00 cm cuvet; a blank solution containing only solvent has an absorbance of 0.0290 at the same wavelength. Find the molar absorptivity of compound A.

b. A concentrated solution of compound A in the same solvent was diluted from an initial volume of 2.00 mL to a final volume of 25.0 mL and then had an absorbance of 0.733. What is the concentration of A in the concentrated solution?

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- **Analysis of Mixture**
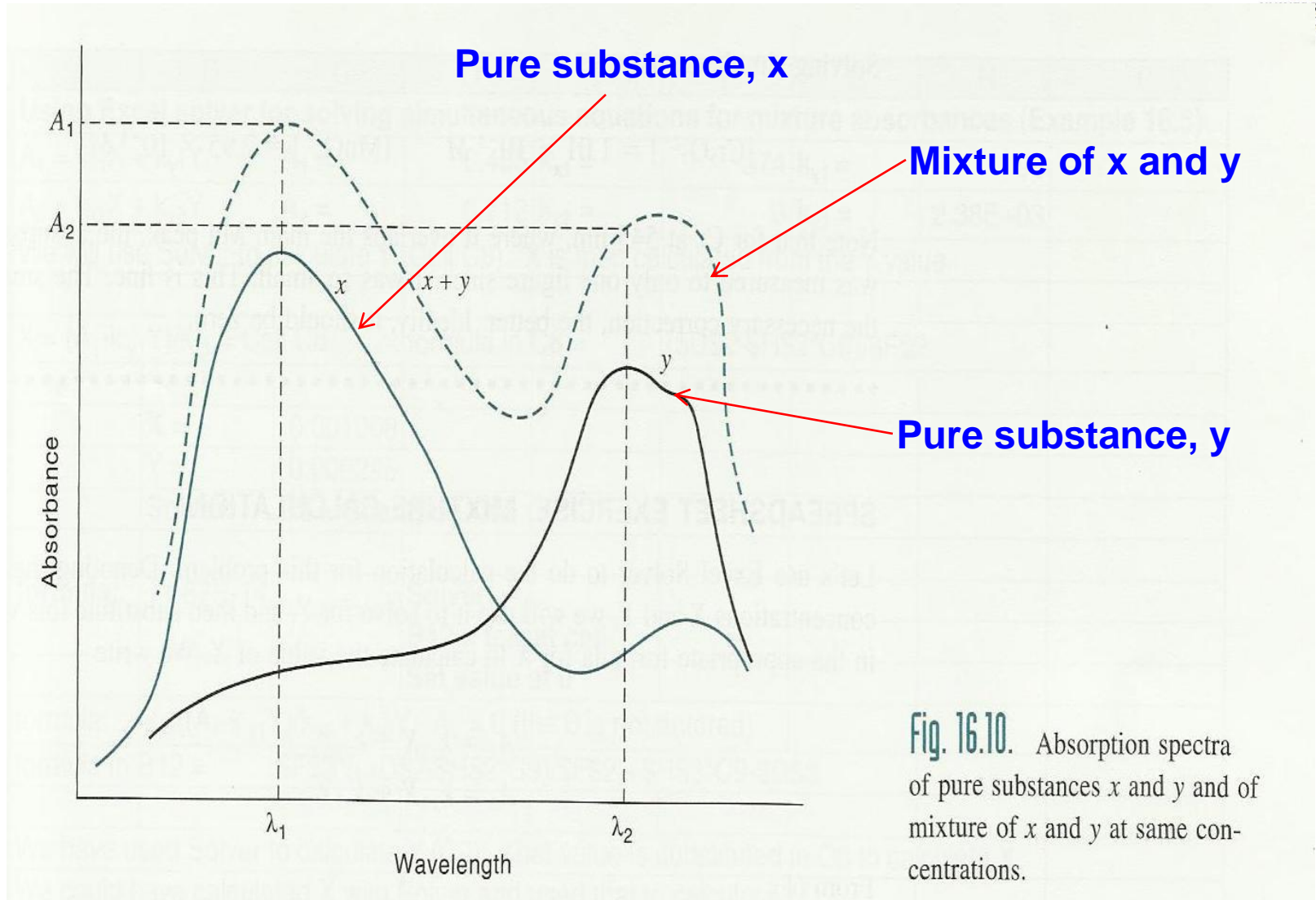
- Spectrometric Instrumentation

Analysis of Mixture

- It is possible to make quantitative calculations when two absorbing species in solution.

- It is apparent from Beer's law that the total absorbance A, at a given wavelength will be equal to the sum of the absorbances of all absorbing species.

- For two absorbing species, if c is in g / L:

$$A = a_x b c_x + a_y b c_y$$

- If c is in mol/ L:

$$A = \varepsilon_x b c_x + \varepsilon_y b c_y$$

Pure substance, x

Mixture of x and y

Pure substance, y

Fig. 16.10. Absorption spectra of pure substances x and y and of mixture of x and y at same concentrations.

- From Figure 16.10 →two unknowns, *x* and *y* → two measurements will have to be made.

- Technique: choose <u>two wavelengths</u> for measurement. (1) occurring at the absorption <u>maximum for *x*</u> (λ_1 in the figure).

  (2) the other <u>maximum for y</u> (λ_2 in the figure)

We can write:

$$A_1 = A_{x1} + A_{y1} = \varepsilon_{x1}bc_x + \varepsilon_{y1}bc_y$$
$$A_2 = A_{x2} + A_{y2} = \varepsilon_{x2}bc_x + \varepsilon_{y2}bc_y$$

$$A_1 = A_{x1} + A_{y1} = \varepsilon_{x1}bc_x + \varepsilon_{y1}bc_y$$
$$A_2 = A_{x2} + A_{y2} = \varepsilon_{x2}bc_x + \varepsilon_{y2}bc_y$$

- A_1 and A_2 are the absorbances for the mixture at wavelength 1 and 2, respectively.

- A_{x1} and A_{y1} are the absorbances contributed by pure substances x and y, respectively at wavelength 1.

- A_{x2} and A_{y2} are the absorbances contributed by pure substances x and y, respectively at wavelength 2.

- ε_{x1} and ε_{y1} are the molar absorptivities contributed by pure substances x and y, respectively at wavelength 1.

- ε_{x2} and ε_{y2} are the molar absorptivities contributed by pure substances x and y, respectively at wavelength 2.

- These molar absorptivities (ε_{x1}, ε_{y1}, ε_{x2} and ε_{y2}) are determined by making absorbance measurements on pure solution (known molar concentrations) of pure substances x and y at wavelength 1 and 2.

- c_x and c_y $\rightarrow$ two unknowns $\rightarrow$ calculated from the solution of the two simultaneous equations

$$A_1 = A_{x1} + A_{y1} = \varepsilon_{x1}bc_x + \varepsilon_{y1}bc_y$$
$$A_2 = A_{x2} + A_{y2} = \varepsilon_{x2}bc_x + \varepsilon_{y2}bc_y$$

Example 6

The molar absorptivitives of compound X and Y were measured with pure samples each

λ (nm)	ε (M⁻¹ cm⁻¹)	
	X	Y
272	16440	3870
327	3990	6420

A mixture of compounds X and Y in a 1 cm cell had an absorbance of 0.957 at 272 nm and 0.559 at 327 nm. Find the concentrations of X and Y in the mixture.

Solution

From Equations analysis of mixture:

$$A_1 = A_{x1} + A_{y1} = \varepsilon_{x1}bc_x + \varepsilon_{y1}bc_y$$

$$A_2 = A_{x2} + A_{y2} = \varepsilon_{x2}bc_x + \varepsilon_{y2}bc_y$$

$$A_{272} = \varepsilon_{x,272}b[X] + \varepsilon_{y,272}b[Y]$$

$$A_{327} = \varepsilon_{x,327}b[X] + \varepsilon_{y,327}b[Y]$$

Substitution: (b = 1 cm)

$$0.957 = 16440\,[X] + 3870\,[Y] \qquad (1)$$

$$0.559 = 3990\,[X] + 6420\,[Y] \qquad (2)$$

Solve Equations (1) and (2) simultaneously:

$0.559 = 3990 [(0.957-3870[Y])/16440] + 6420 [Y]$

$0.3267 = 5481 [Y]$

$[Y] = 5.96 \times 10^{-5} M$

Substitute [Y] into Equation (1) or (2),

$[X] = 4.42 \times 10^{-5} M$

Example 7

Potassium dichromate and potassium permanganate have overlapping absorption spectra. $K_2Cr_2O_7$ has an absorption maximum at 441 nm, and $KMnO_4$ has a band at 545 nm. A mixture is analyzed by measuring the absorbance at these two wavelengths with the following results:

$A_{441} = 0.405$, $A_{545} = 0.712$

The absorbances of pure solution of $K_2Cr_2O_7$ (1.00×10^{-3} M) and $KMnO_4$ (2.00×10^{-4} M), using the same cell gave the following results:

$A_{Cr, 441} = 0.374$, $A_{Cr,545} = 0.009$, $A_{Mn,441} = 0.019$, $A_{Mn, 545} = 0.475$.

Calculate the concentrations of dichromate and permanganate in the sample solution.

Solution

The pathlength b is unknown precisely; but since the same cell is used in all measurements, it is constant. We can calculate εb from the pure substances measurement:

Mixture:
At A =441nm,
$$A_{441} = \varepsilon_{Cr,441} b \, [Cr_2O_7^{2-}] + \varepsilon_{Mn,441} b \, [MnO^{4-}] \text{ ---------------(1)}$$

At A = 545 nm,
$$A_{545} = \varepsilon_{Cr,545} b \, [Cr_2O_7^{2-}] + \varepsilon_{Mn,545} b \, [MnO^{4-}] \text{ ----------------(2)}$$

Pure substances:
At 440 nm,
$$0.374 = \varepsilon_{Cr,441} b \times 1.00 \times 10^{-3}, \; \varepsilon_{Cr,441} b = 374$$
$$0.019 = \varepsilon_{Mn,441} b \times 2.00 \times 10^{-4}, \; \varepsilon_{Mn,441} b = 95$$

At 545 nm,
$$0.009 = \varepsilon_{Cr,545} b \times 1.00 \times 10^{-3}, \; \varepsilon_{Cr,545} b = 9$$
$$0.475 = \varepsilon_{Mn,545} b \times 2.00 \times 10^{-4}, \; \varepsilon_{Mn,545} b = 2.38 \times 10^3$$

Substitution of ε values into Equations (1) and (2) :

$0.405 = 374[Cr_2O_7^{2-}] + 95[MnO^{4-}]$

$0.712 = 9[Cr_2O_7^{2-}] + 2.38 \times 10^3[MnO^{4-}]$

Solving simultaneously,

$[Cr_2O_7^{2-}] = 1.01 \times 10^{-3}$ M

$[MnO^{4-}] = 2.95 \times 10^{-4}$ M

Example 8

Analysis of an unknown mixture of H_2O_2 complexes of Ti(IV) and V(V) in H_2SO_4 Solution.
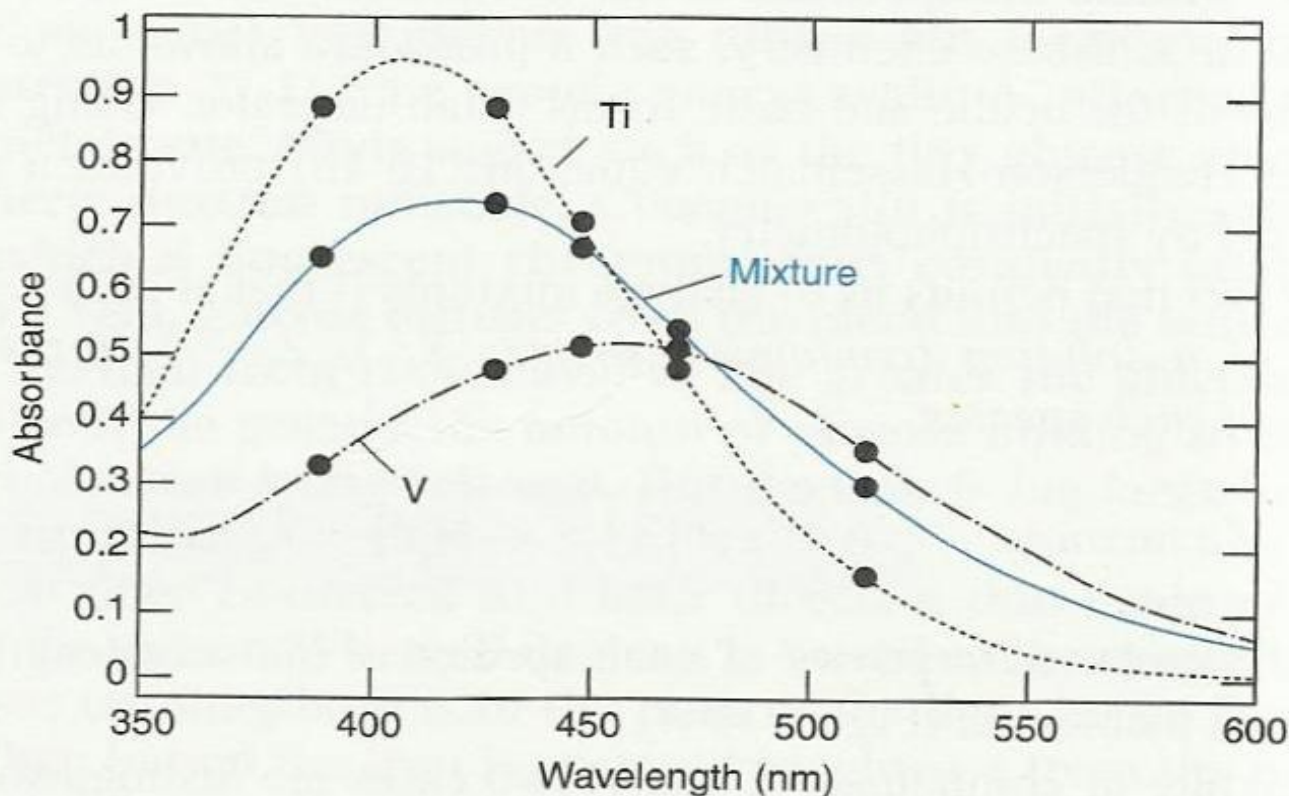
Visible spectra of standard solution: 1.32 mM Ti(IV), 1.89 mM V(V), and an unknown mixture containing both ions. All solution contain 0.5 wt% H_2O_2 and ~ 0.01 M H_2SO_4.

Absorbance Data

Wavelength (nm)	A_{Xs} Titanium standard	A_{Ys} Vanadium standard	A_m Mixture
390	0.895	0.326	0.651
430	0.884	0.497	0.743
450	0.694	0.528	0.665
470	0.481	0.512	0.547
510	0.173	0.374	0.314

Determine the concentration of the unknown mixture.

The absorbance of the mixture (A_m) at any chosen wavelength is

$$A_m = \varepsilon_x b[X] + \varepsilon_y b[Y] \quad \textbf{Mixture}$$

Where X and Y refer to Ti(IV) and V(V), respectively. If a standard solution of species X with concentration $[X]_s$ is prepared, its absorbance will be

$$A_{x_s} = \varepsilon_x b[X]_s$$

Similarly, for species Y, $[Y]_s$

Pure Component

$$A_{y_s} = \varepsilon_y b[Y]_s$$

Solving the above equations for ε_x and ε_y,

$$\frac{A_m}{A_{Xs}} = \frac{[Y]}{[Y]s}\left(\frac{A_{Ys}}{A_{Xs}}\right) + \frac{[X]}{[X]s}$$

How???

Slope   Intercept

A graph of A_m/A_{Xs} versus A_{ys}/A_{Xs} (all of which we have measured) at various wavelengths has a slope of $[Y]/[Y]_s$ and an intercept $[X]/[X]_s$.

We can find the concentration $[X]$ and $[Y]$ on the unknown mixture because we know the concentration $[X]_s$ and $[Y]_s$.

Given in the question

Wavelength (nm)	A_{Xs} Titanium standard	A_{Ys} Vanadium standard	A_m Mixture	A_m/A_{Xs}	A_{Ys}/A_{Xs}
390	0.895	0.326	0.651	0.727	0.364
430	0.884	0.497	0.743	0.840	0.562
450	0.694	0.528	0.665	0.958	0.760
470	0.481	0.512	0.547	1.137	1.064
510	0.173	0.374	0.314	1.815	2.161

$$\frac{A_m}{A_{X_s}} = 0.499 + (0.607)\frac{A_{Y_s}}{A_{X_s}}$$
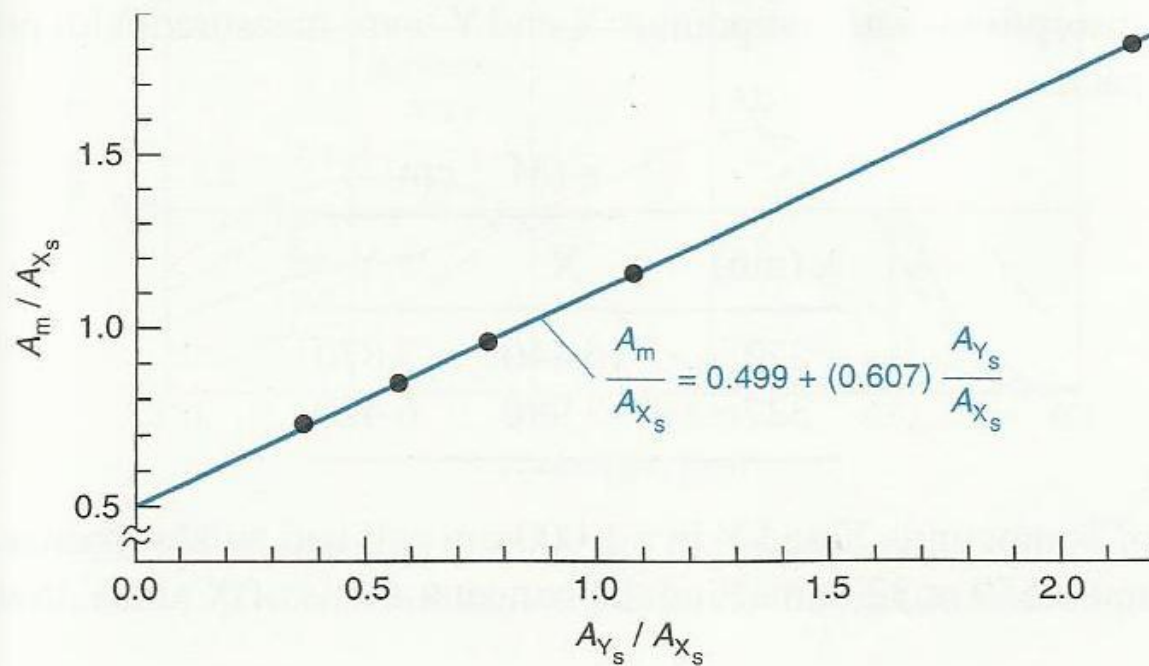
The least-square straight line through the point is:

$$\frac{A_m}{A_{Xs}} = 0.607 \left(\frac{A_{Ys}}{A_{Xs}}\right) + 0.499$$

Therefore,

Slope = 0.607 = [Y]/[Y]$_s$

$\rightarrow$ [Y] = [V(V)] = 0.607 x 1.89 mM = 1.15 mM

Intercept = 0.499 = [X]/[X]$_s$

$\rightarrow$ [X] = [Ti(IV)] = 0.499 x 1.32 mM = 0.659 mM

Outline

- Electromagnetic Radiation
- Absorption Process
- Emission Process
- Qualitative Analysis
- Quantitative Analysis
- Analysis of Mixture
- **Spectrometric Instrumentation**

Spectrometric Instrumentation

- Spectrometer or Spectrophotometer → an instrument/device to measure absorbance of light that resolve polychromatic radiation into different wavelength.

- Consists of
  (1) a source of continuous radiation over the wavelength of interest.
  (2) a monochromator for selecting a narrow band of wavelengths from the source spectrum.
  (3) sample cell for holding sample.
  (4) a detector or transducer → for converting radiant energy into electrical energy.
  (5) a device to read out the response of the detector.

Block diagram of spectrometer/spectrophotometer

Source → Monochromator → Sample → Detector → Readout (meter or recorder)
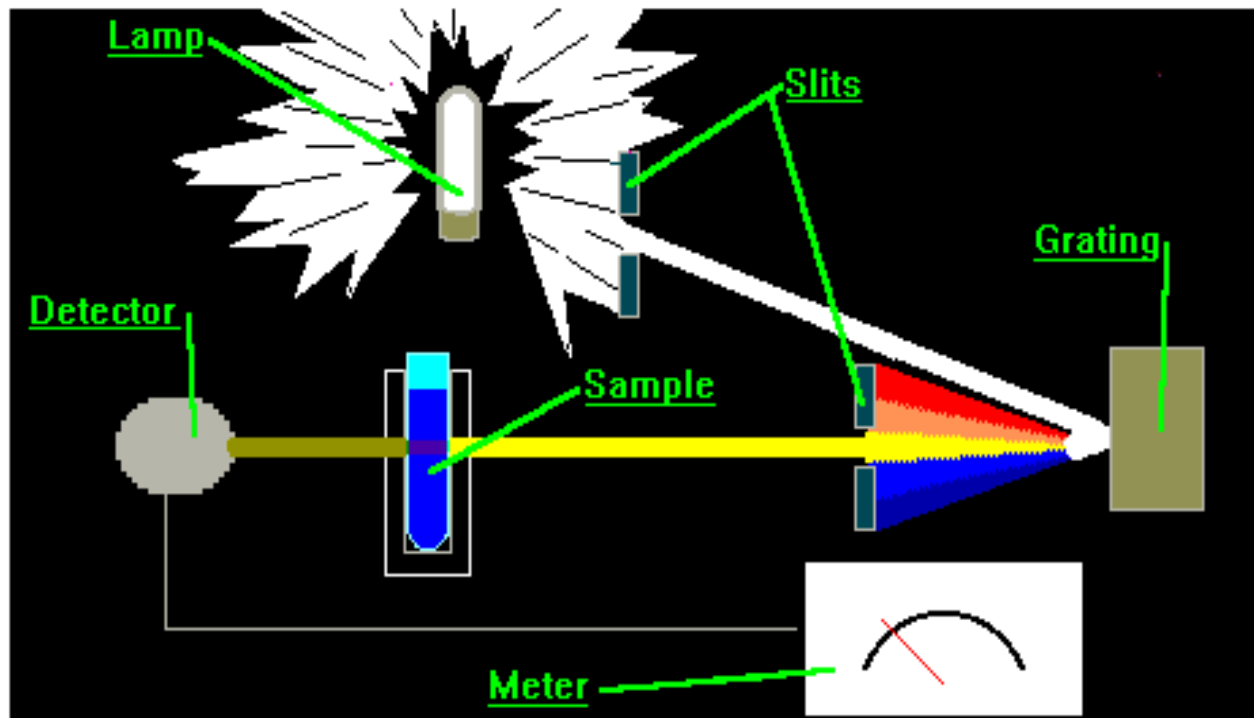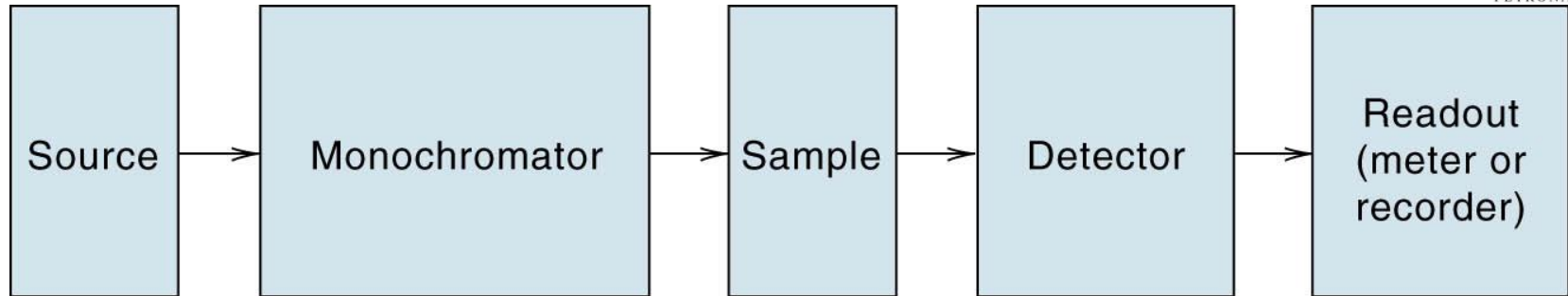
(1) Sources of Light

- It's provides radiation of range of wavelengths.

Source → Monochromator → Sample → Detector → Readout (meter or recorder)
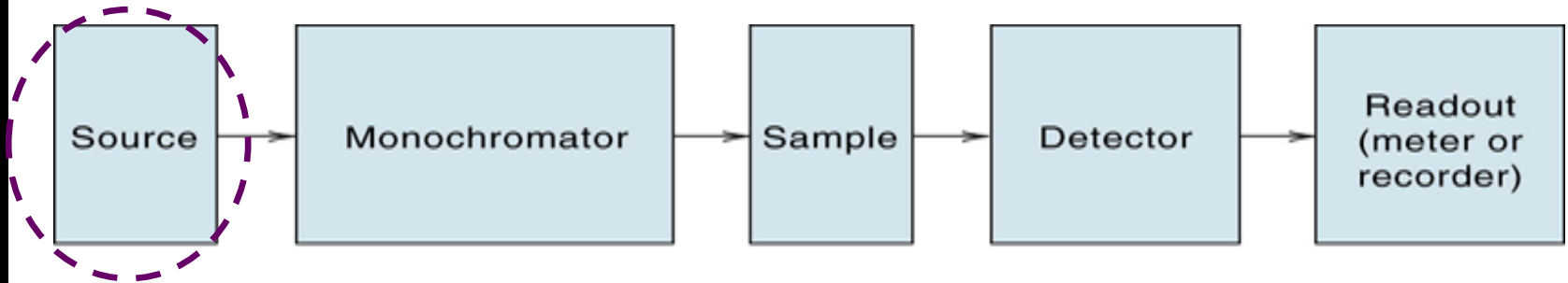
Tungsten lamp:
- Produces visible and near-infrared radiation in the range from 320-2500 nm.

Deuterium Arc Lamp:
- Produces UV radiation in the range from 200 - 400 nm.

Source of light: Lamps
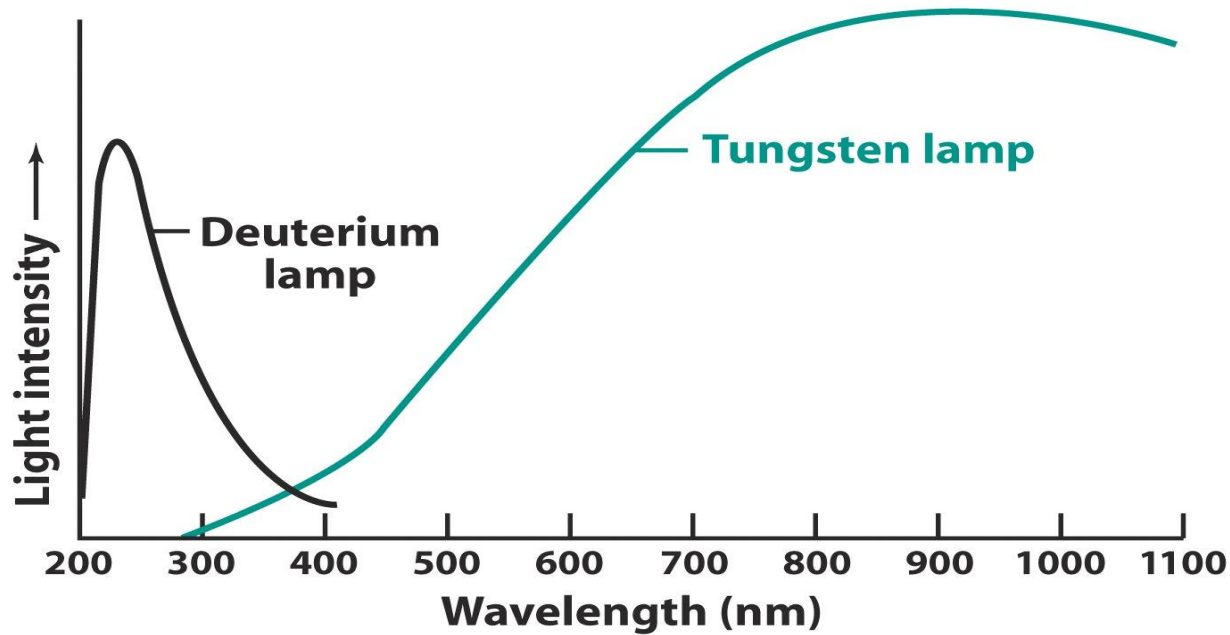
Deuterium Lamp

Tungsten Lamp

(2)Monochromators
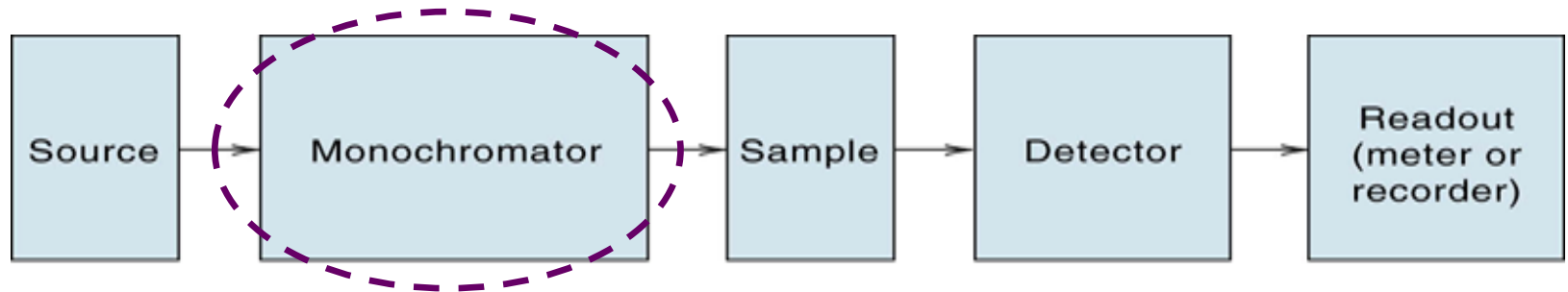
- Disperse light into its component wavelength and selects as a narrow band of wavelengths to pass on to the sample.

- Consists of (1)entrance and exit slits, (2) mirrors, and a (3) grating to disperse the light.

- Two basic types of dispersing elements (1) prism and (2) diffraction grating

Diffraction Grating:
linear dispersion, independent of wavelength , but the intensity varies with wavelength. Eg.: aluminium
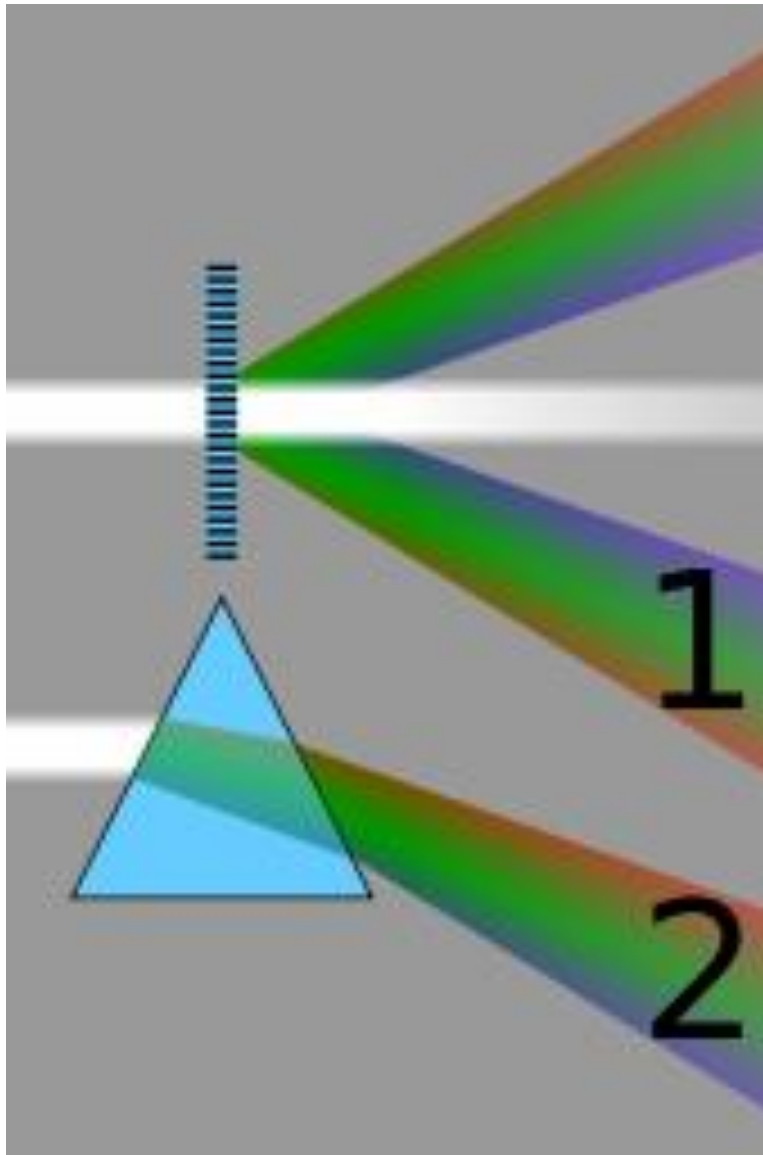
Prism: non-linear
dispersion, good at short wavelength, poor at long wavelength. Eg.: glass or lenses.

(3)Sample Cell
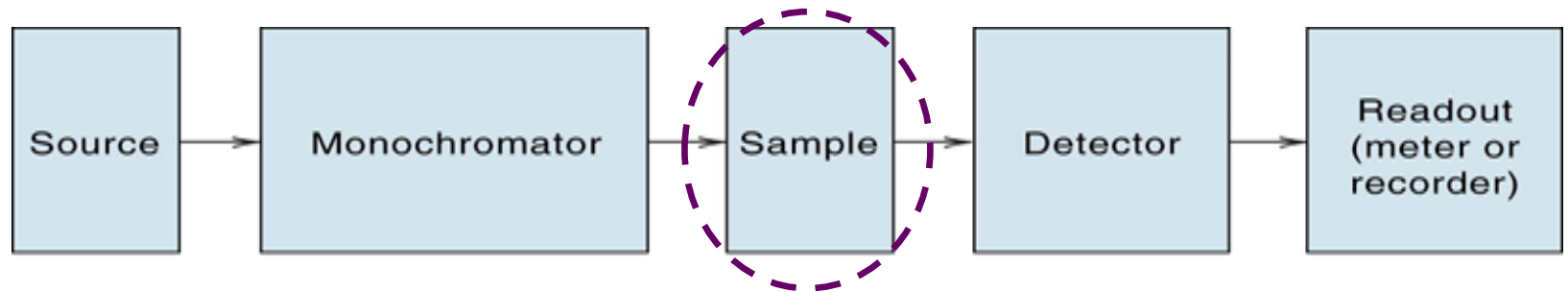
- The cell holding the sample → transparent in the wavelength region being measured.

- For visible and ultraviolet spectrophotometers, a liquid sample is usually contained in a cell called a cuvet → flat, fused silica faces. Most common used cuvet : 1.00 cm pathlength.

- Glass → for visible, not for ultraviolet because it absorbs UV radiation.

- For IR measurement, 1 wt% mixture of solid sample with KBr → grounded to fine powder and pressed into translucent pellet for mounting and measurement.
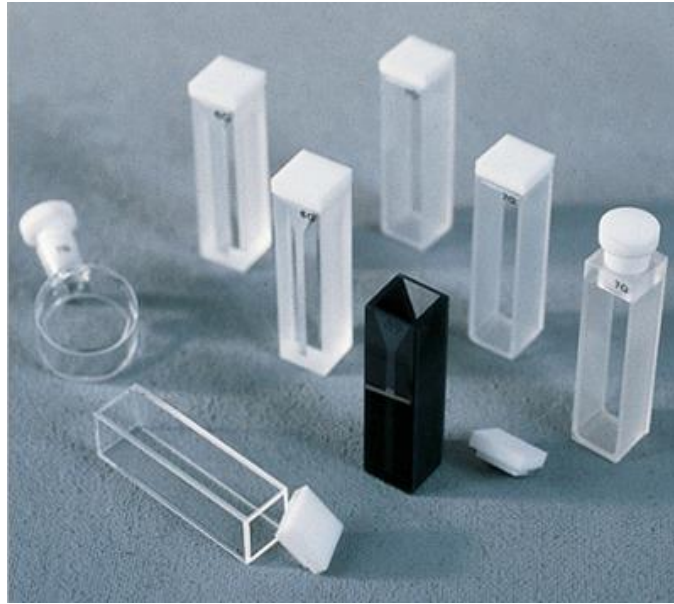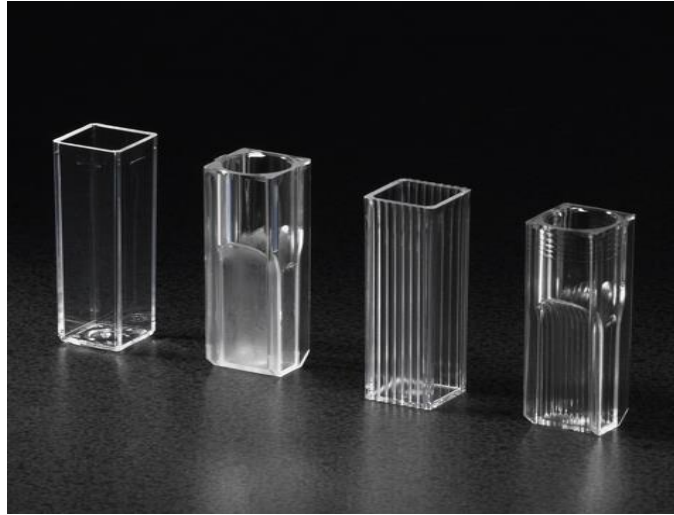
Cuvet for UV/Vis Measurement

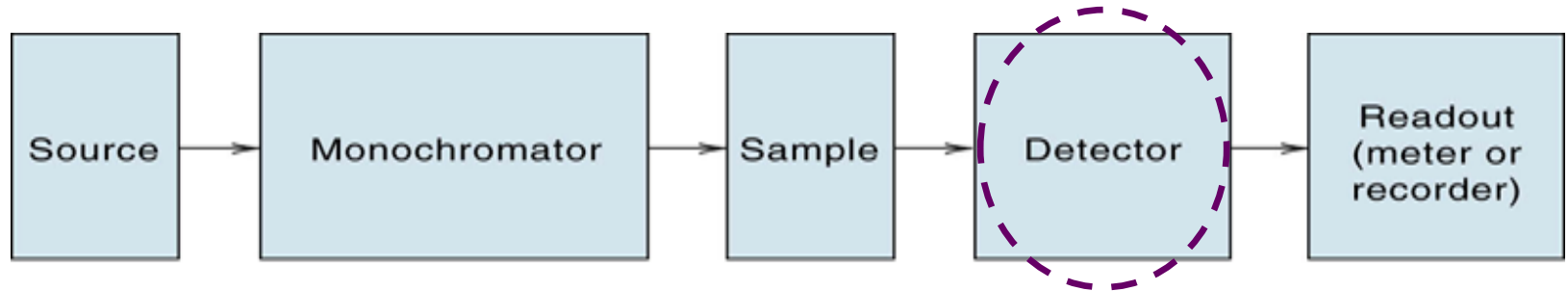# FT-IR Sample Preparation- KBr + Sample Pellet

Pelletizer

Agitate mortar

Sample holder

Die

(4) Detectors

- A detector produces an electric signal when it is struck by photons.
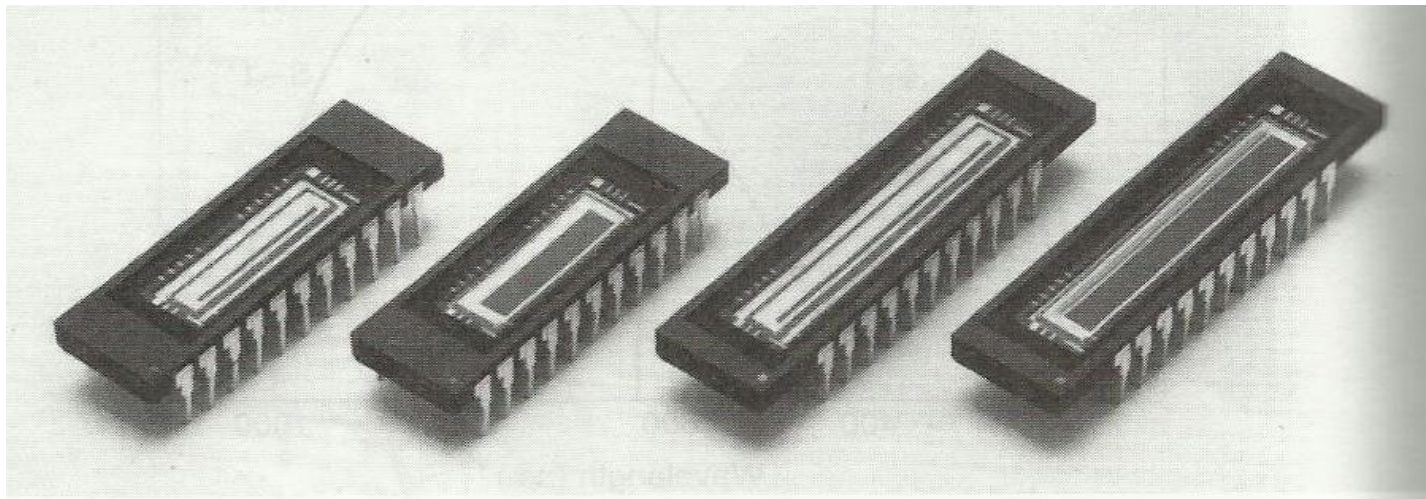
Examples UV-Vis detector:

(1) Phototube or photocell

(2) Photomultiplier (PM) tube

(3) Photodiaode array

Phototubes

Photomultiplier

Photodiaode array

IR detectors:

- Detectors used in the UV-Vis regions do not work in the IR region.

- IR photon do not have sufficient energy to generate a signal in either kind of detector.

- IR radiation possesses the property of heat, and heat detectors that transduce heat into an electrical signal can be used.

Examples IR detector:

(1) Thermocouple

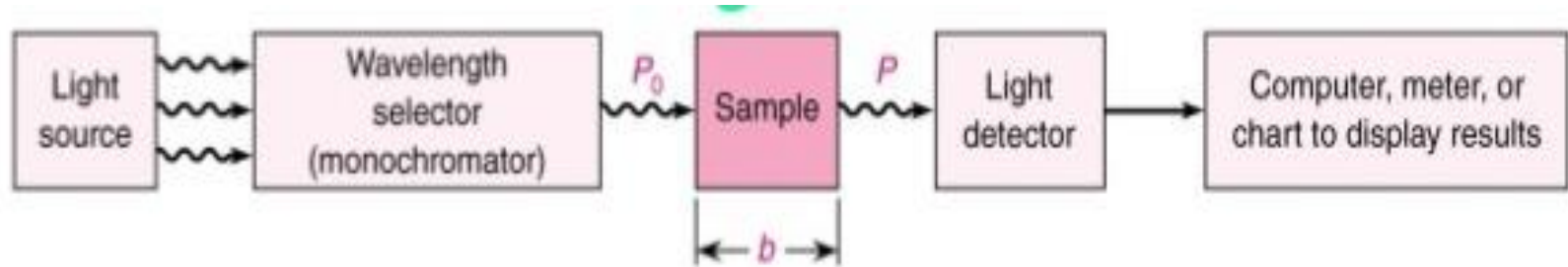(2) Balometers

(3) Thermistors

Thermocouples
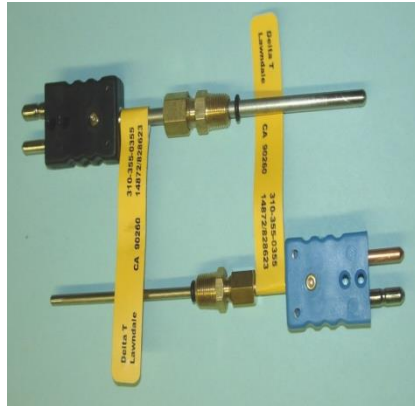
Balometers and Thermistors

MEASUREMENT OF ABSORBANCE AND TRANSMITTANCE

1) Single-beam spectrophotometer
2) Double-beam spectrophotometer
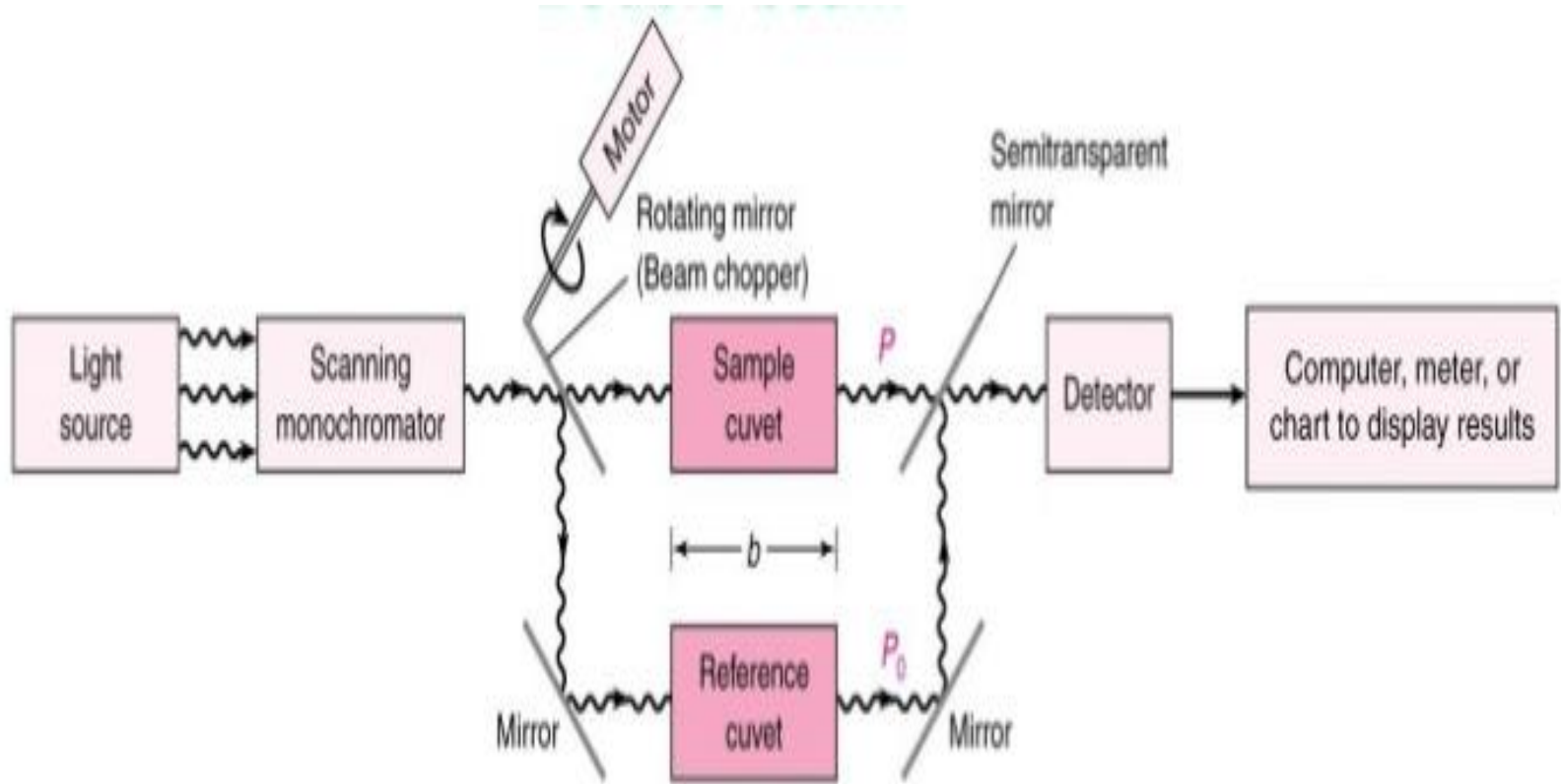
Single- beam Spectrophotometer

General operation:

1) The radiant power of light passing through a reference cuvet containing pure solvent is defined as P_o.

2) The cuvet is then removed and replaced by sample cuvet, the radiant power → P.

3) Knowing P and P_o→ allows T or A to be determined.

4) Any radiation not absorbed by the sample falls on the detector→ intensity converted to an electrical signal.

Single- beam Spectrophotometer

- **One** beam of light.

- **Inconvenient** because the sample and reference must be **placed alternately** in the beam.

- For measurements at multiple wavelength, the reference must be **run at each wavelength**.

- Poorly suited to measuring absorbance as a **function of time**.

Double - beam Spectrophotometer

Double-beam Spectrophotometer

- Has two light path → <u>sample</u> and <u>blank</u> reference.

- Through a rotating mirror, the light beam alternately passes through the reference cell and the sample cell, from each, to the detector.

- Automatically vary the wavelength and record the absorbance as a function of wavelength.

END OF CHAPTER