Spectroscopy

SI Base Units

m - meter - length

s - second - time

kg - kilogram - mass

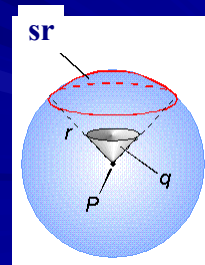K - kelvin - thermodynamic temperature

A - ampere - electric current

cd - candela - luminous intensity

mol - amount of substance

SI Supplementary Units

radian – rad – plane angle

steradian – sr – solid angle

SI Derived Units

N - Newton - Force - 1kg x m/s^2

Pa - Pascal - Pressure, Stress - 1N/m^2

J - Joule -Work, Energy, Amount of Heat -
     1N x m

lm - Lumen - Luminous Flux - 1 cd x sr

^{0}C - Degree Celsius - Temperature –
     (K - 273)

SI Prefixes

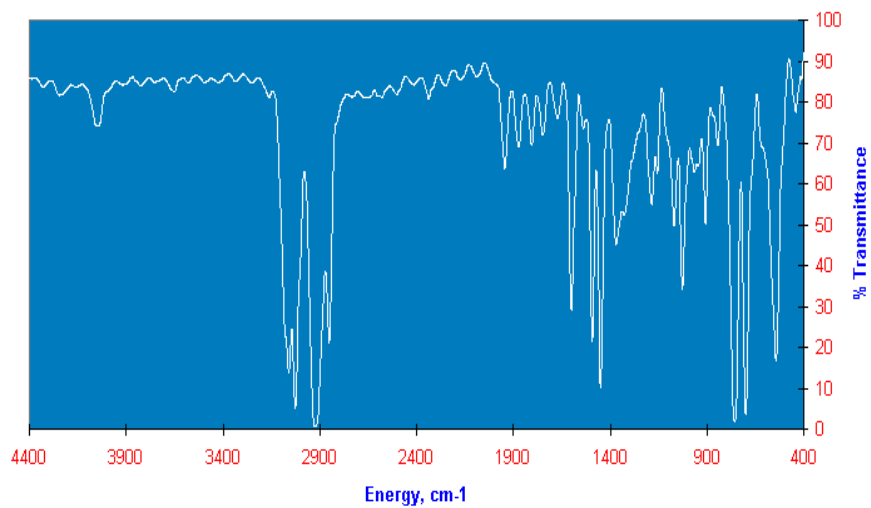|					
deca	10	da	deci	10^{-1}	d
hecto	10^2	h	centi	10^{-2}	c
kilo	10^3	k	milli	10^{-3}	m
mega	10^6	M	micro	10^{-6}	m
giga	10^9	G	nano	10^{-9}	n
tera	10^{12}	T	pico	10^{-12}	p
peta	10^{15}	P	femto	10^{-15}	f
exa	10^{18}	E	atto	10^{-18}	a
zetta	10^{21}	Z	zepto	10^{-21}	z
yotta	10^{24}	Y	yocto	10^{-24}	y

Spectroscopy

Set of methods where interaction of electromagnetic radiation with chemical molecules is measured to obtain characteristics, properties and quantity
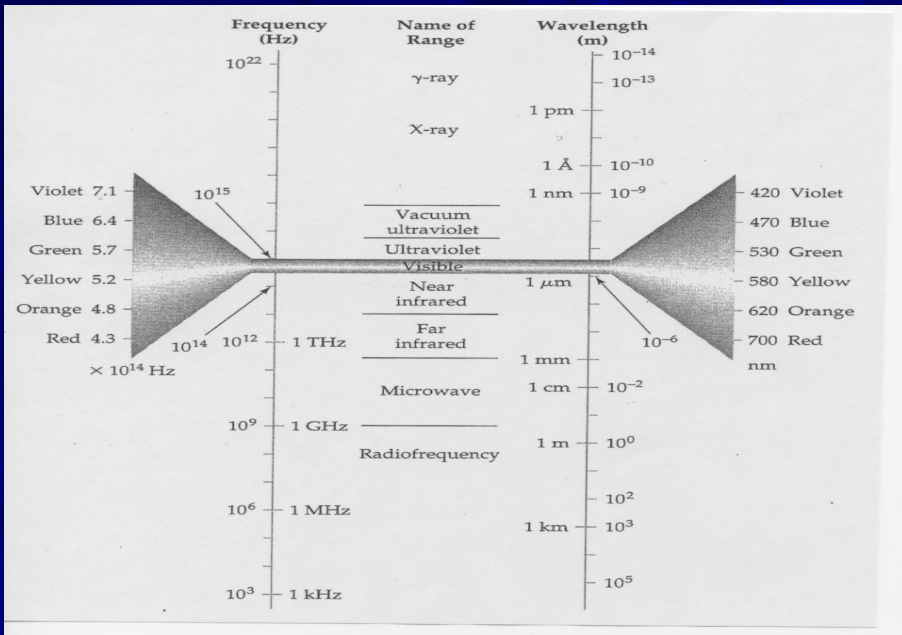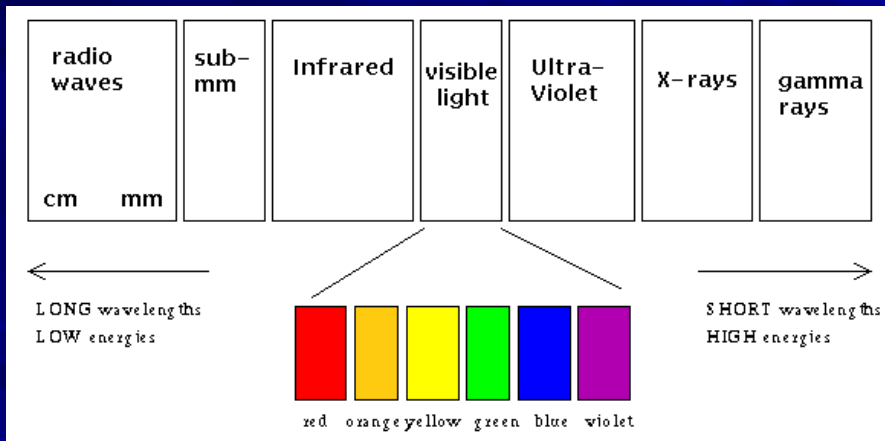
Spectroscopy

Radiation

IR Spectrum

Figure 4-7: Typical Infrared spectrum

Energy, cm-1

% Transmittance

Electromagnetic Radiation

Frequency (Hz)	Name of Range	Wavelength (m)

10^{22}

γ-ray

10^{-14}

10^{-13}

1 pm

X-ray

1 Å 10^{-10}

1 nm 10^{-9}

Violet 7.1 10^{15} — 420 Violet

Blue 6.4 — 470 Blue

Green 5.7 Vacuum ultraviolet — 530 Green

Ultraviolet

Yellow 5.2 Visible — 580 Yellow

Near infrared 1 μm

Orange 4.8 — 620 Orange

Far infrared

Red 4.3 10^{14} 10^{12} — 1 THz 10^{-6} — 700 Red

$\times 10^{14}$ Hz 1 mm nm

Microwave 1 cm 10^{-2}

10^{9} — 1 GHz

Radiofrequency 1 m 10^{0}

10^{2}

10^{6} — 1 MHz 1 km 10^{3}

10^{5}

10^{3} — 1 kHz

Radiation Spectrum

radio waves	sub-mm	Infrared	visible light	Ultra-Violet	X-rays	gamma rays
cm mm						

← LONG wavelengths LOW energies

SHORT wavelengths HIGH energies →
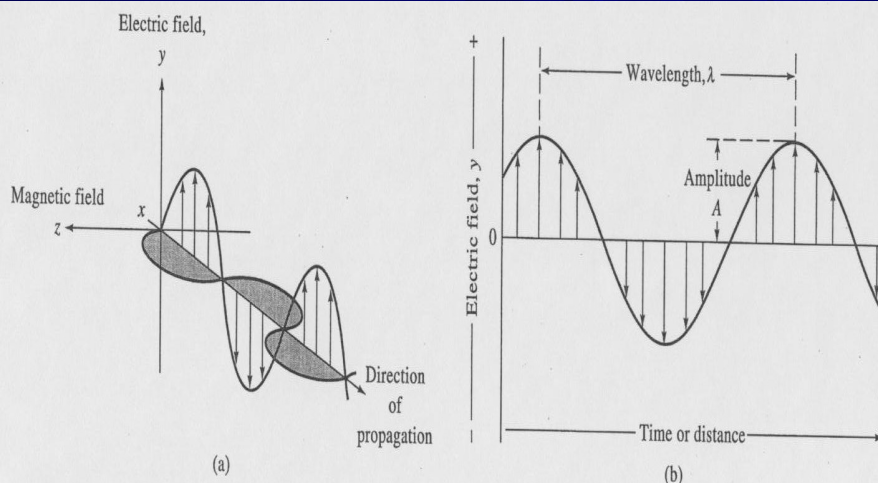
red   orange yellow   green   blue   violet

Spectroscopy - Colours

TABLE 14.1

Colors of Different Wavelength Regions

Wavelength Absorbed, nm	Absorbed Color	Transmitted Color (Complement)
380–450	Violet	Yellow-green
450–495	Blue	Yellow
495–570	Green	Violet
570–590	Yellow	Blue
590–620	Orange	Green-blue
620–750	Red	Blue-green

Spectroscopy – Light Nature

Figure 6-1 Representation of a beam of monochromatic, plane-polarized radiation: (a) electrical and magnetic fields at right angles to one another and direction of propagation, (b) two-dimensional representation of the electric vector.

Spectroscopy – Radiation Terminology

**Wavelength** (λ) - length between two equivalent points on successive waves

Wavenumber – the number of waves in a unit of length or distance per cycle - reciprocal of the wavelength

Frequency (ν) – is the number of oscillations of the field per second (Hz)

Velocity (c) – independent of wavelength – in vacuum is 3.00×10^{10} cm/s (3.00×10^{8} m/s)

Photon (quanta) – quantum mechanics nature of light to explain photoelectric effect

Spectroscopy - Radiation

Wavelength

Vibration

Amplitude

Direction of propagation

FIGURE 14.1 Wave motion of electromagnetic radiation.
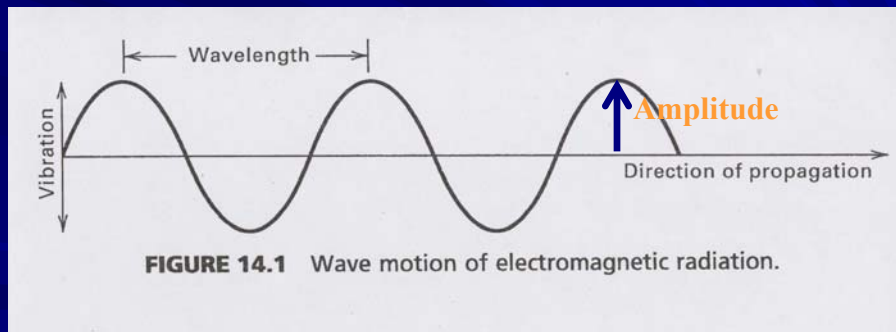
Spectroscopy - Relations

$$\lambda = c/\nu$$

Where: λ (cm); ν (Hz; s^{-1}); c = light velocity

Units used for wavelength:
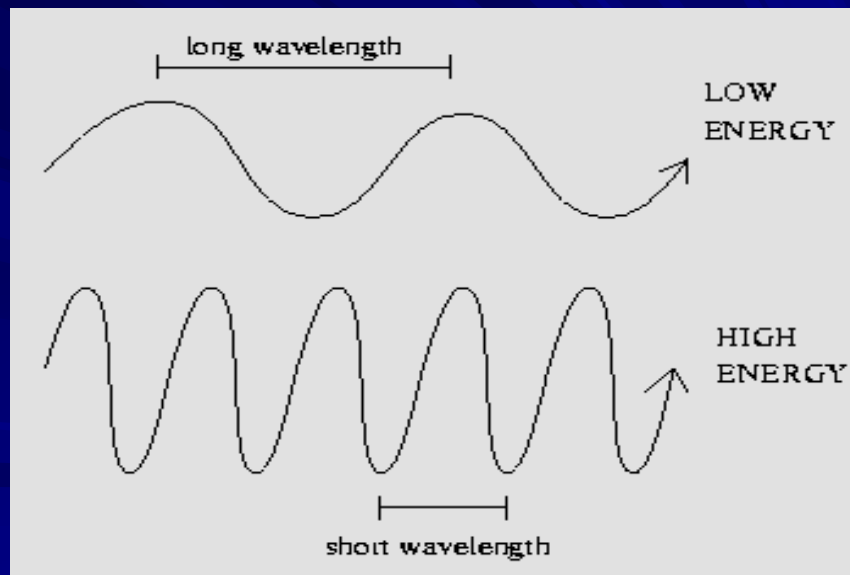**Å = angstrom = 10^{-10} m**
nm = 10^{-9}m
μm = 10^{-6}m

Light Energy

Spectroscopy - Relations

The De-Broglie Relationship – The link between Particle and Wave behavior

$$E = h\nu$$

Where:

h = Planck's constant – 6.62×10^{-34} Js

   Proportionality constant

When $\nu = c/\lambda$ is substituted:

$$E = hc/\lambda$$

Spectroscopy - Relations

The De-Broglie Relationship – The link between Particle and Wave behavior

$$E = mc^2$$

Combining with previous equation

$$mc^2 = hc/\lambda$$

That gives

$$\lambda = h/mc$$

Qualitative Spectroscopy

Spectroscopy Modes

TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type 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	0.75–3.75 mm	13–27	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 Å = 10^{-10} nm = 10^{-8} cm
1 nm = 10^{-9} m = 10^{-7} cm
1 μm = 10^{-6} m = 10^{-4} cm

Spectroscopy – Electron Distribution

(a) σ orbital

(c) σ^* orbital

(b) π orbital
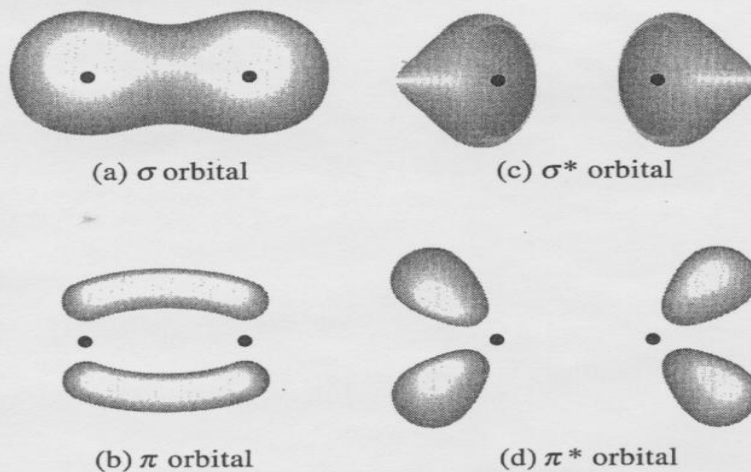
(d) π^* orbital

Figure 14-1 Electron distribution in sigma and pi molecular orbitals.

Spectroscopy – Molecules and Radiation

Absorption:

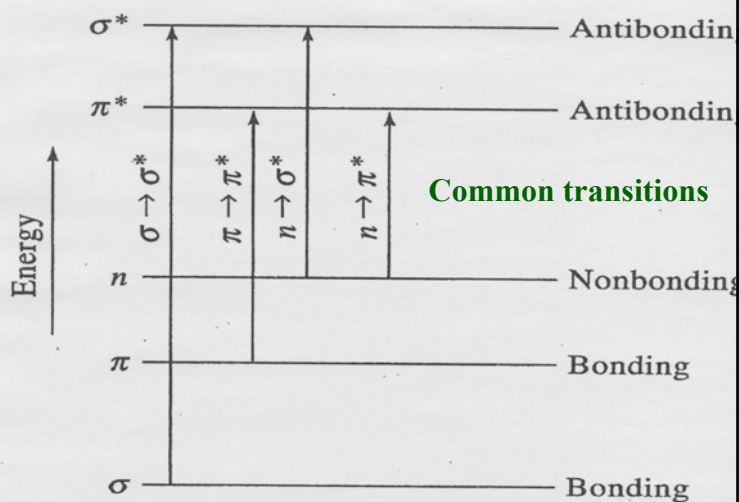$$M + h\nu \longrightarrow M^*$$

Change in nuclear energy level – X-rays (high energy)

Changes in nuclear spin state (Low energy – magnetic field)

Radiation exited species – lifetime 10^{-8} to 10^{-9} s

Release – return to lower energy state:

$M^* \longrightarrow M + heat$ (collision with neighbours)

$M^* \longrightarrow M + h\nu$ (emission, highly probable at high frequency)

Spectroscopy – Molecular Energy

Figure 14-3 Electronic molecular energy levels.

Spectroscopy – Energy Transitions

❖ σ ➡ σ*

Observed only at the highest energy – vacuum ultraviolet. Rarely, never observed in normal UV/VIS

❖ n ➡ σ*

Saturated compounds containing atoms with unshared electron pairs (nonbonding electrons) capable this transition. This transition requires less energy – happen in 150 to 250 nm (most absorption peaks below 200nm). Molar absorptivity are low $100 – 3000$ L cm^{-1} mol^{-1}

Spectroscopy – Absorption Maxima

TABLE 14-1 Some Examples of Absorption due to $n \rightarrow \sigma^*$ Transitions[a]

Compound	λ_{max}(nm)	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S$[b]	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

[a]Samples in vapor state.

Spectroscopy – Energy Transitions

n ⟶ **π^*** Molar absorptivity 10 – 100 L cm^{-1} mol^{-1}

π ⟶ **π^*** Molar absorptivity 1000 to 10,000 L cm^{-1} mol^{-1}

Applications of absorption spectroscopy to organic compounds are based upon this transitions to excited state of π^*.

Energy required for those excitation states is within 200 to 700 nm.

Chromophores involved are unsaturated functional groups to provide the π orbitals.

n π^* transitions are **hypsochromic** (shift towards blue) with increasing polarity of solvent

π π^* transition often is **bathochromic** (shift to red) with increased solvent polarity

Spectroscopy – Interaction Molecule & Radiation
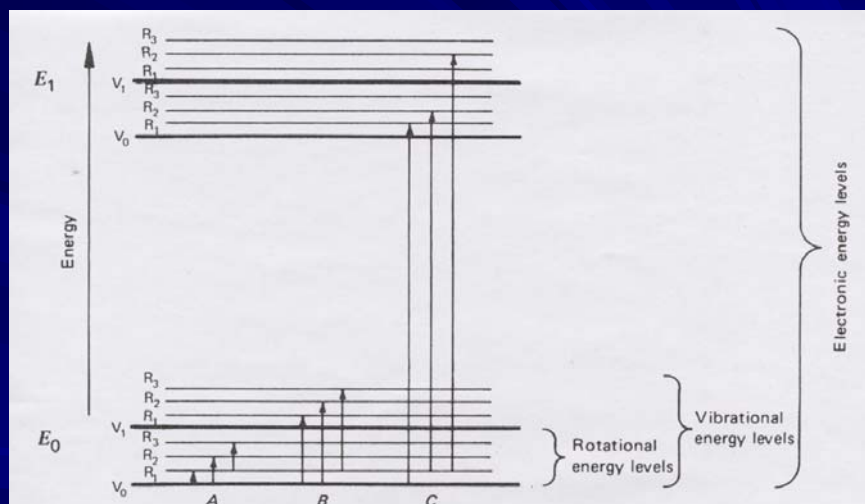
FIGURE 14.3 Energy level diagram illustrating energy changes associated with absorption of electromagnetic radiation: A, pure rotational changes (far infrared); B, rotational–vibrational changes (near infrared); C, rotational–vibrational–electronic transitions (visible and ultraviolet). E_0 is electronic ground state and E_1 is first electronic excited state.

Spectroscopy - Chromophors

TABLE 14-2 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	$\lambda_{max}(nm)$	ϵ_{max}	Type of Transition
Alkene	$C_6H_{13}CH=CH_2$	n-Heptane	177	13,000	$\pi \to \pi^*$
Alkyne	$C_5H_{11}C\equiv C-CH_3$	n-Heptane	178	10,000	$\pi \to \pi^*$
			196	2,000	—
			225	160	—
Carbonyl	CH_3CCH_3 (O)	n-Hexane	186	1,000	$n \to \sigma^*$
			280	16	$n \to \pi^*$
	CH_3CH (O)	n-Hexane	180	large	$n \to \sigma^*$
			293	12	$n \to \pi^*$
Carboxyl	CH_3COH (O)	Ethanol	204	41	$n \to \pi^*$
Amido	CH_3CNH_2 (O)	Water	214	60	$n \to \pi^*$
Azo	$CH_3N=NCH_3$	Ethanol	339	5	$n \to \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \to \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \to \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \to \pi^*$

14

Spectroscopy – Chromophores

TABLE 14.2

Electronic Absorption Bands for Representative Chromophores[a]

Chromophore	System	λ_{max}	ϵ_{max}
Amine	$-NH_2$	195	2,800
Ethylene	$-C=C-$	190	8,000
Ketone	$\diagdown C=O \diagup$	195	1,000
		270–285	18–30
Aldehyde	$-CHO$	210	Strong
		280–300	11–18
Nitro	$-NO_2$	210	Strong
Nitrite	$-ONO$	220–230	1,000–2,000
		300–400	10
Azo	$-N=N-$	285–400	3—25
Benzene		184	46,700
		202	6,900
		255	170
Naphthalene		220	112,000
		275	5,600
		312	175
Anthracene		252	199,000
		375	7,900

[a]From M. M. Willard, L. L. Merritt, and J. A. Dean, *Instrumental Methods of Analysis*, 4th ed. Copyright© 1948, 1951, 1958, 1965, by Litton Educational Publishing, Inc., by permission of Van Nostrand Reinhold Company.

Spectroscopy

- **Conjugation** – electron are delocalized; lower energy required to exite electrons;

Absorption maxima will shift to longer wavelength

Spectroscopy - Multichromophors

TABLE 14-3   Effect of Multichromophores on Absorption

Compound	Type	λ_{max}(nm)	ϵ_{max}
$CH_3CH_2CH_2CH=CH_2$	Olefin	184	~10,000
$CH_2=CHCH_2CH_2CH=CH_2$	Diolefin (unconjugated)	185	~20,000
$H_2C=CHCH=CH_2$	Diolefin (conjugated)	217	21,000
$H_2C=CHCH=CHCH=CH_2$	Triolefin (conjugated)	250	—
$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$	Ketone	282	27
$CH_2=CHCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$	Unsaturated ketone (unconjugated)	278	30
$CH_2=CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3$	α,β-Unsaturated ketone (conjugated)	324	24
		219	3,600

UV Spectroscopy – Absorption Maxima

**TABLE 14-4**   Absorption Characteristics of Aromatic Compounds

| Compound		E_2 Band		B Band	
		λ_{max}(nm)	ϵ_{max}	λ_{max}(nm)	ϵ_{max}
Benzene	C_6H_6	204	7,900	256	200
Toluene	$C_6H_5CH_3$	207	7,000	261	300
m-Xylene	$C_6H_4(CH_3)_2$	—	—	263	300
Chlorobenzene	C_6H_5Cl	210	7,600	265	240
Phenol	C_6H_5OH	211	6,200	270	1,450
Phenolate ion	$C_6H_5O^-$	235	9,400	287	2,600
Aniline	$C_6H_5NH_2$	230	8,600	280	1,430
Anilinium ion	$C_6H_5NH_3^+$	203	7,500	254	160
Thiophenol	C_6H_5SH	236	10,000	269	700
Naphthalene	$C_{10}H_8$	286	9,300	312	289
Styrene	$C_6H_5CH=CH_2$	244	12,000	282	450

Spectroscopy

❖ **Auxochrome** – functional group that does not absorb radiation itself in the UV range but has a shifting effect on main chromophore peaks to longer wavelength as well as increasing their intensity.

❖ Example: -OH and –NH_2 on benzene chromophore

Mid-range IR Spectra
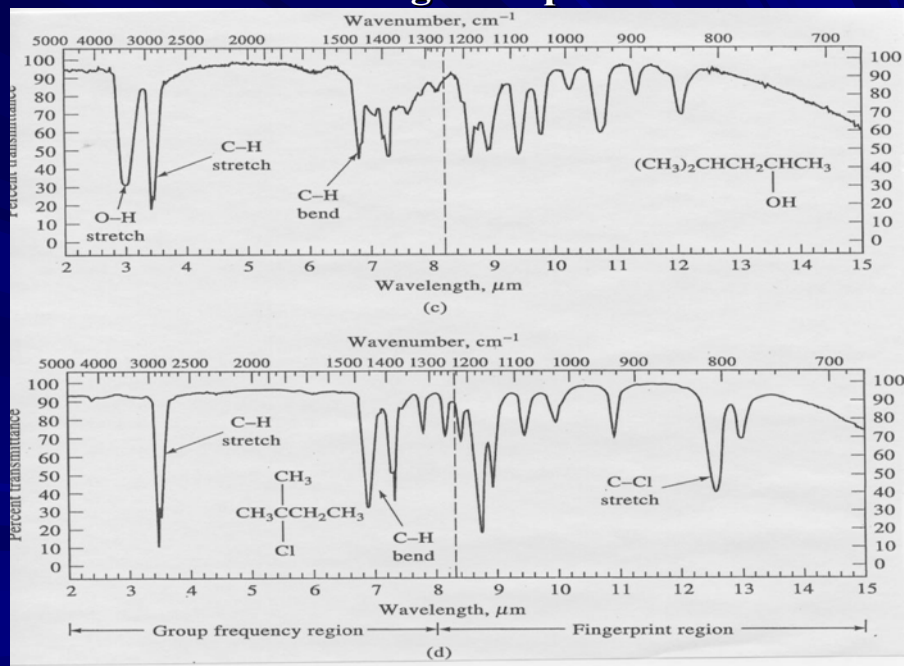
Spectroscopy Typical UV Spectra
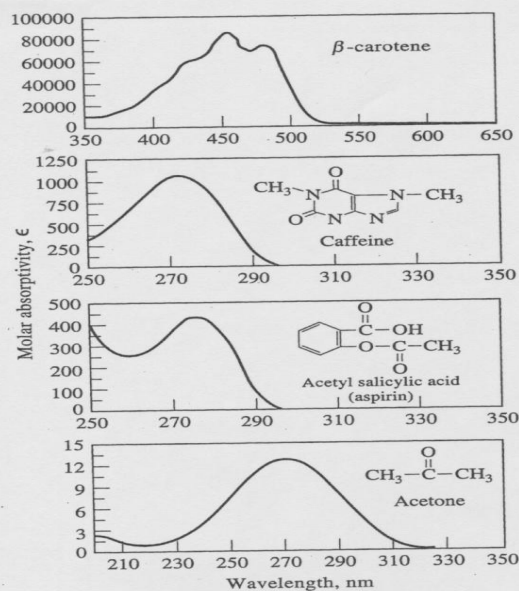
Figure 14-4 Ultraviolet spectra for typical organic compounds.

Spectroscopy

■ **Inorganic Anions**

  A number of inorganic anions exhibit Uv absorption as consequence of $\pi \rightarrow \pi*$ transition

Example:

nitrate – 313nm; nitrite – 360 and 280 nm

carbonate - 217nm; azide – 230nm
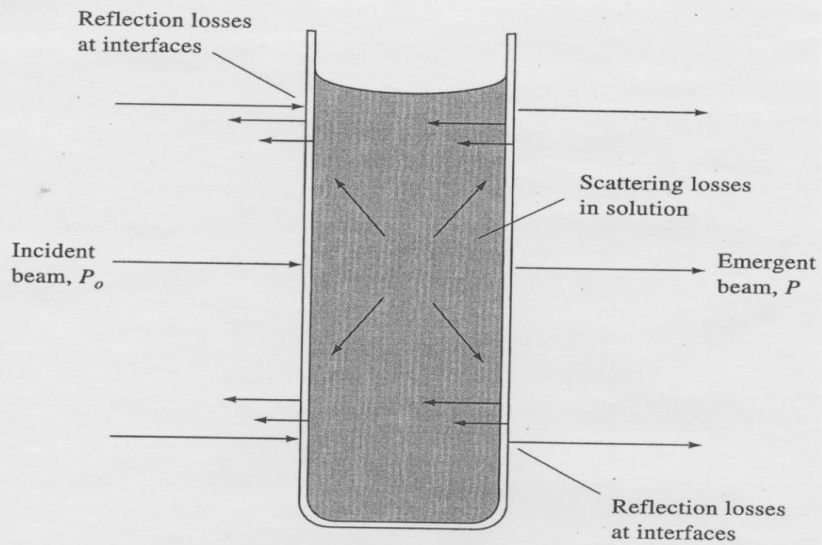
trithiocarbonate – 500nm

UV/VIS - Solvents

TABLE 14-6 Solvents for the Ultraviolet and the Visible Regions

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.

Quantitative Spectroscopy

Spectroscopy – Light Properties

Reflection losses at interfaces

Scattering losses in solution

Incident beam, P_o

Emergent beam, P

Reflection losses at interfaces

Figure 13-1 Reflection and scattering losses.

Spectrophotometer

Model of light interaction with matrix and how spectrophotometer works

http://www.chm.davidson.edu/java/spec/spec.html

Spectroscopy – Quantification Terms

➢ **Transmittance (T)** – the fraction of incident radiation transmitted by the medium:

$$T = P/P_0$$

➢ **Absorbance (A)** – the amount of incident radiation absorb by the medium and expressed by:

$$A = \log(1/T) = -\log T = \log P_0/P$$

Transmittance and Absorbance
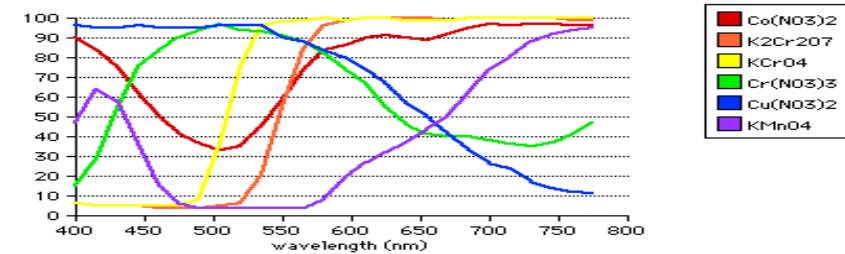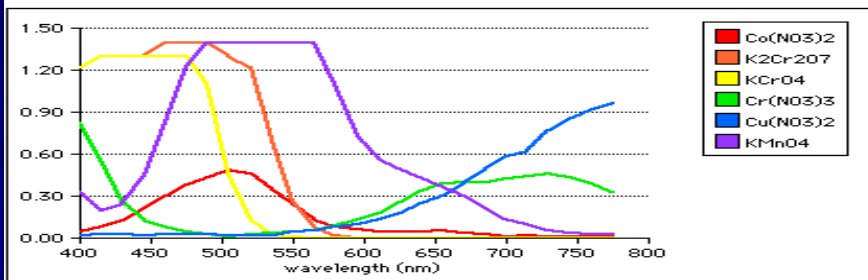
Spectroscopy - Quantification

Beer's Law (Beer – Bourguer – Lambert Law)

Radiation energy decays exponentially

$$T = P/P_0 = 10^{-kb}$$

Where:

k – constant

T – the transmittance – the fraction of transmitted radiant energy

b – the pathlength of the medium

Spectroscopy - Quantification

If we present in logarithmic form:

$$\log T = \log P/P_0 = -kb$$

The same stands for concentration:

$$\log T = \log P/P_0 = -k'c$$

Spectroscopy - Quantification

$$\log T = \log P/P_0 = -k'c$$

Because A = - log T, then:

$$A = k'c$$

Where: k' = ab

$$A = abc$$

Where:
a – proportionality constant called <u>absorptivity</u>
b – pathlength of the medium

Spectroscopy - Quantification

$$A = abc$$

If:

c - is expressed in *moles per liter*

b – pathlength (cell length) in *cm*
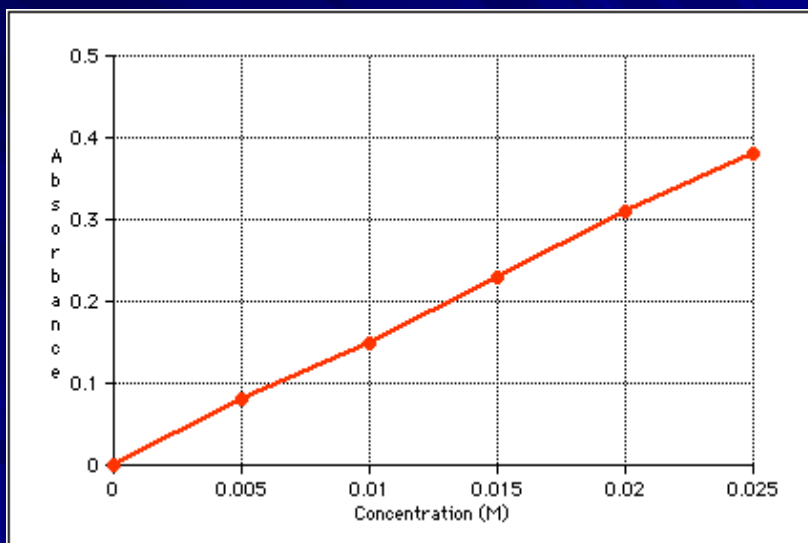
Then **a** is called the *molar absorptivity* and

has the special symbol ε and units: $L\ mol^{-1}\ cm^{-1}$

Spectroscopy

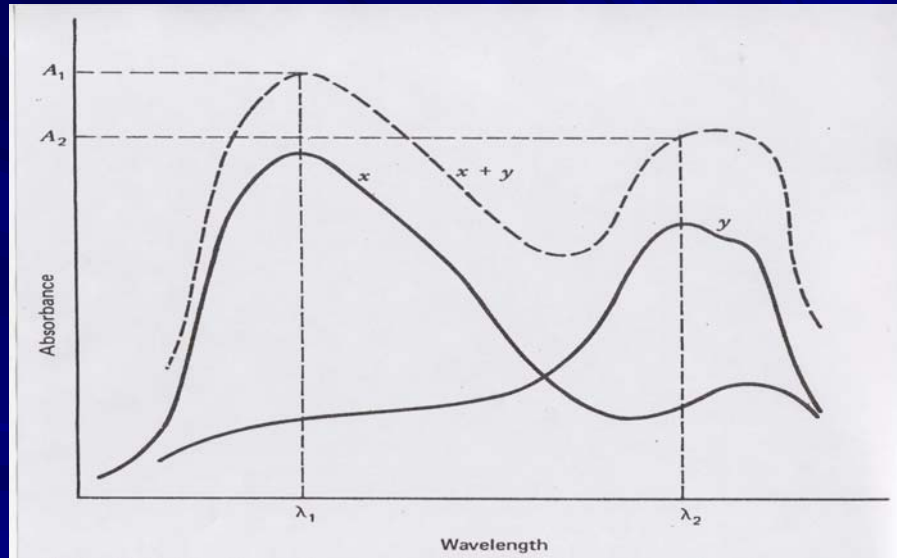- **Molar absorptivity**

  Range for UVVIS – 0 to 10^5

Beer Law Chart

Spectroscopy – Multimolecules Effect

FIGURE 14.10 Absorption spectra of pure substances *x* and *y* of a mixture of *x* and *y* at the same concentrations.

Spectroscopy - Mixture

Multi-component mixture:

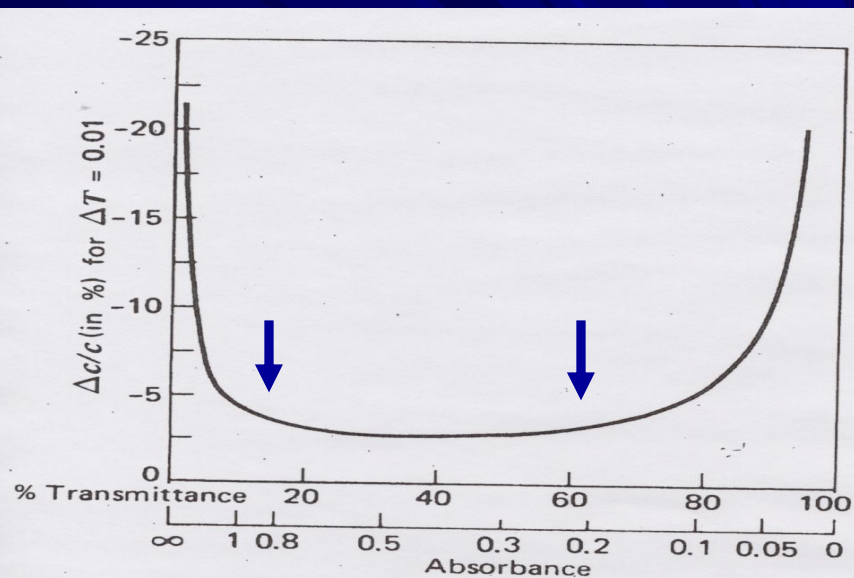$$A_T = A_1 + A_2 + A_3 + A_n$$

$$A_T = \varepsilon_1 bc_1 + \varepsilon_2 bc_2 + \varepsilon_3 bc_3 + \varepsilon_n bc_n$$

Where: 1,2,3,….,n – refer to absorbing components

Spectroscopy – Beer's Law Limitations

- **Deviations from the direct proportionality (b=const)**

- **Instrumental Deviations**

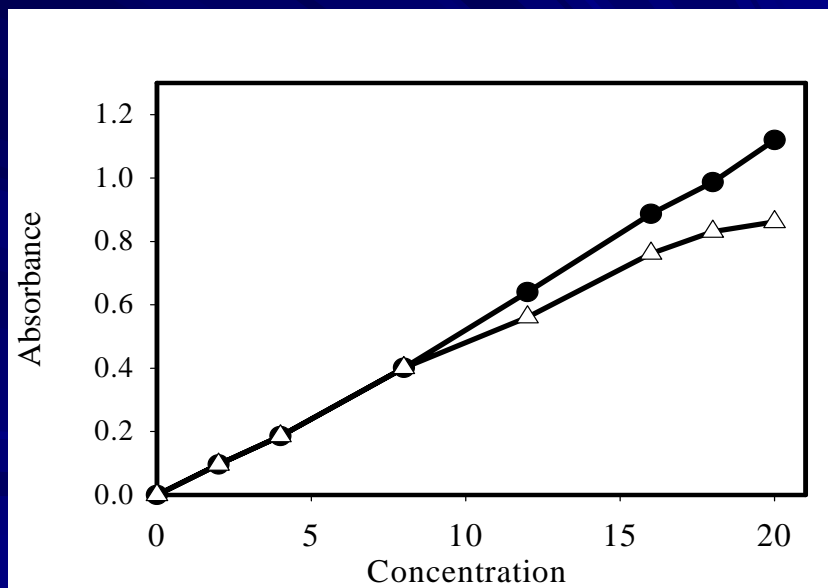- **Chemical Deviations**

Spectroscopy – Beer's Law Compliance

FIGURE 14.27 Relative concentration error as a function of transmittance for a 1% uncertainly in %T.

Beer's Law Limitations

■ **Deviations from the direct proportionality (b = const)**

❖ Valid at concentration usually below 0.01M

❖ Molecules interference – distance between molecules affects charge distribution of molecules (ions)

❖ Effect of refractive index – concentration affects refractive index ε is affected (low, less important)
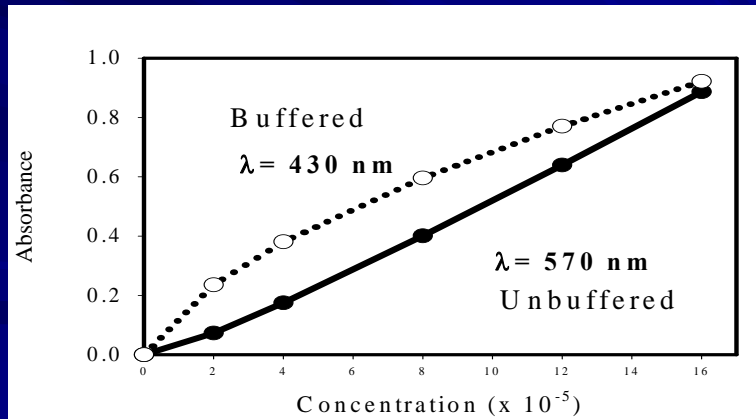
Spectroscopy - Deviations

Beer's Law Limitations

■ **Chemical Deviations**

  ❖ **Association, dissociation and reaction with solvent and other molecules**

Beer's Law Limitations

■ **Instrumental Deviations**

  ❖ **monochromatic radiation – quality of monochromator and control of bandwidth and slit**

  ❖ **Instrumental noise – accuracy of measurement of transmittance – quality of detector**