

# ***ADVANCED PHARMACEUTICAL ANALYSIS***

## ***INTRODUCTION***

***Optical activity***

***Fifth stage***

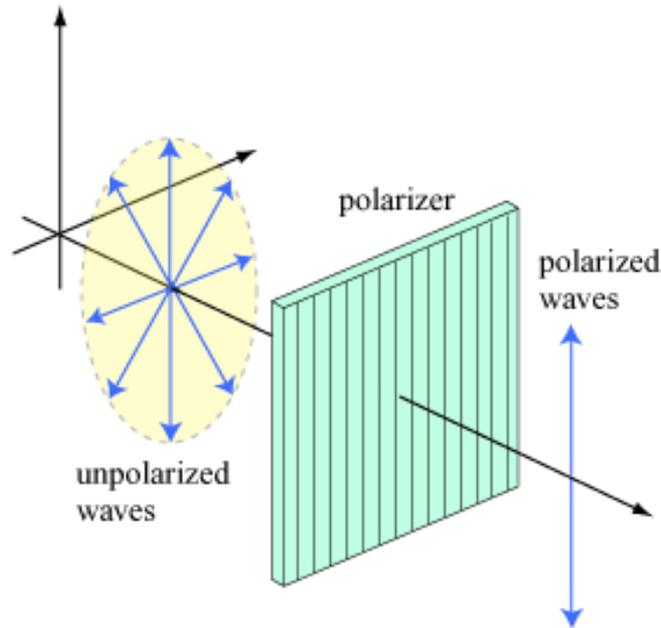
***Created By  
A. L. : Abdulkareem Hamad***

# Optical activity

A beam of ordinary light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of light travel. When a beam of ordinary light is passed through a device called a *polarizer*, however, only the light waves oscillating in a single plane pass through and the light is said to be *plane-polarized*. Light waves in all other planes are blocked out.

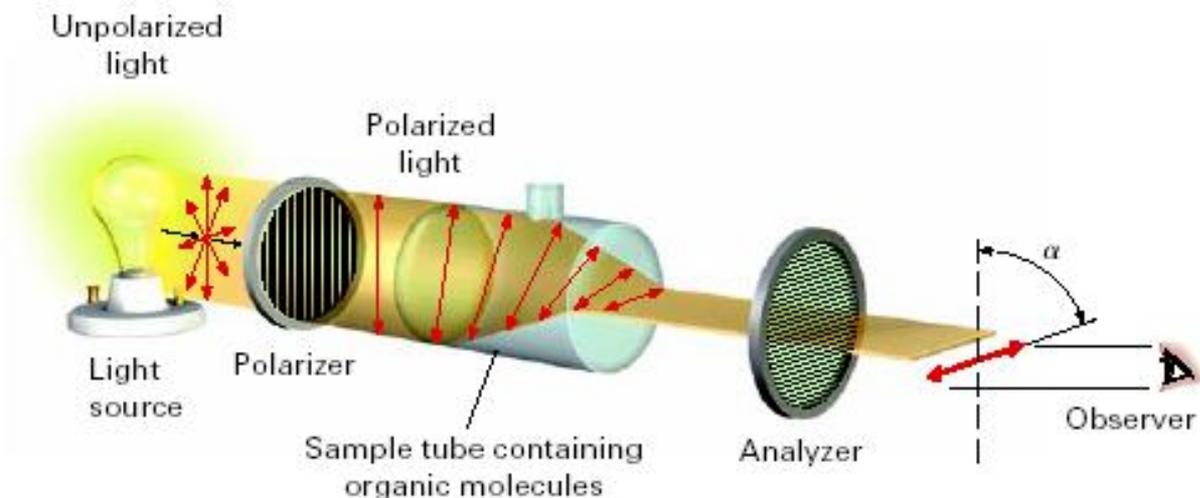
**Biot** made the remarkable observation that when a beam of plane-polarized light passes through a solution of certain organic molecules, such as sugar or camphor, the plane of polarization is *rotated* through an angle. Not all organic substances exhibit this property, but those that do are said to be **optically active**.

Oscillation of the electrical field of ordinary light occurs in all possible planes perpendicular to the direction of propagation.



The plane of oscillation of the electrical field of plane-polarized light. In this example the plane of polarization is vertical.

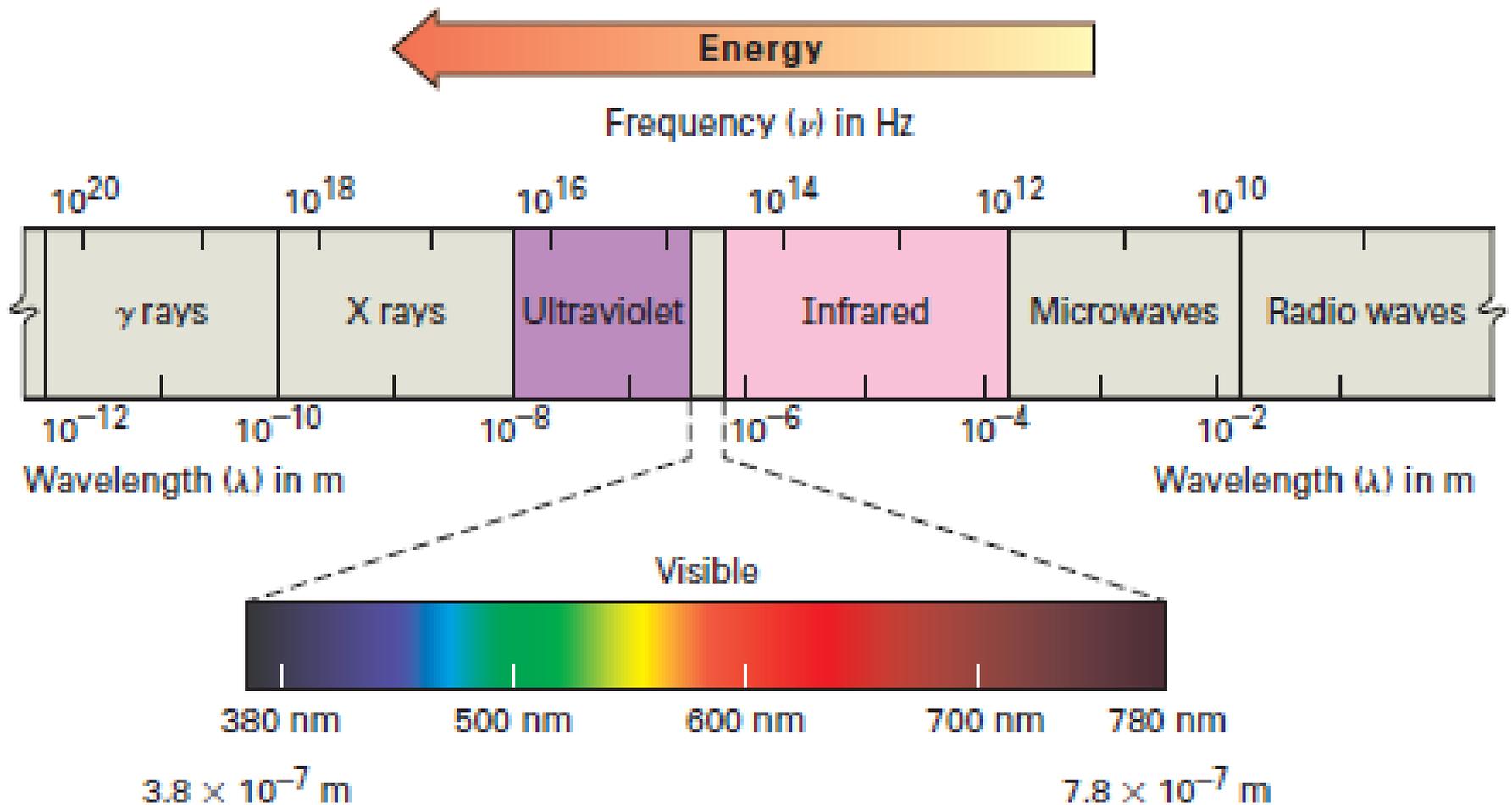
The angle of rotation can be measured with an instrument called a *polarimeter*. A solution of optically active organic molecules is placed in a sample tube, plane-polarized light is passed through the tube, and rotation of the polarization plane occurs. The light then goes through a second polarizer called the *analyzer*. By rotating the analyzer until the light passes through it, we can find the new plane of polarization and can tell to what extent rotation has occurred.



To express optical rotations in a meaningful way so that comparisons can be made, we have to choose standard conditions. The **specific rotation**,  $[\alpha]_D$ , of a compound is defined as the observed rotation when light of 589.6 nm (1 nm=  $10^{-9}$  m) wavelength is used with a sample path length  $l$  of 1 decimeter (dm; 1 dm= 10 cm) and a sample concentration  $c$  of 1 g/cm<sup>3</sup>.

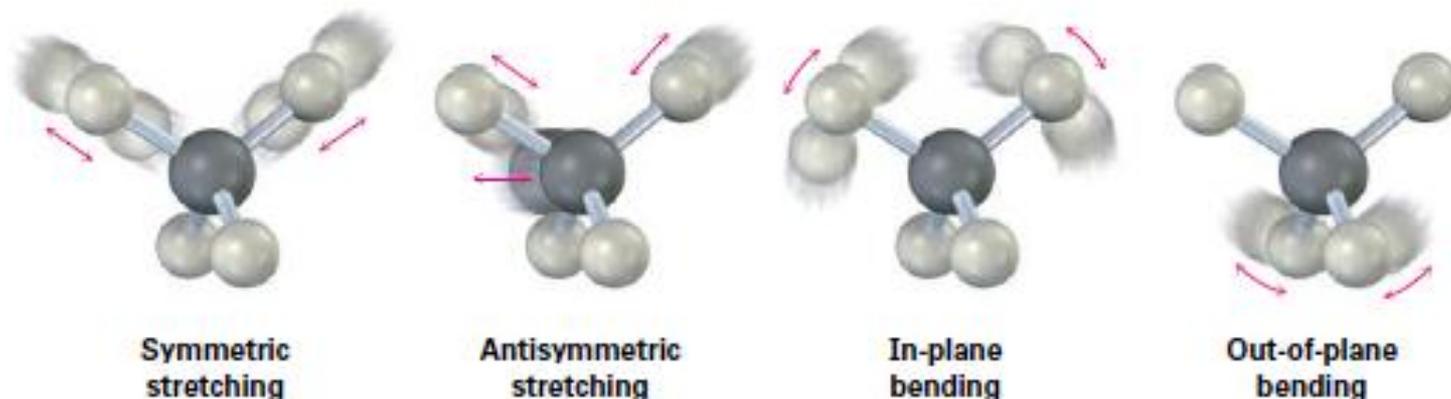
$$[\alpha]_D = \frac{\text{Observed rotation (degrees)}}{\text{Pathlength, } l \text{ (dm)} \times \text{Concentration, } c \text{ (g/cm}^3\text{)}} = \frac{\alpha}{l \times c}$$

# Electromagnetic spectrum



# IR spectroscopy

All molecules have a certain amount of energy and are in constant motion. Their bonds stretch and contract, atoms wag back and forth, and other molecular vibrations occur. Some of the kinds of allowed vibrations are shown below:



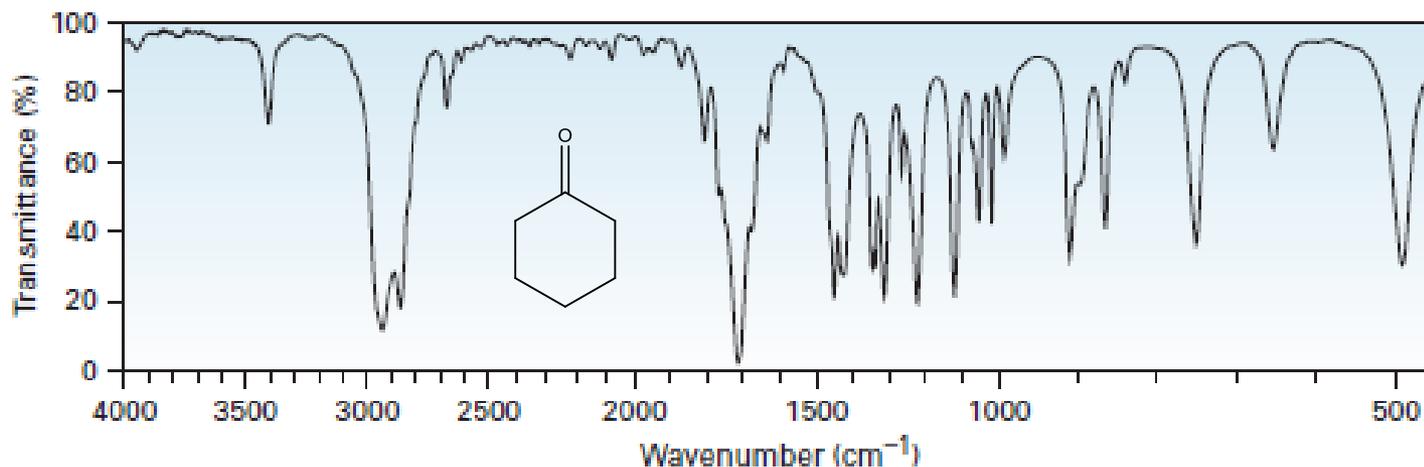
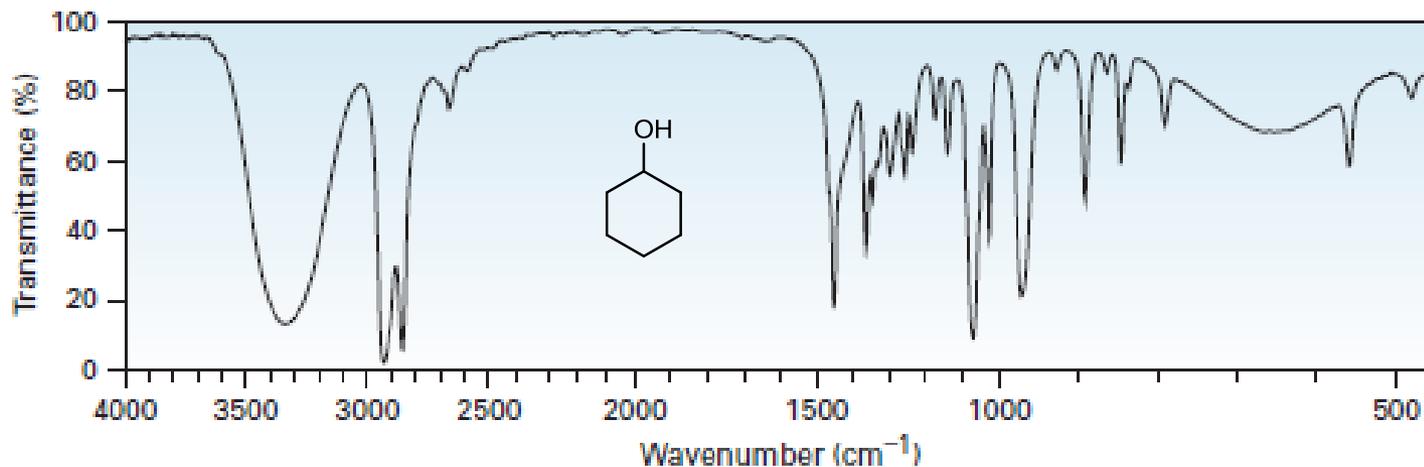
The amount of energy a molecule contains is not continuously variable but is *quantized*. That is, a molecule can stretch or bend only at specific frequencies corresponding to specific energy levels. Take bond stretching, for instance.

Although we usually speak of bond lengths as if they were fixed, the numbers given are really averages. In fact, a typical C-H bond with an average bond length of 110 pm is actually vibrating at a specific frequency, alternately stretching and contracting as if there were a spring connecting the two atoms.

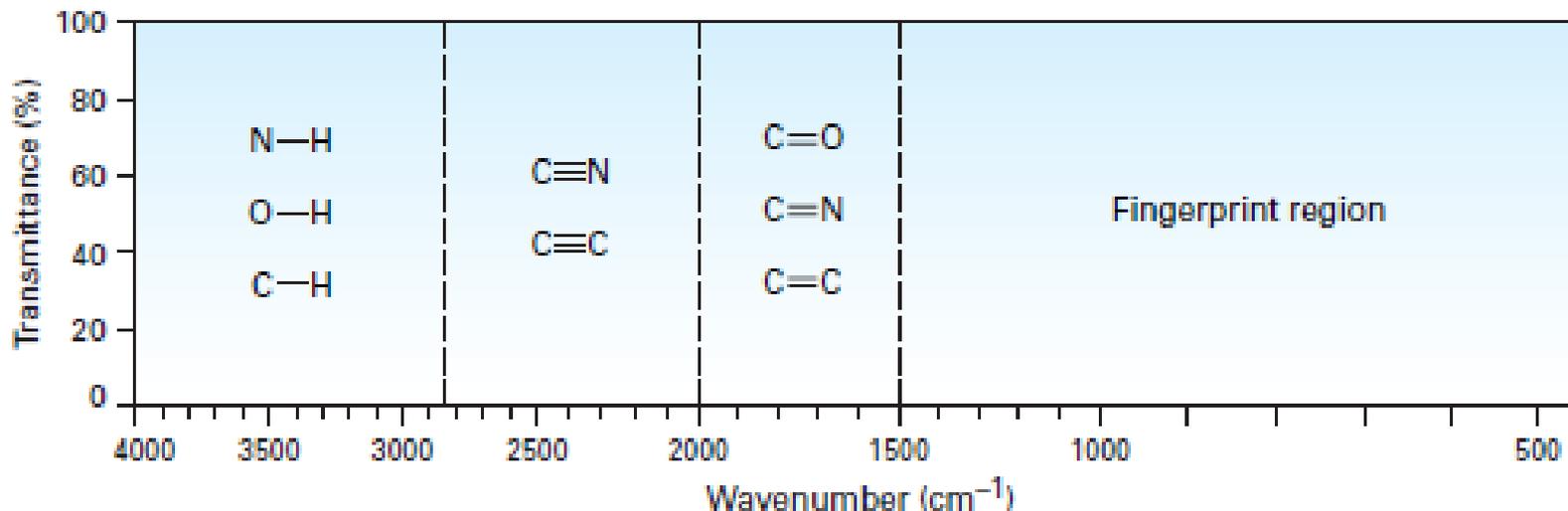
**Table 13.1** Characteristic Infrared Absorptions of Some Functional Groups

Functional Group	Absorption ( $\text{cm}^{-1}$ )	Intensity	Functional Group	Absorption ( $\text{cm}^{-1}$ )	Intensity
Alkane			Amine		
C–H	2850–2960	Medium	N–H	3300–3500	Medium
Alkene			C–N	1030–1230	Medium
=C–H	3020–3100	Medium	Carbonyl compound		
C=C	1640–1680	Medium	C=O	1670–1780	Strong
Alkyne			Aldehyde	1725	Strong
=C–H	3300	Strong	Ketone	1715	Strong
C=C	2100–2260	Medium	Ester	1735	Strong
Alkyl halide			Amide	1690	Strong
C–Cl	600–800	Strong	Carboxylic acid	1710	Strong, broad
C–Br	500–600	Strong	Carboxylic acid		
Alcohol			O–H	2500–3100	Strong, broad
O–H	3400–3650	Strong, broad	Nitrile		
C–O	1050–1150	Strong	C=N	2210–2260	Medium
Arene			Nitro		
C–H	3030	Weak	NO <sub>2</sub>	1540	Strong
Aromatic ring	1660–2000	Weak			
	1450–1600	Medium			

The spectra of cyclohexanol and cyclohexanone show how IR spectroscopy can be used. Although both spectra contain many peaks, the properties absorptions of the different functional groups allow the compounds to be distinguished. Cyclohexanol shows a properties alcohol O-H absorption at  $3300\text{ cm}^{-1}$  and a C-O absorption at  $1060\text{ cm}^{-1}$ ; cyclohexanone shows a properties ketone C=O peak at  $1715\text{ cm}^{-1}$ .



- The region from 4000 to 2500  $\text{cm}^{-1}$  corresponds to absorptions caused by N-H, C-H, and O-H single-bond stretching motions. N-H and O-H bonds absorb in the 3300 to 3600  $\text{cm}^{-1}$  range; C-H bond stretching occurs near 3000  $\text{cm}^{-1}$ .
- The region from 2500 to 2000  $\text{cm}^{-1}$  is where triple-bond stretching occurs. Both  $\text{C}\equiv\text{N}$  and  $\text{C}\equiv\text{C}$  bonds absorb here.
- The region from 2000 to 1500  $\text{cm}^{-1}$  is where double bonds ( $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ , and  $\text{C}=\text{C}$ ) absorb. Carbonyl groups generally absorb in the range 1670 to 1780  $\text{cm}^{-1}$ , and alkene stretching normally occurs in the narrow range 1640 to 1680  $\text{cm}^{-1}$ .
- The region below 1500  $\text{cm}^{-1}$  is the fingerprint portion of the IR spectrum. A large number of absorptions due to a variety of C-C, C-O, C-N, and C-X single-bond vibrations occur here, forming a unique pattern that acts as an identifying fingerprint of each organic compound.



# UV-spectroscopy

A typical UV spectrum – that of buta-1,3-diene – is shown below. Unlike IR spectra, which generally have many peaks, UV spectra are usually quite simple. Often, there is only a single broad peak, which is identified by noting the wavelength at the very top, indicated as max. For buta-1,3-diene,  $\lambda_{\text{max}} = 217 \text{ nm}$ . Note that UV spectra differ from IR spectra in the way they are presented. For historical reasons, IR spectra are usually displayed so that the baseline corresponding to zero absorption runs across the top of the chart and a valley indicates an absorption, whereas UV spectra are displayed with the baseline at the bottom of the chart so that a peak indicates an absorption.

