Ch. 6: Introduction to Spectroscopic methods

<u>Spectroscopy:</u>

A branch of science that studies the interaction between EM radiation and matter.

<u>Spectrometry and Spectrometric methods :</u>

Measurement of the intensity of radiation with a photoelectric transducer or other types of electronic device.

What is Electromagnetic Radiation?

- EMR is a form of energy that has both <u>Wave</u> and <u>Particle</u> Properties.
- Many of the properties of electromagnetic radiation are conveniently described by means of a classical sinusoidal wave model, which embodies such parameters as wavelength, frequency, velocity, and amplitude.
- In contrast to other wave phenomena, such as sound, electromagnetic radiation *requires no supporting medium* for its transmission and thus passes readily a vacuum.

EMR as a Wave

For many purposes, electromagnetic radiation is conveniently represented as electric and magnetic field that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation.



Figure-6.1(a) Representation of a single ray of plane-polarized electromagnetic radiation. The term plane polarized implies that all oscillations of either the electric or the magnetic fields lie within a single plane.



Figure -6.1(b) is a two –dimensional representation of the electric vector component of the ray in 6(a).

Properties of electromagnetic radiation



- <u>Period</u> (p) the time required for one cycle to pass a fixed point in space.
- Frequency (V) the number of cycles which pass a fixed point in space per second. =1/p
- <u>Amplitude</u> (A) The maximum length of the electric vector in the wave (Maximum height of a wave).
- <u>Wavelength</u> (λ) The distance between two identical adjacent points in a wave (usually maxima or minima).
- <u>*Wavenumber* (1/ λ)</u> The number of waves per cm in units of cm⁻¹.

Douglas A. Skoog, et al. Principles of Instrumental Analysis, Thomson, 2007

Velocity of propagation = $v_i = v \cdot \lambda_i$

Speed of light = Frequency x Wavelength

- Frequency of a beam of radiation is determined by the source and invariant
- Velocity of radiation depends upon the composition of the medium through which it passes.

For electromagnetic waves the Speed (*c*) in vacuum is a Constant Speed of light in vacuum = $c = 2.99792x10^8$ m/s = $c = v \cdot \lambda$ Speed of light in air = only 0.03% less than the one in vacuum. Therefore for either air or vacuum; $c = 3.00 \times 10^8$ m/s

In any medium containing matter, propagation of radiation is slowed by the interaction between the electromagnetic field of the radiation and the bound electrons in the matter. Since the radiant frequency is invariant and fixed by the source, the wavelength must decrease as radiation passes from a vacuum to another medium.

Effect of the Medium on a Light Wave



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- Frequency remains the same.
- Velocity and Wavelength change.

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 This constant speed means a direct, Inverse Relationship Between Wavelength and Frequency

 $\nu \propto 1/\lambda$

The relationship between frequency v of light and energy E,

Planck's Equation: $E = h_V$;Whereh = Planck's constant= 6.6 x 10^{-27} erg.sec = 6.6 x 10^{-34} joule.sec

In vacuum, velocity of light = $c = v\lambda = 3 \times 10^{10}$ cm/s which gives, $v = c/\lambda$ E = h(c/ λ) = hcv (where, $v = 1/\lambda$ = wavenumber)

Energy directly proportional to wavenumber

The Electromagnetic Spectrum

The Higher the Frequency the Shorter the Wavelength The Longer the Wavelength, Lower the Frequency.



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

TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

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Mathematical Description of a Wave



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Sine waves with different amplitudes and with a phase different of 90 degree

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Mathematical Description of a Wave

A wave can be described by an equation for a sine wave



 $Y = A \sin(\omega t + \phi)$

Y= magnitude of the electric field at time t,

- A = Amplitude
 - ϕ = phase angle

 ω = angular velocity

$$\omega = 2\pi v = 2\pi v$$

 $\frac{2\pi v}{\lambda}$

The angular velocity is related to the frequency of the radiation

$$Y = A \sin(2\pi v t + \phi)$$

Superposition of Waves

□ If two plane-polarized waves overlap in space, the resulting electromagnetic disturbance is the algebraic sum of the two waves.



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Superposition of sinusoidal wave: (a) A1 < A2, $(\Phi 1 - \Phi 2) = 20^{\circ}$, v1 = v2; (b) A1 < A2, $(\Phi 1 - \Phi 2) = 200^{\circ}$, v1 = v2

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Optical Interference

Optical Interference: The interaction of two or more light waves yielding an irradiance that is not equal to the sum of the irradiances.





-Constructive Interference

1) Have identical frequency

2)
$$\phi_2 - \phi_1 = \delta = \pm m 2\pi$$

 $\phi_2 - \phi_1 = 0$, or 360 deg or integer multiple of 360 deg.

- Destructive Interference 1) Have identical frequency 2) $\phi_2 - \phi_1 = \delta = (2m+1)\pi$

 $\phi_2 - \phi_1 = 180 \text{ deg or } 180 + \text{integer multiple of 360 deg.}$

Figure 3-4 – Ingle and Crouch,

Periodicity or Beat

✓ Superposition of two sinusoidal wave of different frequencies but identical amplitudes.

✓ The resultant wave is no longer sinusoidal but exhibit a periodicity

✓ wave1 period= $1/v_1$, wave2 period= $1/1.25 v_1$; result: $1/\Delta v_1$



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An important aspect of superposition is that:

- > a complex waveform can be broken down into simple components
- by a mathematical operation called the Fourier transformation.
 - Jean Fourier (1768-1830) demonstrated that, any periodic function, regardless of complexicity, can be described by a sum of simple sine or cosine terms.
 - of the original signal. The Fourier transform decomposes
 - a <u>function</u> of time (a *signal*) into the frequencies that make it up.
 - The Fourier transform is called the *frequency domain*

representation

FT is a tedious and time consuming when done by hand.
 Efficient computer programs are necessary.

Diffraction:





(b)

The Bending of Light as It Passes Through an Aperture or Around a Small Object

Diffraction is a consequence of interference

not only observed for EMR but also for mechanical or acoustical waves

Figure 6-7 Propagation of waves through a slit: (a) $xy >> \lambda$; (b) $xy = \lambda$.

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Diffraction of Waves in a Liquid

> Diffraction increases as aperture size $\rightarrow \lambda$



FIGURE 10.2 Diffraction through an aperture with varying λ as seen in a ripple tank. (Photo courtesy PSSC *Physics*, D. C. Heath, Boston, 1960.)

Eugene Hecht, Optics, Addison-Wesley, Reading, MA, 1998.

Diffraction Pattern From Multiple Slits

- If the radiation is monochromatic, a series of dark and light images is observed.



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Diffraction Pattern From Multiple Slits



If slit width $\rightarrow \lambda$

The band intensities decrease only gradually with increasing distances from the central band. If slit width $>\lambda$

The decrease is much more pronounced

Diffraction Pattern From Multiple Slits



Example 6.1. OE = 2.0 m, BC = 0.3 mm, n=4 $\lambda = ?$ If DE = 15.4 mm $0.3 \text{ mm x } 15.4 \text{ mm} = 4 \text{ x } \lambda$ 2.0 m x 1000 mm/mBC. $DE = n\lambda$ OD = OE

The conditions for maximum constructive interference can be derived. θ =diffraction angle BD and CD are the light paths from the slits B and C to the point D. Assumption: OE >>> BC then, BD // OD // CD BF \perp CD and forms BCF triangle And BCF \approx DOE Angle CBF = θ =diffraction angle

 $\mathbf{CF} = \mathbf{BC} \sin \theta = \mathbf{n}\lambda$

 $DE = OD \sin \theta \rightarrow Sin \theta = DE/OD$



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Coherent Radiation

Coherency: When two waves have an initial phase difference of zero or constant for a long time, they are considered coherent.

Conditions for coherency of two sources of radiation are:

- 1. They must have identical frequencies and
- 2. The phase relationships between the two remains constant with time

Incoherency test: Illuminate the slits with W-lampresult is ;

- disappearance of the dark and light patterns
- more or less uniform illumination of the screen

This behaviour is the consequence of the incoherent character of W-lamp.

Incoherent sources

Light is emitted by individual atoms or molecules

- resulting beam is the summation of countless individual events
- ➤ phase differences are variable
- constructive and destructive interferences occur randomly
- > average of the emissions are observed as an illumination

Coherent sourses

 \succ optical lasers, rf oscilators, microwave sources.

6B-7 Transmission of Radiation: The Refractive Index

- Radiation interacts with the matter.
- Refractive index of a medium is one measure of its interaction with radiation,
- n is wavelength (frequency) dependent.



 η , In glass n increases as λ decreases.

TABLE 4.1 Approximate Indices of Refraction of Various Substances*

	1 000 20	
Air	1.000 29	
Ice	1.51	
Water	1.333	
Ethyl alcohol (C2 H5 OH)	1.36	
Fused quartz (SiO ₂)	1.4584	
Carbon tetrachloride (CCl ₄)	1.46	
Turpentine	1.472	
Benzene ($C_6 H_6$)	1.501	
Plexiglass	1.51	
Crown glass	1.52	
Sodium chloride (NaCl)	1.544	
Light flint glass	1.58	
Polystyrene	1.59	
Carbon disulfide (CS ₂)	1.628	
Dense flint glass	1.66	
Lanthanum flint glass	1.80	
Zircon (ZrO ₂ ·SiO ₂)	1.923	
Fabulite (SrTiO ₃)	2.409	
Diamond (C)	2.417	
Rutile (TiO ₂)	2.907	
Gallium phosphide	3.50	

*Values vary with physical conditions—purity, pressure, etc. These correspond to a wavelength of 589 nm

Eugene Hecht, Optics, Addison-Wesley, Reading, MA, 1998.

Refractive index (n)

- the velocity (v) of EM radiation depends on the medium through which it travels
- $n_i = c/v_i$ (>1).
 - the ratio of the velocity in vacuum over the velocity in the medium
- n depends on the frequency of the light

Dispersion and Prisms

Dispersion: The variation in refractive index of a substance with wavelength or frequency





Normal Dispersion:

A region where gradual increase in n wrt increase in frequency.

Anomalous Dispersion: Frequency ranges in which a sharp change in n is observed.

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Dispersion curves are imp. when choosing materials for the optical components of spectrometer. ND(lenses) AD(prisms)



FIGURE 35.17 (a) Dispersion of white light by a prism. Because *n* varies with wavelength, the prism disperses the white light into its various spectral components. (b) Different colors are refracted at different angles because the index of refraction of the glass depends on wavelength. Violet light deviates the most; red light deviates the least. (*Photograph courtesy of Bausch and Lomb*)

6B-8 Refraction of Radiation

What happens when light hits a boundary between two media?

<u>Refraction</u>: an abrupt *change in direction of radiation as it passes from one medium to another with different densities.*

Conservation Law

- $\alpha(\lambda) + \rho(\lambda) + T(\lambda) = 1$
- $\alpha(\lambda)$ = Fraction Absorbed
- $\rho(\lambda)$ = Fraction Reflected
- $T(\lambda)$ = Fraction Transmitted



FIGURE 4.13 A beam of plane waves incident on a distribution of molecules constituting a piece of clear glass or plastic. Part of the incident light is reflected and part refracted.

Eugene Hecht, *Optics*, Addison-Wesley, Reading, MA, 1998. 28

Refraction:

- **Refraction** is the change in direction of propogation of a wave due to a change in its transmission medium.
- Refraction of light in passing from less dense to a more dense medium, bending is towards the normal.
- If the beam passes from more dense to a less dense medium, bending away from the normal occurs



- The extent of refraction is given by,

<u>Snell's Law:</u> $n_1 \sin\theta_1 = n_2 \sin\theta_2$ $v_2 \sin\theta_1 = v_1 \sin\theta_2$ $\frac{\sin\theta_1}{\sin\theta_2} = \frac{v_1}{v_2}$

Douglas A. Skoog, et al. Principles of Instrumental Analysis, Thomson, 2007

Refraction:



An object (in this case a pencil) partially immersed in water looks bent due to refraction



6B-9 Reflection of Radiation

Reflection is the change in direction of a <u>wavefront</u> at an <u>interface</u> between two different <u>media</u> so that the wavefront returns into the medium from which it originated.



For monochromatic light hitting a flat surface at 90⁰

$$\frac{I_r}{I_0} = \frac{(n^2 - n^1)^2}{(n^2 + n^1)^2}$$

I₀: intensity of incident light I_r: reflected intensity

Laws of reflection:

- 1. The incident ray, the reflected ray and the normal to the reflection surface at the point of the incidence lie in the same plane.
- 2. The reflected ray and the incident ray are on the opposite sides of the normal.

Reflection of Radiation

Specular reflection: Reflection of light from a smooth surface (mirror like)



Reflections on still water are an example of specular reflection

Diffuse reflection: Reflection of light from a rough surface. (retaining the energy but losing the image)

$\rho(\lambda)$ at different interfaces

Reflectance is the fraction of the incident radiant energy reflected.

TABLE B-2 Reflectances for several interfaces				
Interface	Spectral reflectance	Interface	Spectral reflectance	
Glass-air	0.0403	NaCl-air	0.045	
Glass-H ₂ O	0.0035	KCl-air	0.038	
Glass-1 M KC1	0.0031	Sapphire-air	0.076	
Glass-benzene	1.1×10^{-7}	Sapphire-H ₂ O	0.0198	

TABLE B-	1
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Material	η at 589 nm	Material	η at 589 nm
Air	1.003	AgCl	2.000 (3.9 μm)
H ₂ O	1.333	Sapphire	1.769 (579 nm)
Fused silica	1.458	NaCl	1.544
	1.513 (240 nm)		1.522 (4.0 µm)
Borosilicate	1.517	ZnS	2.35
Crown glass	1.548 (313 nm)	Cryolite	1.34
KCI	1.490	ADP	1.525 (m., 579 nm)
	1.471 (4.71 μm)		1.479 (n., 579 nm)
KI	1.666	KDP	1.510 (n., 579 nm)
	1.627 (4.13 µm)		1.469 (n., 579 nm)
MgF ₂	$1.378 (\eta_{o})$	Calcite	1.658 (m.)
	$1.390 (\eta_e)$		1.486 (m_)
Crystal quartz	$1.544 (\eta_{o})$	MgO	1.773 (361 nm)
	1.553 (n _e)	0	1.723 (1.01 µm)
KBr	1.560	Benzene	1.500
	1.535 (4.26 µm)		
1 M KCl (aq)	1.342		

Ingle and Crouch, Spectrochemical Analysis

6B-10 Scattering of Radiation

The fraction of radiation transmitted at all angles from its original path

- Rayleigh scattering : Molecules or aggregates of molecules with dimensions significantly smaller than λ of radiation. Intensity is proportional to the inverse fourth power of the wavelength. I α 1/ λ^4
 - Blue color of the sky.
- Scattering by big molecules (Tyndall effect):

➤Colloidal dimensions particles, scattering can be seen by naked eye.

> used for measuring particle size and shapes of polymer molecules

Raman Scattering:

➢Involves quantized frequency changes. These changes are the results of vibrational energy level transitions that occur in the molecule as a consequence of the polarization process.

6B-11 Polarization of Radiation

- Ordinary radiation consists of a bundle of electromagnetic waves in which the vibrations are equally distributed among a huge number of planes centered along the path of the beam. Viewed end on, a beam of monochromatic radiation can be visualized as an infinite set of electric vectors that fluctuate in length from zero to a maximum amplitude *A*.
- Figure 6-11b depicts an end-on view of these vectors at various times during the passage of one wave of monochromatic radiation through a fixed point in space (Figure 6-11a).

FIGURE 6-11 Unpolarized and plane-polarized radiation: (a) cross-sectional view of a beam of monochromatic radiation, (b) successive end-on view of the radiation in (a) if it is unpolarized, (c) successive end-on views of the radiation of (a) if it is plane polarized on the vertical axis.

•Figure 6-12a shows a few of the vectors depicted in Figure 6-11b at the instant the wave is at its maximum. The vector in anyone plane, say *XY* as depicted in Figure 6-12a. can be resolved into two mutually perpendicular components *A B and CD as shown in Figure* 6-12b.

•If the two components for all of the planes shown in Figure 6-12a are combined, the resultant has the appearance shown in Figure 6-12c. Removal of one of the two resultant planes of vibration in Figure 6-12c produces a beam that is *plane polarized.*

FIGURE 6-12 (a) A few of the electric vectors of a beam traveling perpendicular to the page. (b) The resolution of a vector in a plane XY into two mutually perpendicular components. (c) The resultant when all vectors are resolved (not to scale). *The resultant* electric vector of a planepolarized beam then occupies a single plane. Figure 6-11c shows an end-on view of a beam of planepolarized radiation after various time intervals.

Polarizers:

- the *wire-grid polarizer*, which consists of a regular array of fine parallel metallic wires, placed in a plane perpendicular to the incident beam. Electromagnetic waves which have a component of their <u>electric fields</u> aligned parallel to the wires induce the movement of <u>electrons</u> along the length of the wires. Since the electrons are free to move in this direction, the polarizer behaves in a similar manner to the surface of a <u>metal</u> when reflecting light, and the wave is reflected backwards along the incident beam (minus a small amount of energy lost to joule heating of the wire).^[5]

a Nicol prism- Birefringent polarizer that consists of a crystal of calcite which has been split and rejoined with <u>Canada balsam</u>. The crystal is cut such that the *o*- and *e*-rays are in orthogonal linear polarization states

A <u>Wollaston prism</u> is another birefringent polarizer consisting of two triangular calcite prisms with orthogonal crystal axes that are cemented together. At the internal interface, an unpolarized beam splits into two linearly polarized rays which leave the prism at a divergence angle of 15°–45°.

6C-Quantum-Mechanical Properties of EMR 6C-1 The Photoelectric Effect

FIGURE 6-13

Apparatus for studying the photoelectric effect. Photons enter the phototube, strike the cathode, and eject electrons.

The photoelectrons are attracted to the anode when it is positive with respect to the cathode.
When the anode is negative as shown, the electrons are "stopped", and no current passes.

- The negative voltage between the anode and the cathode when the current is zero is the stopping potential.

FIGURE 6-14 Maximum kinetic energy of photoelectrons emitted from three metal surfaces as a function of radiation frequency. The *y-intercepts (-\omega) are the work* functions for each metal. If incident photons do not have energies of at least hv= ω , no photoelectrons are emitted from the photocathode.

 $KE_m = hv - \omega$ h: Planck's constant = 6.6254 x 10-34 joule-sec. ω : work function

: energy required to remove an e⁻ from the surface

 $E = hv = KE_m + \omega$

•Current is proportional to the intensity of the radiation

- •V₀ depends on the frequency of the radiation and the chemical composition of the coating on the photocathode
- •V₀ independent of the intensity of the incident radiation

Energy States of Chemical Species

- Quantum theory by Planck (1900)
- Black body radiation
- Atoms, ions, and molecules exist in discrete states
- Characterized by definite amounts of energy
- Changes of state involve absorption or emission of energy

•
$$E_1-E_0 = h_V = hc/\lambda$$

Interaction of Radiation and Matter:

Emission and Chemiluminescence Process

In (a), the sample is excited by the application of thermal, electrical, or chemical energy.

In the energy level diagram (b), the dashed lines with upwardpointing arrows symbolize these non-radiative excitation processes, while the solid lines with downward-pointing arrows indicate that the analyte loses its energy by emission of a photon.

In (c), the resulting spectrum is shown as a measurement of the radiant power emitted *PE as a function of wavelength, \lambda.*

Interaction of Radiation and Matter

Absorption Process

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).

Interaction of Radiation and Matter

Photoluminescence method (Fluorescence and phosphorescence)

In (b). the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, the excess energy can be lost by emission of a photon (luminescence, shown as solid line) or by nonradiative processes (dashed lines).

FIGURE 6-17(a) Photoluminescence methods (fluorescence and phosphorescence). Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then dissipation of the energy emission of radiation

The emission occurs over all angles, and the wavelengths emitted (c) correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt and phosphorescence being delayed.

Interaction of Radiation and Matter Inelastic Scattering in Raman Spectroscopy

Emission of Radiation

• Emission • $X^* \rightarrow X + hy$ Excitation needs energy!

•Particle bombardment (e-)

•Electrical currents (V)

•Fluorescence

•Heat

Douglas A. Skoog, F. James Holler and Timothy A. Nieman, Principles of Instrumental Analysis, Saunders College Publishing, Philadelphia, 1998.

Emission: Saltwater in a flame

Line Spectra

Individual atoms, well separated, in a gas phase

Band Spectra

Small molecules and radicals

Continuum Spectra

- Produced when solid are heated to incandescence.
- Blackbody Radiation (Thermal Radiation)

Blackbody Radiation

- A <u>blackbody</u> is a theoretical object, (i.e. <u>emissivity</u> = 1.0), which is both a perfect absorber and emitter of radiation. Common usage refers to a source of infrared energy as a "blackbody" when it's emissivity approaches 1.0 (usually e = 0.99 or better) and as a "graybody" if it has lower emissivity.
- Important sources of infrared, visible, and long wavelength UV for analytical instruments

http://www.electro-optical.com/bb_rad/bb_rad.htm

Blackbody Radiation

Figure 13.2 Blackbody radiation curves. The hyperbola passing through peak points corresponds to Wien's Law.

Both Imax and radiation power (P) are related to TEMPERATURE and current!

Eugene Hecht, Optics, Addison-Wesley, Reading, MA, 1998.

2000