

CHAPTER 3

INFRARED SPECTROSCOPY

Expected Outcomes

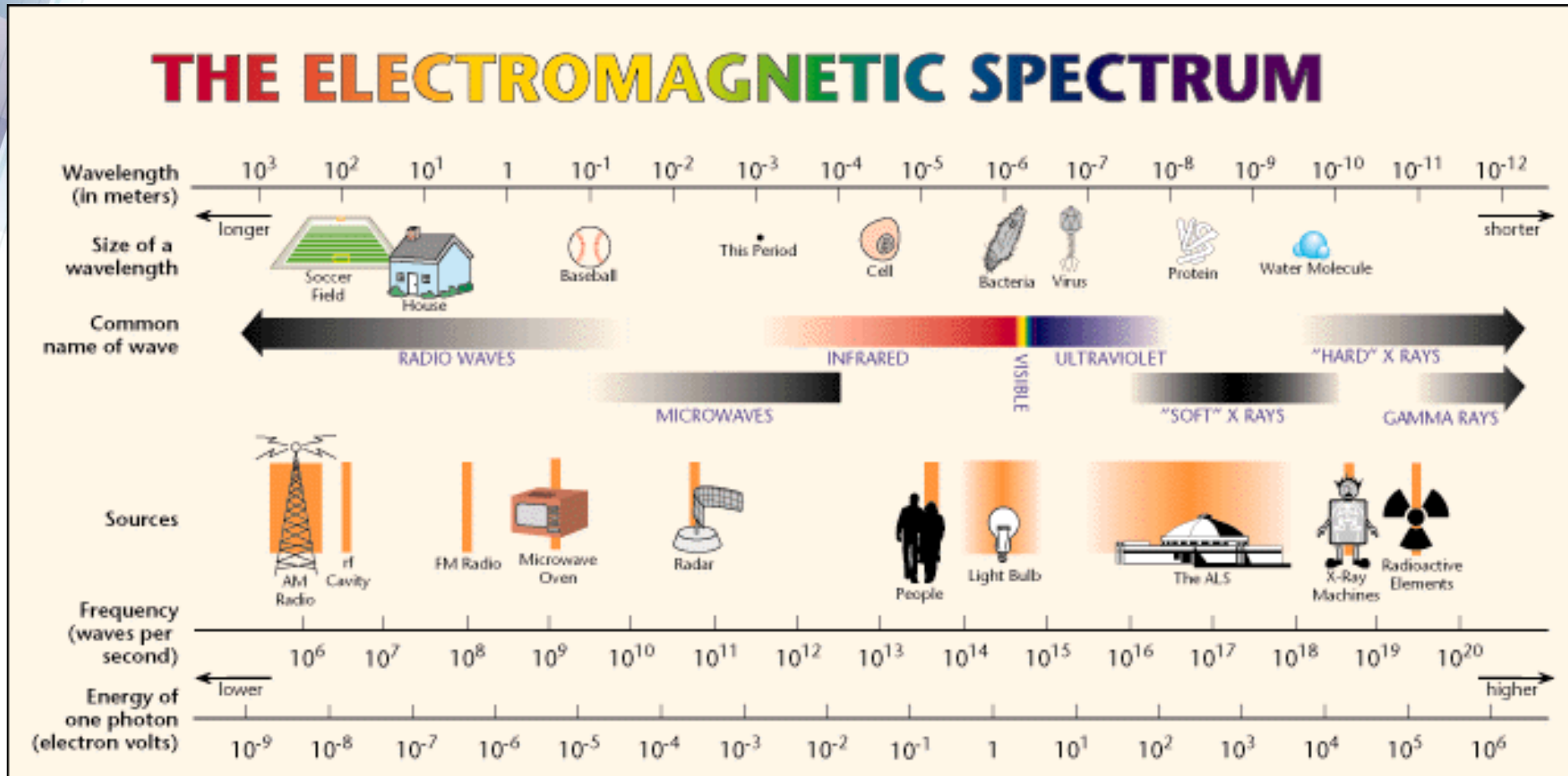
Able to explain the theory of IR spectroscopy

Able to state the function of each components of IR spectroscopy instrumentation

Able to discuss the applications of IR spectroscopy

Electromagnetic spectrum

THE ELECTROMAGNETIC SPECTRUM



<http://mail.colonial.net/~hkaite/electromagspectrum.html>

IR spectrum

Region	Energy (kJ/mol)	Wavenumber (cm ⁻¹)	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

3.1 Theory of Infrared Spectroscopy

- Two major types of molecular vibrations:
 1. **Stretching** vibration
 2. **Bending** vibration

Theory of Infrared Spectroscopy

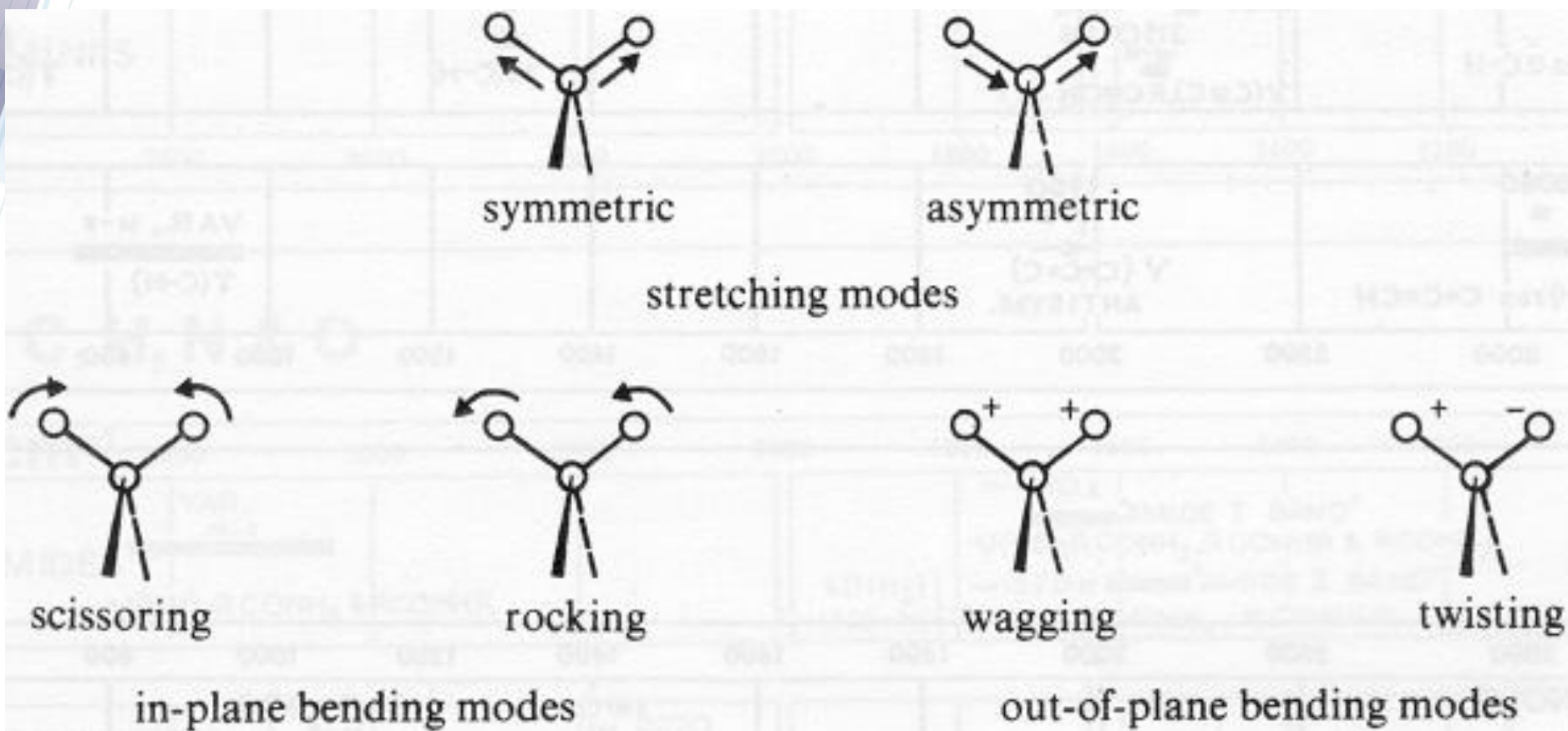
Stretching vibration

- a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing

Bending vibration

- Consist of a change in bond angle between two atoms and a third atom

Theory of Infrared Spectroscopy



(Picture taken from Principles and Practice of Analytical Chemistry by FW Fifield & D Kealey Pg 385)

Theory of Infrared Spectroscopy

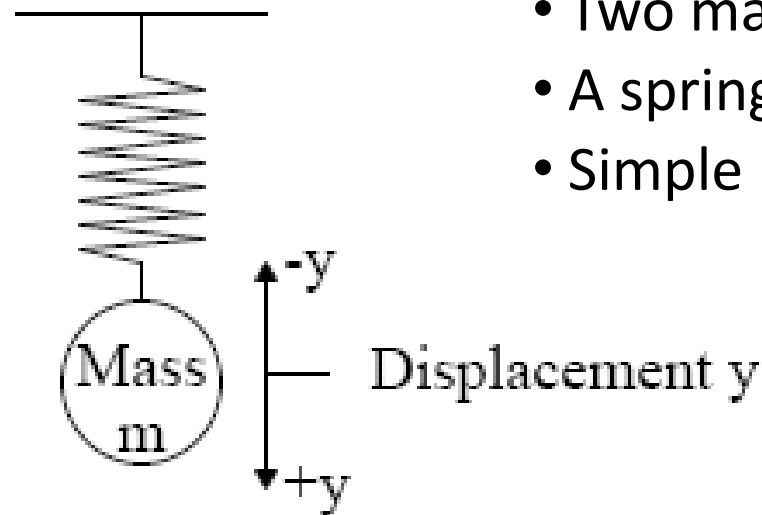
Conditions for IR spectra

- Molecules have a natural frequency of vibration equal to the frequency of incident radiation.
- Change in bond length or bond angle due to vibration must cause a change in the dipole moment of the molecule.
- Radiation energy absorbed must correspond to the energy difference of the ground and excited states of the molecules i.e $E = h\nu$ must be satisfied

Classical vibrational motion

- Mechanical model

- Two masses
- A spring
- Simple harmonic motion



Force required to displace m is

$$F = -k \cdot y$$

Hooke's Law

spring constant (N/m)

Energy of the Hooke's law

Energy is force \times distance

$$dE = -Fdy$$

$$dE = kydy$$

Total Energy

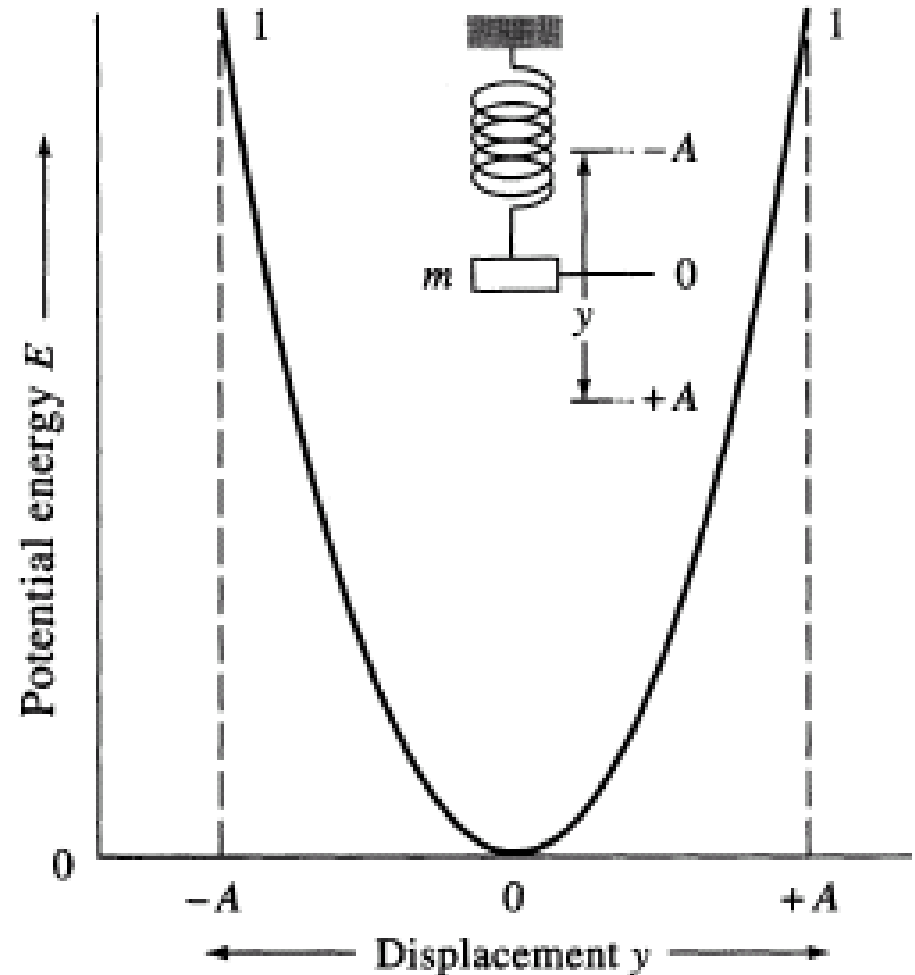
$$\int_0^E dE = k \int_0^y ydy$$

$$E = \frac{1}{2}ky^2$$

- Negative sign force
 - Restoring force
 - Direction of the force is opposite to the displacement

Harmonic Oscillator Potential

- Potential high
 - When the spring is compressed or stretched
- Parabola function
 - $E = (1/2)ky^2$
 - Minimum at equilibrium position
 - Maximum at max amplitude A



Classical vibrational frequency

- $F = ma = m(d^2y/dt^2)$
- $F = -ky$
- Solution of differential equation
 - $Y = A \cos(2\pi\nu t)$
 - $D^2y/dt^2 = -4\pi^2\nu^2 A \cos(2\pi\nu t)$
 - Reduced mass for two masses

$$\nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \nu \text{ independent of energy}$$

Two masses?

$$\nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad \text{reduced mass}$$

Quantum treatment of vibrations

$$E = \left(\nu + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = \left(\nu + \frac{1}{2} \right) h \cdot \nu_{\text{classical}}$$

Vibrational quantum number (0, 1, 2...)

$$E_0 = \frac{1}{2} h \nu_{\text{classical}}$$

Ground vibrational state ($\nu = 0$)

$$E_1 = \frac{3}{2} h \nu_{\text{classical}}$$

First excited state ($\nu = 1$)

$$\Delta E = h \nu_{\text{classical}}$$

$$\nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$E_{\text{radiation}} = h\nu = \Delta E = h\nu_{\text{classical}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\nu = \nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Quantum treatment of vibrations

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}$$

$$\nu = \nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Frequency, $\nu = c / \lambda$

Wavenumber, $\bar{\nu} = 1 / \lambda$

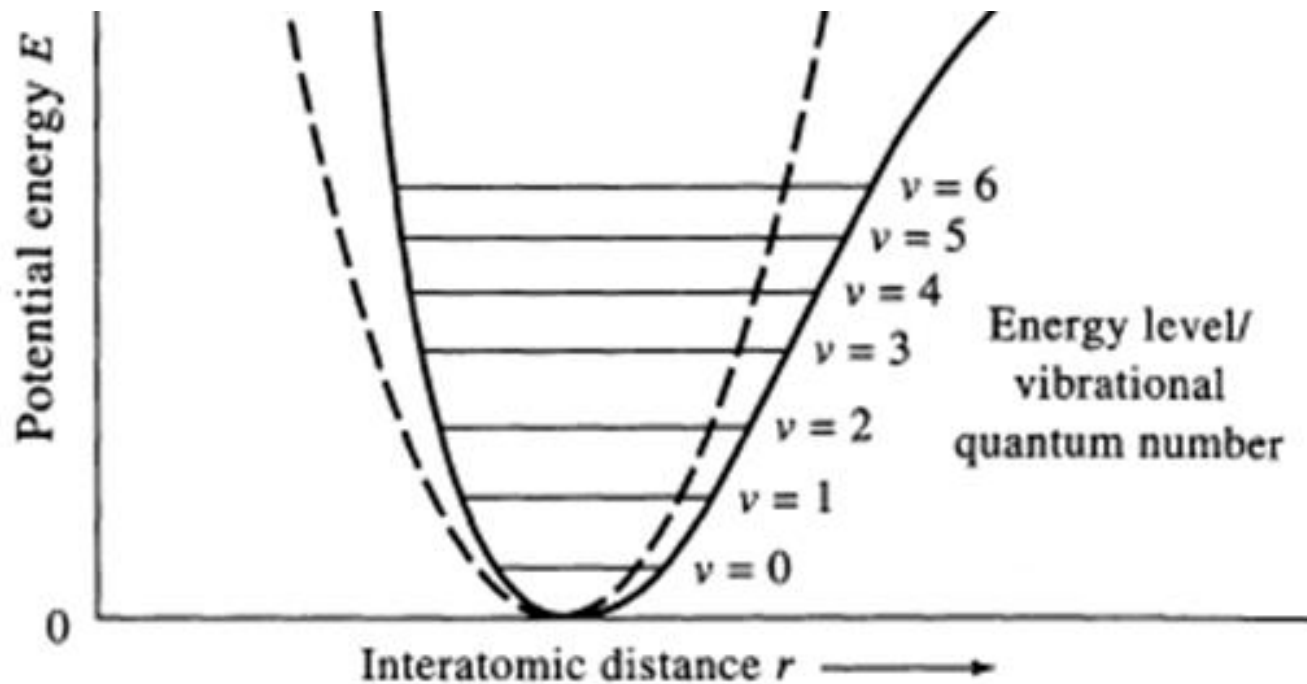
$$\therefore \bar{\nu} = \nu / c$$

- $\bar{\nu}$ = wavenumber = cm^{-1}
- k = force constant = N m^{-1}
 - Single bond $\sim 5 \times 10^2 \text{ N m}^{-1}$
 - Double bond $\sim 1 \times 10^3 \text{ N m}^{-1}$
 - Triple bond $\sim 1.5 \times 10^3 \text{ N m}^{-1}$
- c = velocity of light = cm s^{-1}
- μ = reduced mass = kg

Quantum treatment of vibrations

(2) $\Delta v = \pm 1$ Vibrational Selection Rule

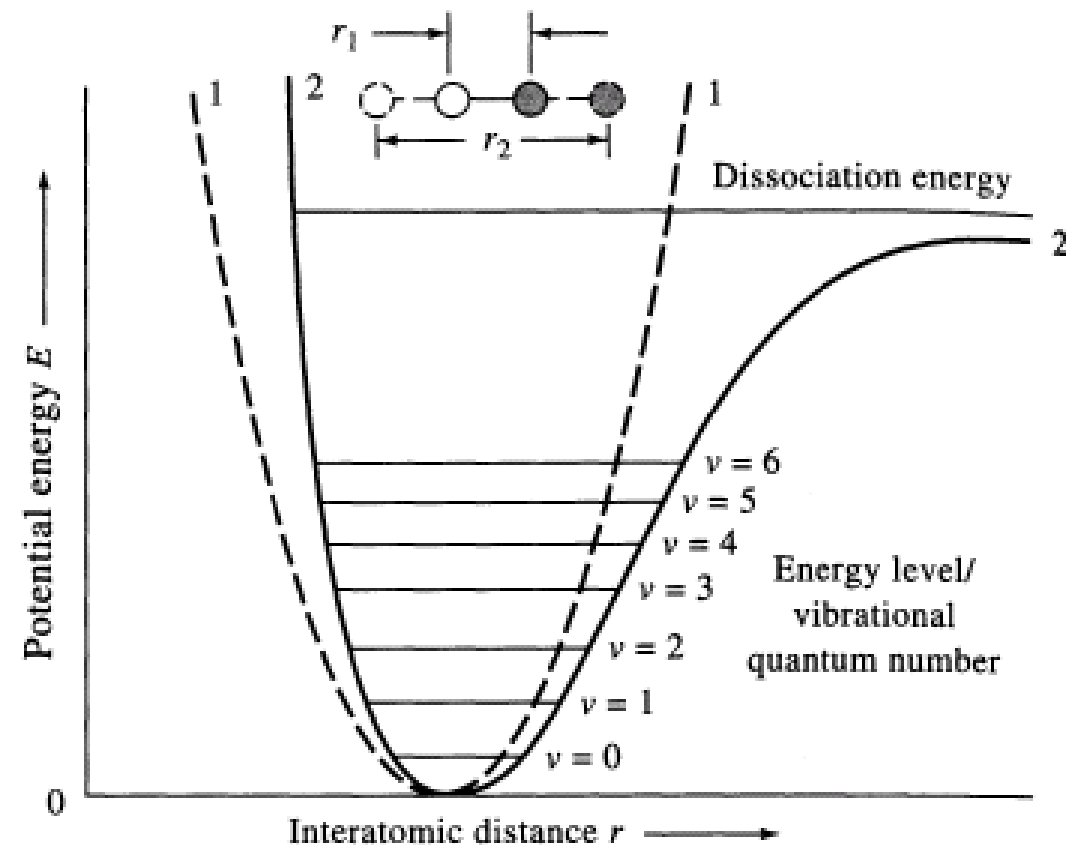
Since levels equally spaced - should see one absorption frequency



Anharmonic Oscillator

- Must modify harmonic oscillator potential for
 - electron repulsion
 - Potential energy increases rapidly at small distances
 - dissociation
 - bond breaks at large distances

Anharmonicity



- Harmonic at low v
- ΔE becomes smaller at high v
 - broadens band
- Selection rule fails $\Delta v = \pm 1$ and $\Delta v = \pm 2 \dots$
 - overtones

Vibrational Normal modes

- $3N$ degrees of freedom for N atoms
 - 3 translation
 - 3(or 2) rotation – rotation about the bond axis is not possible
 - Others are "Normal modes"

- Number of possible vibrations in a polyatomic molecule
 - 2 atoms (H_2) - 1 vibration
 - 3 atoms (H_2O) - 3 vibrations
 - 3 atoms (CO_2) - 4 vibrations
 - 4 atoms (H_2CO) - 6 vibrations
 - 5 atoms ...
 - **$3N - 6$ Non - linear molecule**
 - **$3N - 5$ Linear molecule**

Fewer experimental peaks

- Fewer peaks
 - Symmetry of the molecule
 - Degenerate
 - Energies of two or more vibrations are identical
 - Or nearly identical
 - Undetectable low absorption intensity
 - Out of the instrumental detection range
- More peaks
 - Overtone
 - Combination bands

Vibrational coupling

- Coupling of different vibrations shifts frequencies
- Energy of a vibration is influenced by coupling
- Coupling likely when
 - common atom in stretching modes
 - common bond in bending modes
 - common bond in bending+stretching modes
 - similar vibrational frequencies
- Coupling not likely when
 - atoms separated by two or more bonds
 - symmetry inappropriate

3.2 Instrumentation of IR Spectroscopy

Instrument Components

- Radiation source
- Monochromator
- Sample cells
- Detector

Instrumentation of IR Spectroscopy

Radiation source

Three popular sources are:

1. Nernst glower – constructed of rare earth oxides.
2. Globar – constructed of silicon carbide.
3. Nichrome coil.

Instrumentation of IR Spectroscopy

1. Nernst Glower

- Rod made up of mixture of rare earth oxides.
- These oxides have negative temperature resistance and is non-conducting at room temperature.
- Heat is required to excite the element to emit radiation. (Heated temperature is 1500 – 2000°C).

Instrumentation of IR Spectroscopy

2. Globar

- Bar of sintered silicon carbide heated to 1500-1700°C.
- Less intense source than nernst glower but is more useful for wavelength longer than 15 μm .

Instrumentation of IR Spectroscopy

Nernst glower and Globar

- These 2 sources fulfill 2 requirements:
 - Constant over long periods of time
 - Provide whole range of Infrared region ($2\ \mu\text{m}$ to $15\ \mu\text{m}$)

Instrumentation of IR Spectroscopy

Monochromator

- Prisms or gratings are the dispersive components used in conjunction with variable-slit mechanisms, mirrors, and filters.
- Prisms used: Made up of metal halide prism
 - NaCl – for region from 2.5 to 15.4 μm .
 - KBr – for 10 to 25 μm .
 - CsCl – for 10 to 38 μm .

Instrumentation of IR Spectroscopy

Limitations

- Mechanical and thermal instability
- Water soluble

Note : Glass prism cannot be used as glass absorbs Infrared radiation.

Instrumentation of IR Spectroscopy

Sample cell

- Materials containing the sample must always be transparent to IR
e.g. NaCl, KBr
- Material depends on wavelength range to be studied
 - 2.5 – 15.0 μm NaCl
 - 2.1 – 26.0 μm KBr
 - 0.26 – 55.0 μm CsI

Instrumentation of IR Spectroscopy

Detector

- Thermal detectors – measure the heating effect produced by IR radiation, e.g. thermocouples and Golay detectors.
- Photon detectors – rely on the interaction of IR radiation and a semiconductor material.

Instrumentation of IR Spectroscopy

Two types of instrument

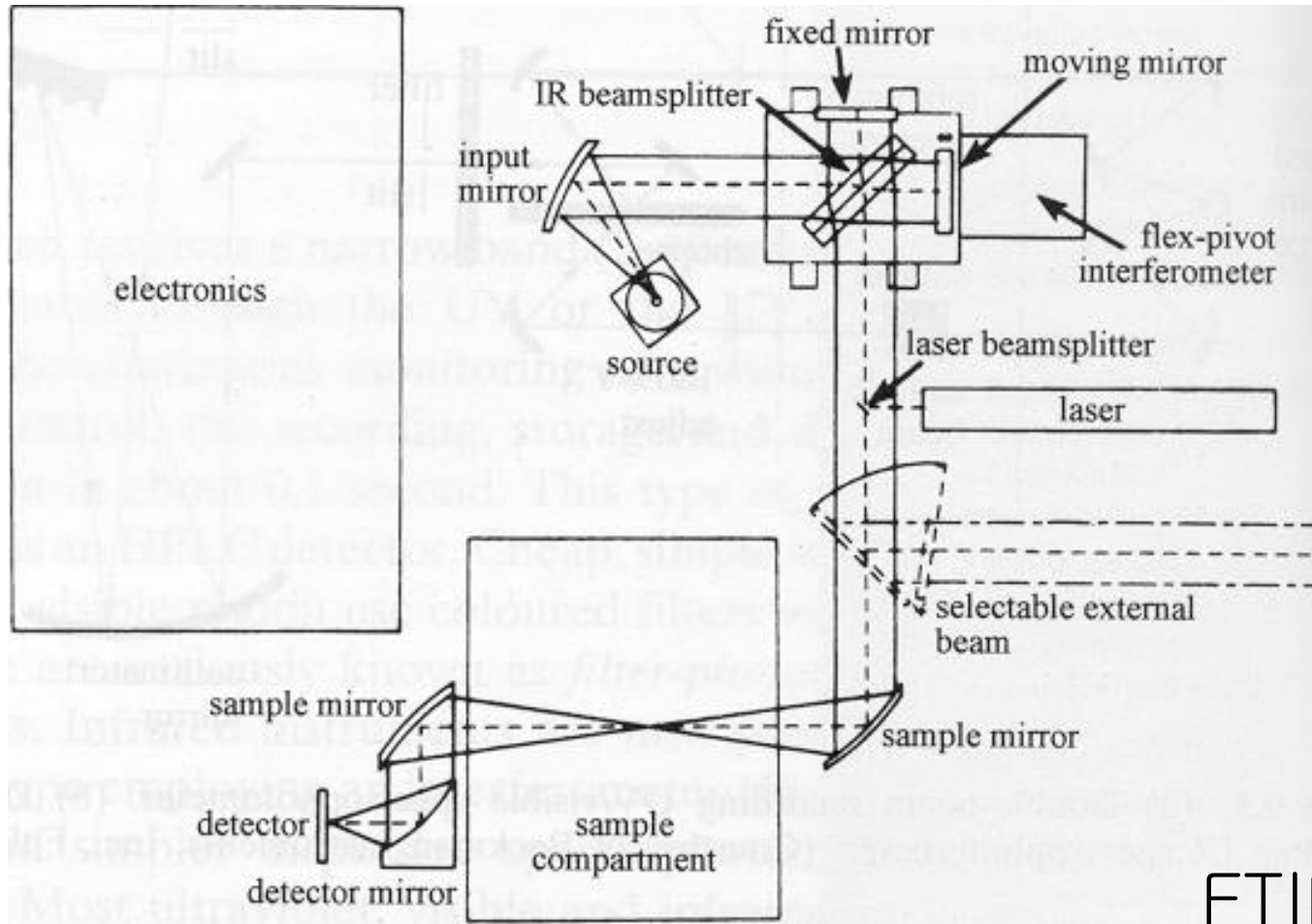
1. Dispersive instrument
2. Fourier Transform IR Spectrometers (FTIR)

Instrumentation of IR Spectroscopy

Fourier Transform IR Spectrometers (FTIR)

- Have recently replaced dispersive instrument for most applications due to their superior speed and sensitivity.
- 10 to 400 cm^{-1} is hard to access by conventional IR spectrometers.
- The Michelson interferometer is a basic component of the Fourier transform instrument.

Instrumentation of IR Spectroscopy



FTIR

(Picture taken from Principles and Practice of Analytical Chemistry by FW Fifield & D Kealey, page 358)

Instrumentation of IR Spectroscopy

- Dispersive instrument uses a monochromator to select each wavenumber in turn in order to monitor its intensity after the radiation has passed through the sample
- In a Fourier transform IR instrument the principles are the same except that the monochromator is replaced by an interferometer.
- An interferometer uses a moving mirror to displace part of the radiation produced by a source thus producing an interferogram.

Advantage of the FT-IR

- Full spectra can be acquired in 1 sec compared to the 2-3 min required for a dispersive instrument to acquire a spectrum.
- The instrument is attached to a computer thus several spectral scans can be taken and averaged in order to improve the signal:noise ratio for the spectrum.

Instrumentation of IR Spectroscopy

Sample Preparation

- Solid sample
- Liquid sample
- Gas sample

Instrumentation of IR Spectroscopy

SOLID sample

1. Mull method
2. KBr disc method
3. Cast Film method

Instrumentation of IR Spectroscopy

1) Mull method

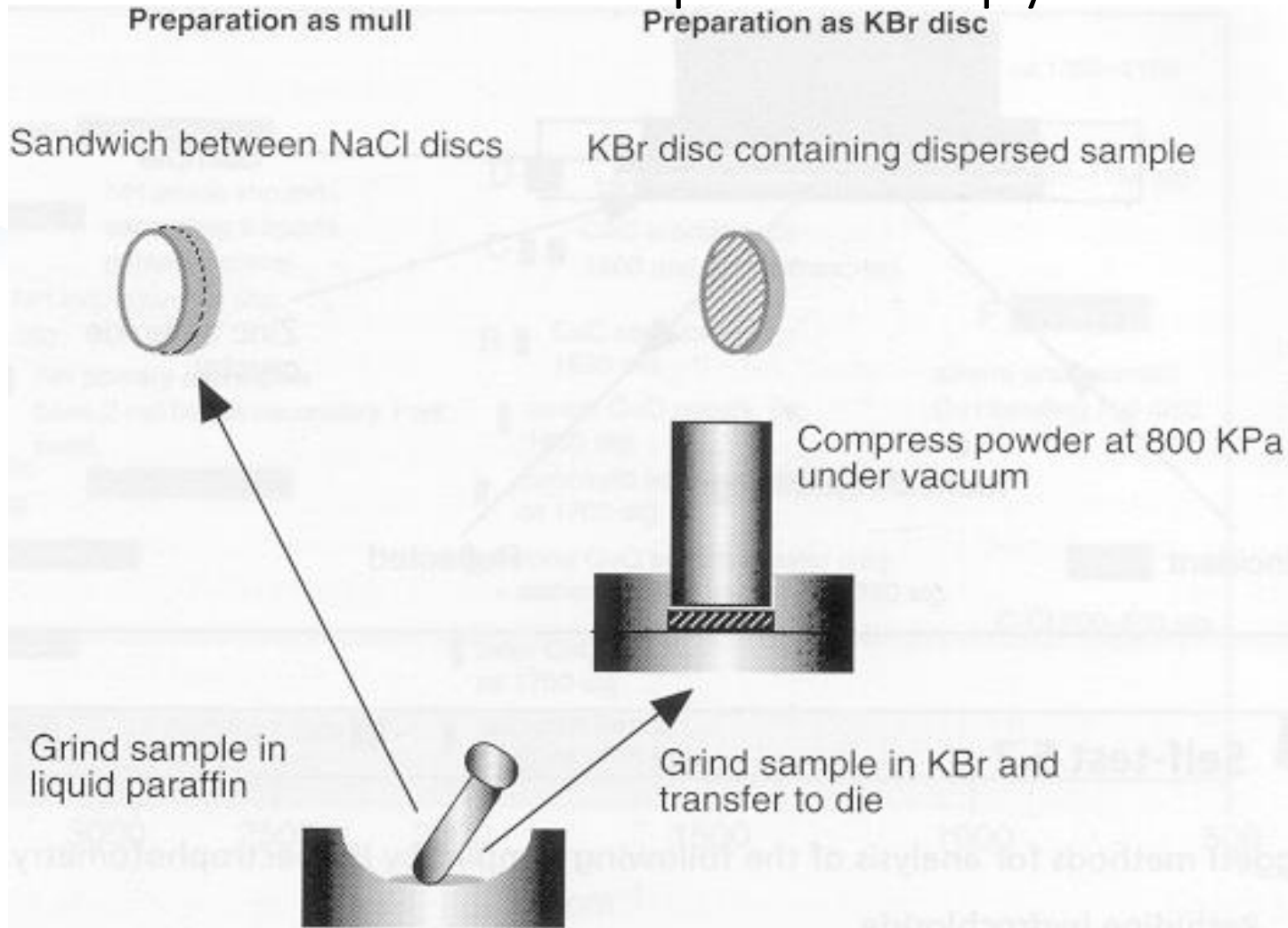
- Grind powder and mix powder into a thick slurry or mull with a greasy, viscous liquid (e.g Nujol[®], paraffin oil) or chlorofluorocarbon (Fluorolube[®]).
- Smear mull on NaCl disc.
- Quick, but the resulting spectra are more complicated.
- Good for qualitative but not quantitative analysis.

Instrumentation of IR Spectroscopy

2) KBr Disc method

- Mix 1 part finely ground solid sample with 100 parts powdered KBr.
- Press mixture under high pressure to form small disc about 1 cm in diameter and 1 to 2 mm thickness.
- The KBr becomes transparent when subjected to pressures of 10,000 to 15,000 psi.
- Disc is transparent to IR radiation and analyzed directly.

Instrumentation of IR Spectroscopy



(Picture taken from Pharmaceutical Analysis by David G. Watson, page 103)

Instrumentation of IR Spectroscopy

3) Cast Film method

- Mainly for polymeric compounds
- Dissolve sample in a suitable, non-hygroscopic solvent
- Deposit a drop of this solution on the surface of KBr or NaCl cell.
- Evaporate solution to dryness to form a film for analysis
- Suitable only for qualitative analysis

Instrumentation of IR Spectroscopy

LIQUID Sample

- Pour the liquid sample into circular cells made up of NaCl and KBr
- Determine directly
- Qualitative and quantitative analysis
- No single solvent is transparent in mid IR region
- Water & alcohols are not favored to be used.

Instrumentation of IR Spectroscopy

GAS sample

- Gas sample cell made up of KBr or KCl
- Cells are 10cm to 1m to compensate for the small number of molecules in the sample.
- Suitable only for qualitative analysis.

3.3 Applications of IR spectroscopy

- **Chemical Analysis:**
 - Match spectra to known databases
 - Identifying an unknown compound, Forensics, etc.
 - Monitor chemical reactions *in-situ*
- **Structural ideas:**
 - Can determine what chemical groups are in a specific compound
- **Electronic Information:**
 - Measure optical conductivity
 - Determine if Metal, Insulator, Superconductor, Semiconductor
 - Band Gaps, Drude model

Qualitative application of IR

- To determine the structure, identity, of organic compounds.
- Each molecule has a distinctive IR absorption spectrum or ‘fingerprint’.
- For a wide range of sample types: gases, liquids, and solids.

Qualitative application of IR

- Most molecules are in constant modes of rotation and / or vibration at temperatures above absolute zero.
- This rotation, stretching, and bending of molecular bonds happens to occur at frequencies found in the IR spectral region.
- These vibrational frequencies will vary as the bonded atoms, functional groups, and bond strengths are changed;
- Typically an organic compound is ultimately identified by comparing its IR absorption spectrum to that of a known compound.
- Functional-group region - relatively easy to assign structures to the absorption bands.

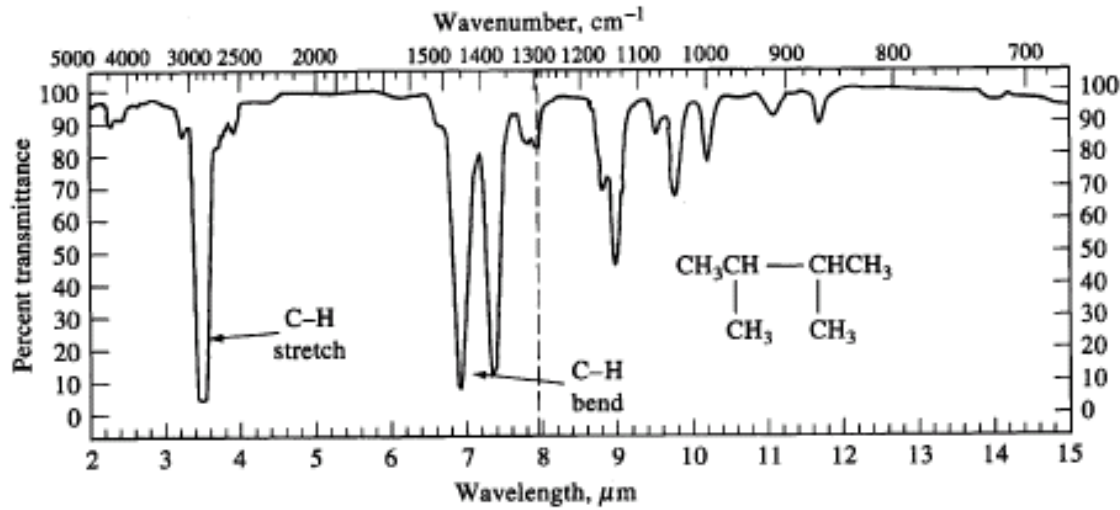
Qualitative application of IR

- A qualitative fingerprint check for the identity of raw material used in manufacturing and for identifying drugs.
- Used in synthetic chemistry as preliminary check for compound identity particularly for carbonyl group
- Can be used to characterize samples in the solid and semi-solid states such as creams and tablets
- Used as a fingerprint test for films, coatings and packaging plastics.

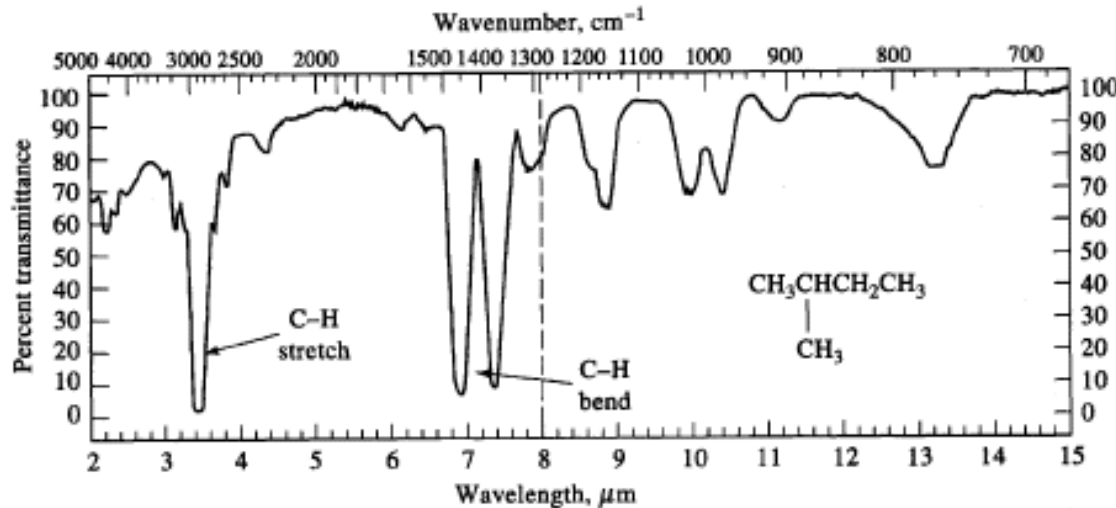
Qualitative analysis of IR

- Step One : Identify functional groups (group frequency region)
 - 1200 - 3600 cm^{-1}
- Step Two : Compare with standard spectra containing these functional groups
 - fingerprint region – sensitive to the structure
 - 600 – 1200 cm^{-1}

Group frequency and fingerprint region



(a)



(b)

Group frequency region Fingerprint region

Group frequencies

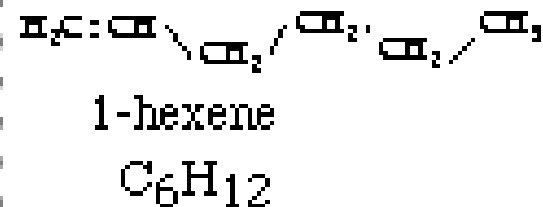
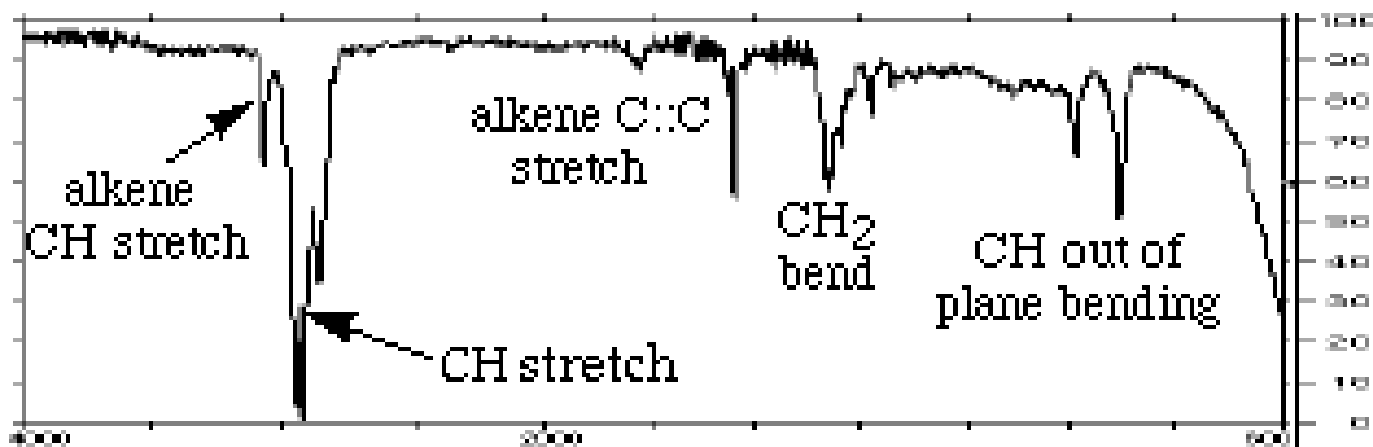
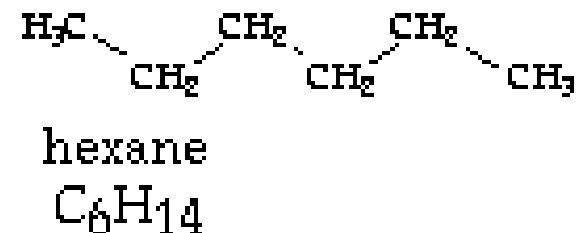
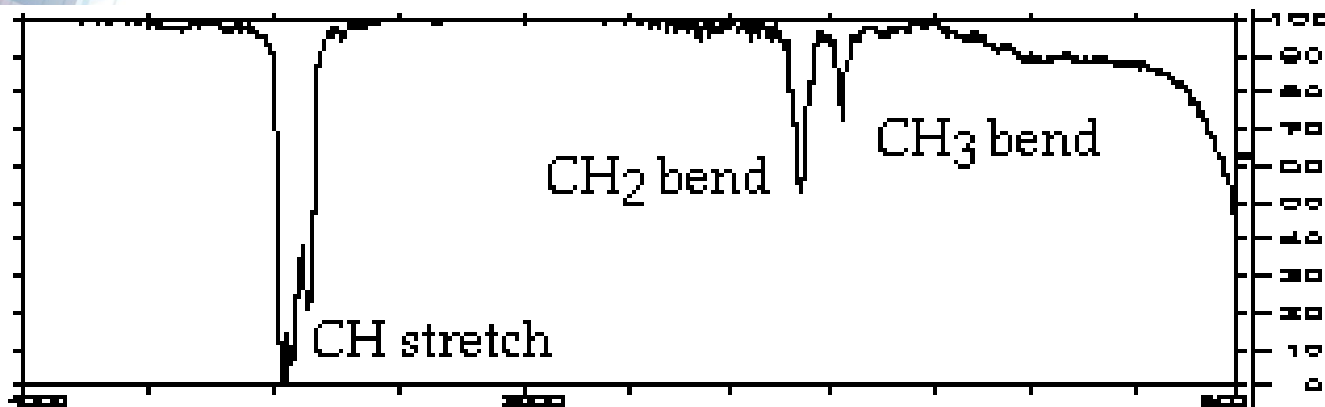
- Approximately calculated from masses and spring constants
 - Variations due to coupling
 - Compared to correlation charts/databases
 - Bond force constant

Group frequency table for organic groups

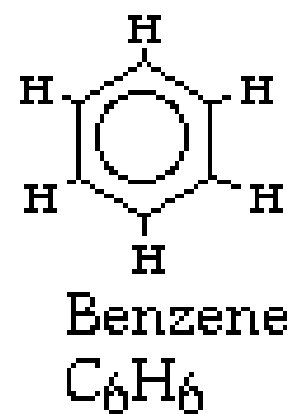
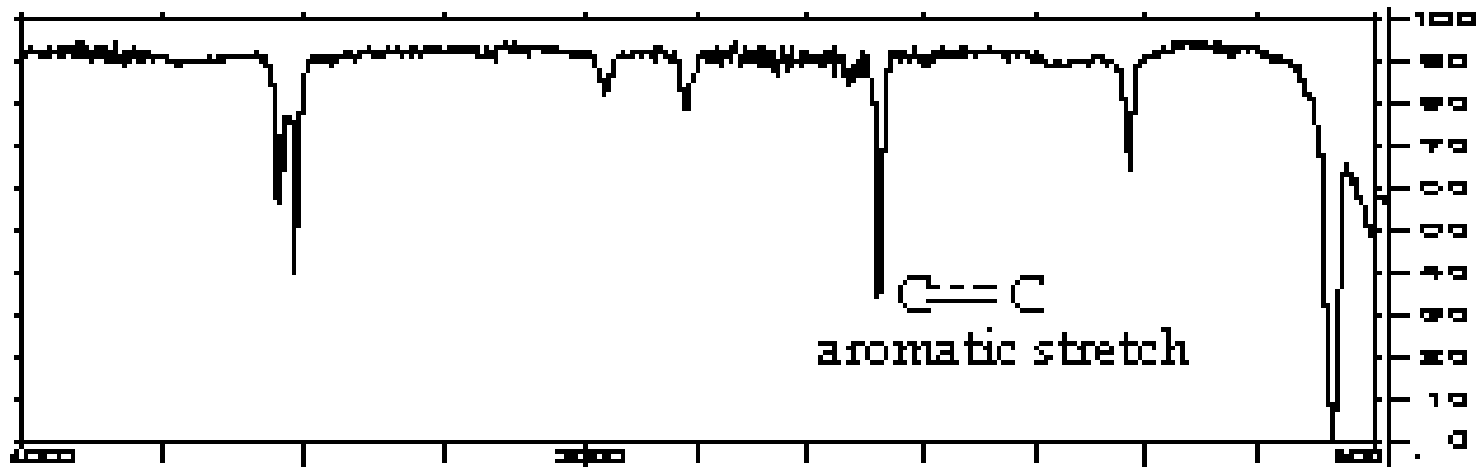
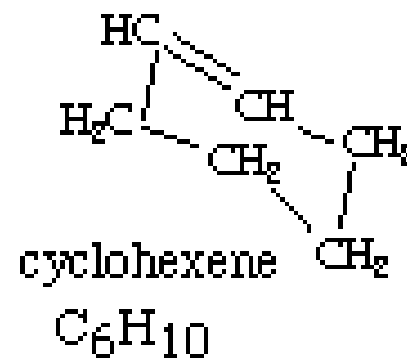
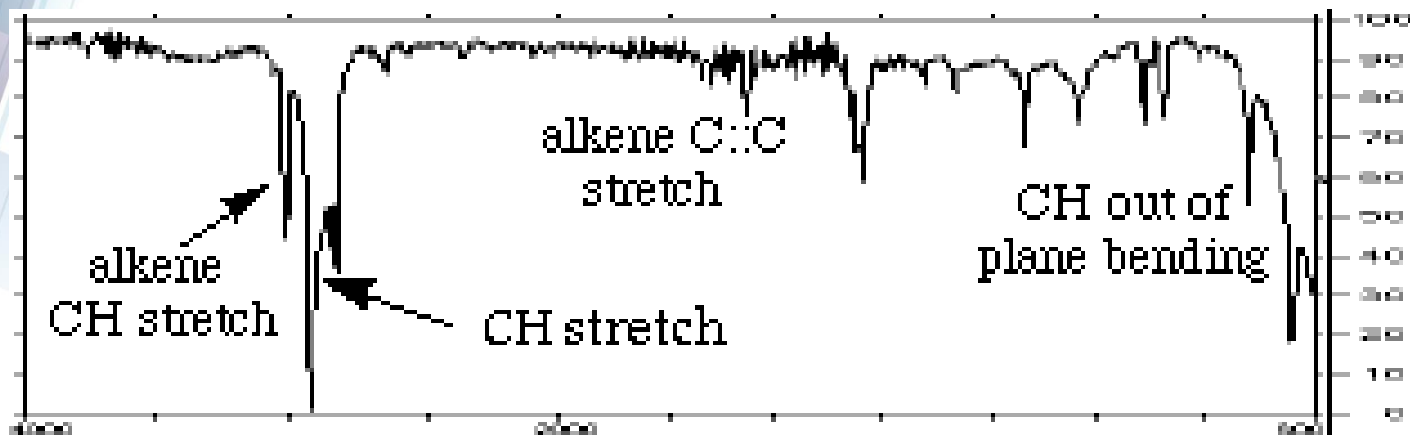
TABLE 17-2 Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<H)	3010–3095	Medium
		675–995	Strong
C—H	Alkynes ($\text{—C}\equiv\text{C—H}$)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO ₂	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

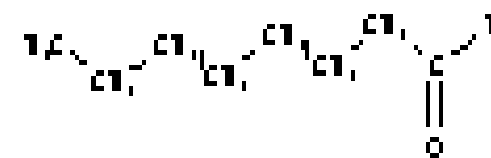
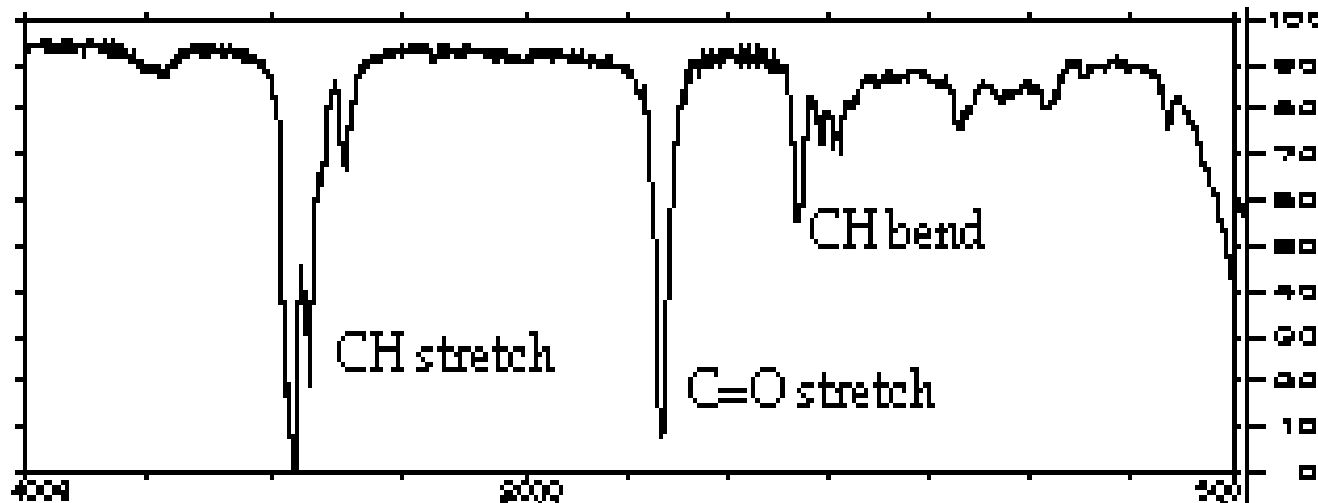
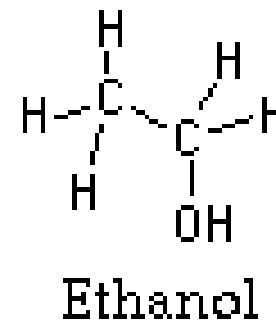
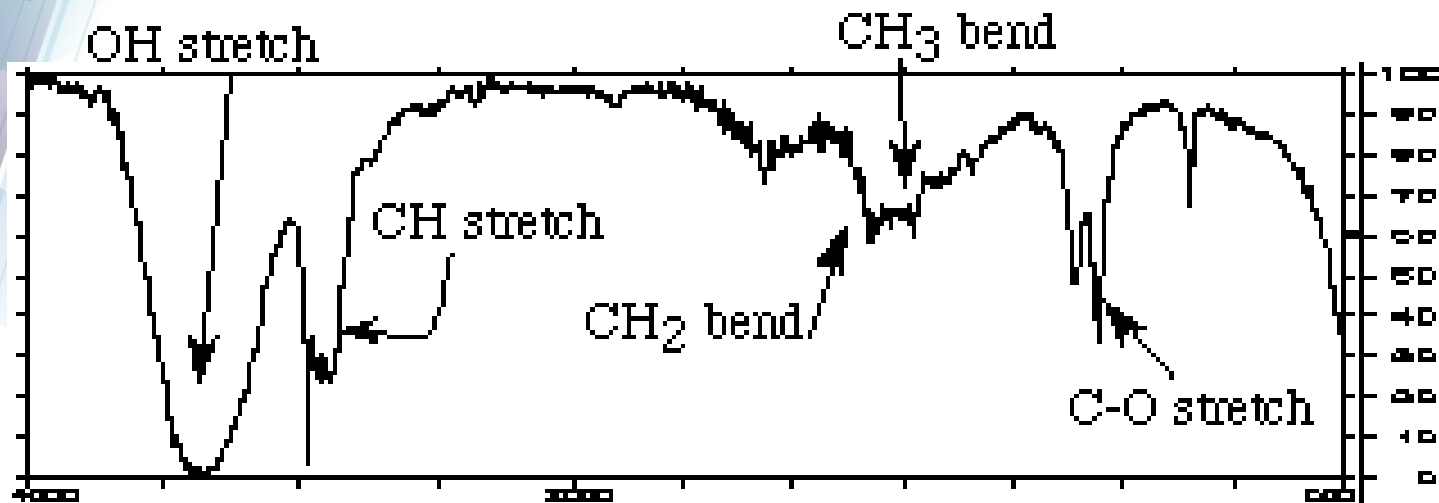
IR Peaks Assignment



IR Peaks Assignment

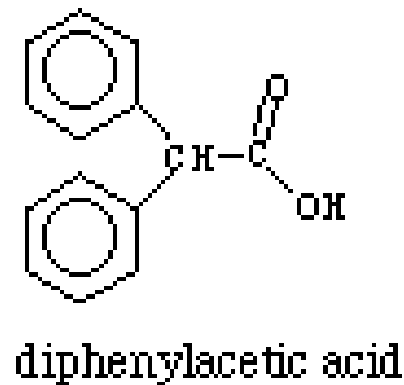
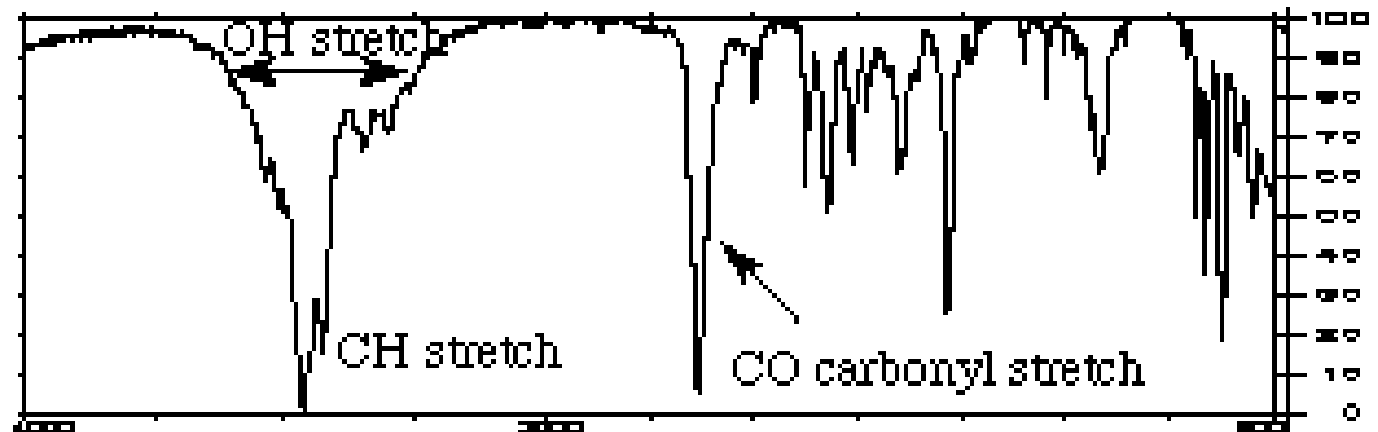
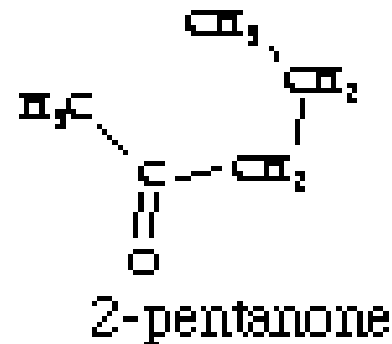
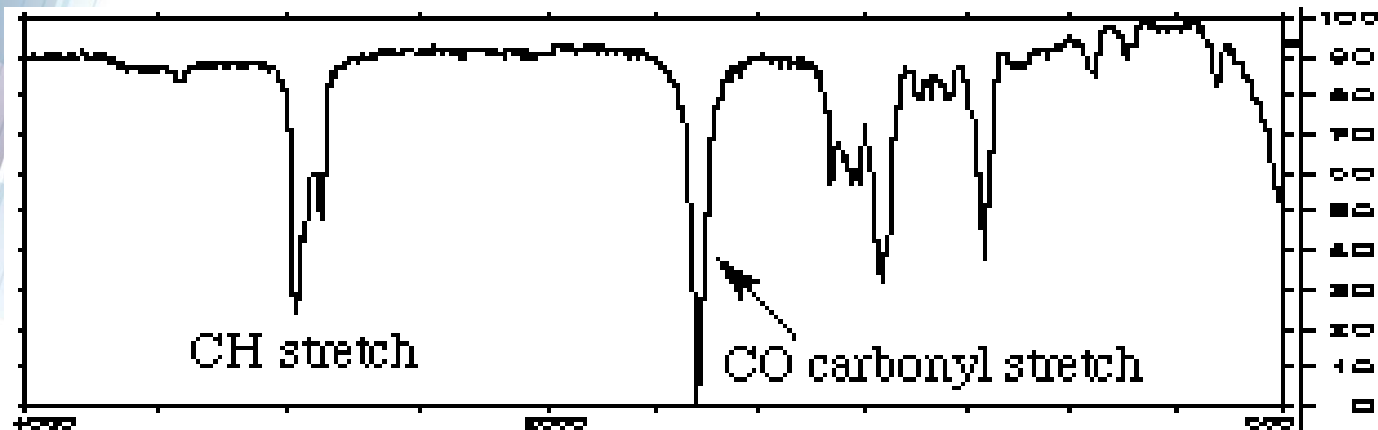


IR Peaks Assignment



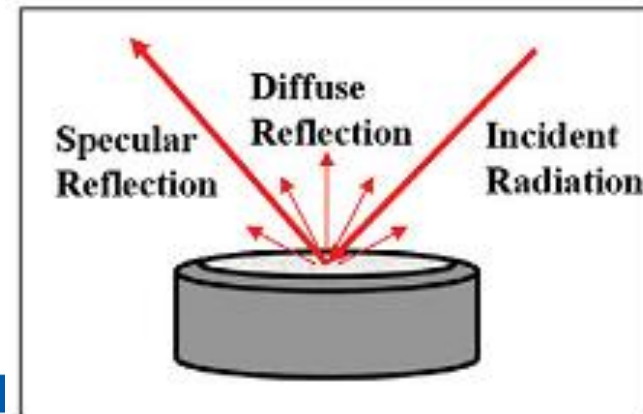
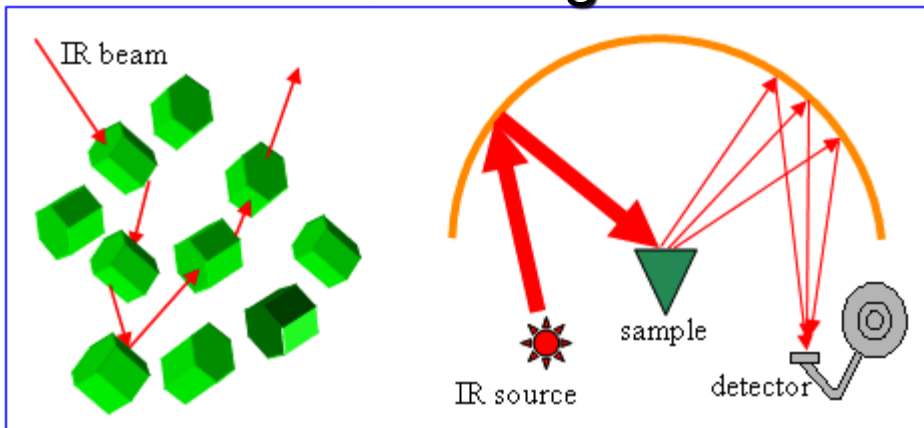
octanal
C₈H₁₆O

IR Peaks Assignment



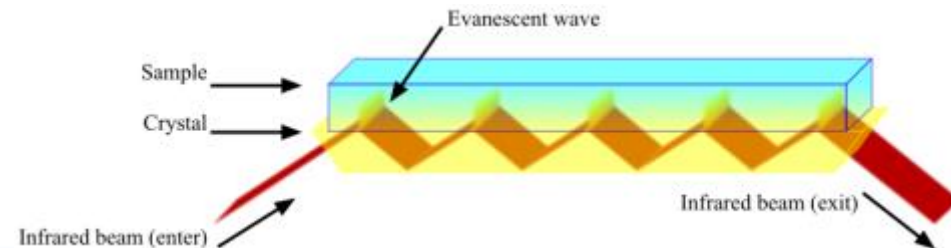
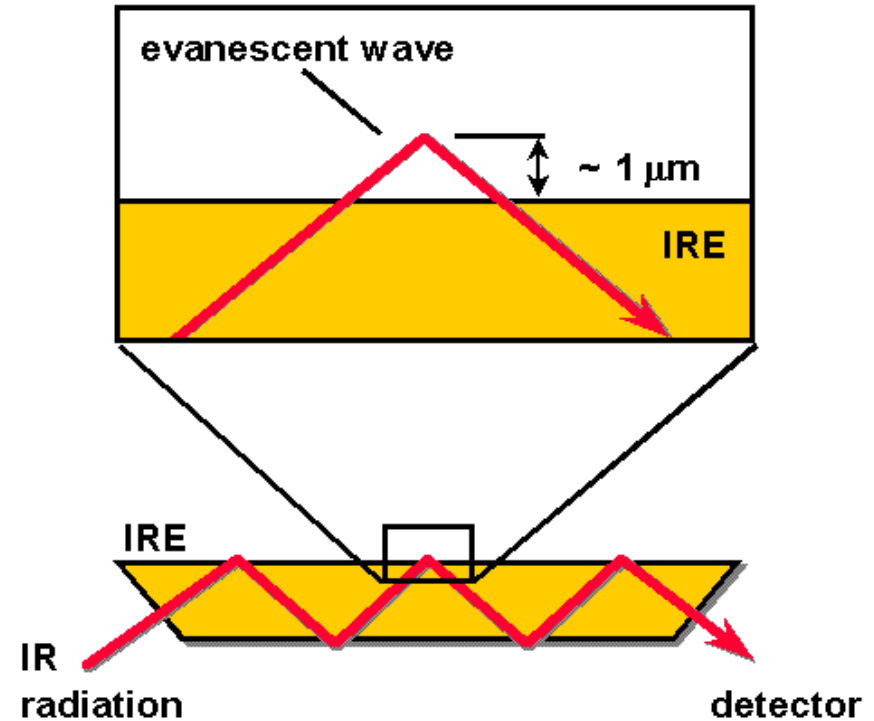
DRIFTS (Diffuse Reflectance IR FT Spectroscopy)

- Powder samples are ground and mixed with IR transparent salt (KBr)
 - to ensure deeper penetration of incident radiation
 - to increase scattering
 - to minimize the specular reflection
- Sample particle size less than 50 microns
- Larger particle size – scattering of energy – baseline shift – IR bands broadening

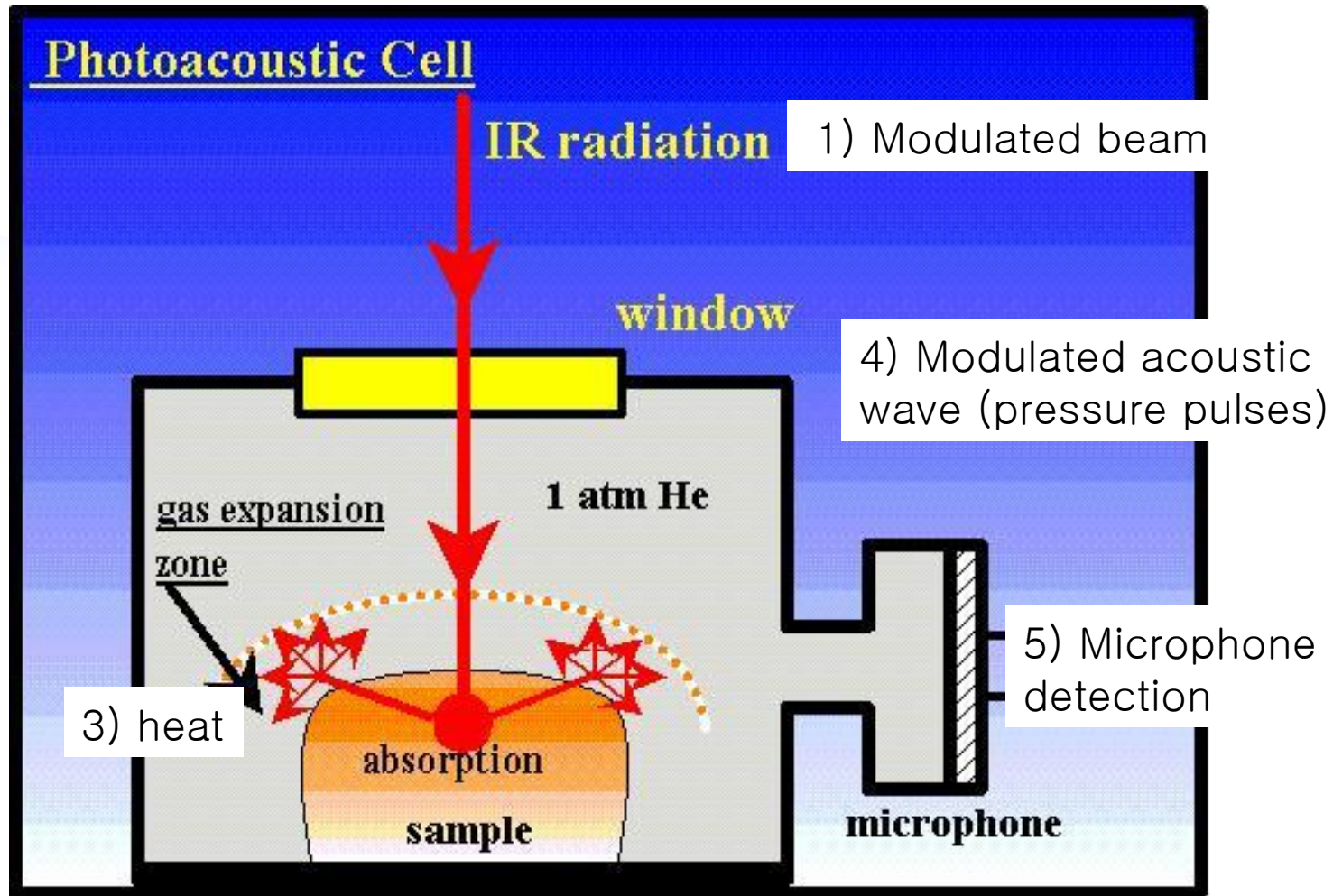


ATR (Attenuated Total Reflectance)

- Sample – wide variety of types
 - solids of limited solubility, Films, Threads, Pastes, Adhesives, Powders
- Principles of the method
 - At a certain angle, total reflection can occur
 - Depth of penetration when reflected
 - Evanescent wave can be absorbed by the sample
- High refractive index ATR crystal
 - Thallium bromiodide (KRS-5)
 - Germanium



Photoacoustic IR Spectroscopy



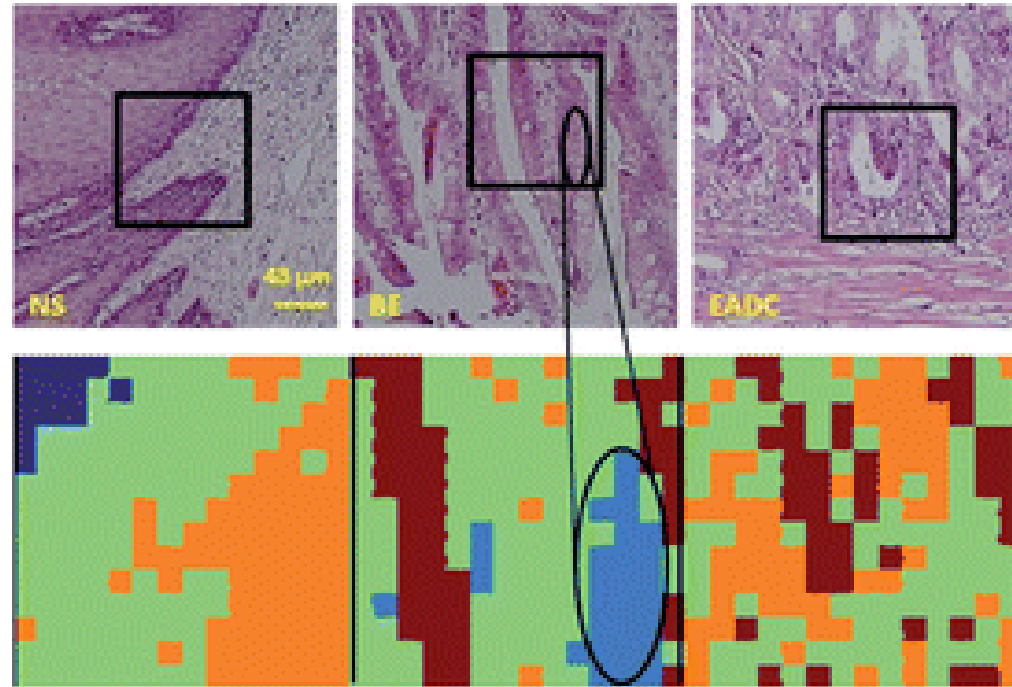
2) Absorption of IR by sample causes nonradiative decay of excited vibration states

Near IR Spectroscopy

- Spectrum
 - 770-2500 nm
 - 13000 – 4000 cm^{-1}
 - Overtone or combination of fundamental stretching modes
 - C-H, N-H, O-H
 - Weaker absorption than fundamental bands
- Disadvantages
 - Low molar absorption coefficient
 - Detection limit 0.1%
- Application
 - Mostly qualitative analysis
 - Water, protein, low mw carbohydrates, food, petroleum

IR microscopy

- IR abs or reflection spectra
- Sample dimensions in 10 -500 μm
- Instrument
 - Ordinary optical microscope
 - FT-IR with small IR beam size



FTIR microscopy tissue screening
for biomarkers

Luca Quaroni and Alan G. Casson, *Analyst*, 2009, 134, 1240

Nicolet Magna 760 with Nic-Plan IR Microscope

