About this part of the module:

Topics to be covered:

1. Introduction to infra Red spectroscopy
2. Effects on IR bands (H-bonding effect).
3. Sampling techniques.
4. Interpretation of IR spectra.
5. Characteristic group frequencies of organic compounds.
6. Fingerprint regions.
7. Application of IR spectroscopy.
8. Problems and solutions.

IR Spectroscopy

I. Introduction

A. **Spectroscopy** is the study of the interaction of matter with the electromagnetic spectrum

1. Electromagnetic radiation displays the properties of both particles and waves

2. The particle component is called a ***photon***

3. The energy (**E**) component of a photon is proportional to the frequency. Where **h** is Planck's constant and ν is the frequency in Hertz (cycles per second)

$$\mathbf{E = h\nu}$$

4. The term "photon" is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light – we will use this terminology in the course

IR Spectroscopy

I. Introduction

5. Because the speed of light, ***c***, is constant, the ***frequency, ν***, (number of cycles of the wave per second) can complete in the same time, must be inversely proportional to how long the oscillation is, or ***wavelength***:

$$\nu = \frac{c}{\lambda} \qquad \therefore E = h\nu = \frac{hc}{\lambda}$$

$$c = 3 \times 10^{10} \text{ cm/s}$$

6. Amplitude, ***A***, describes the wave height, or strength of the oscillation

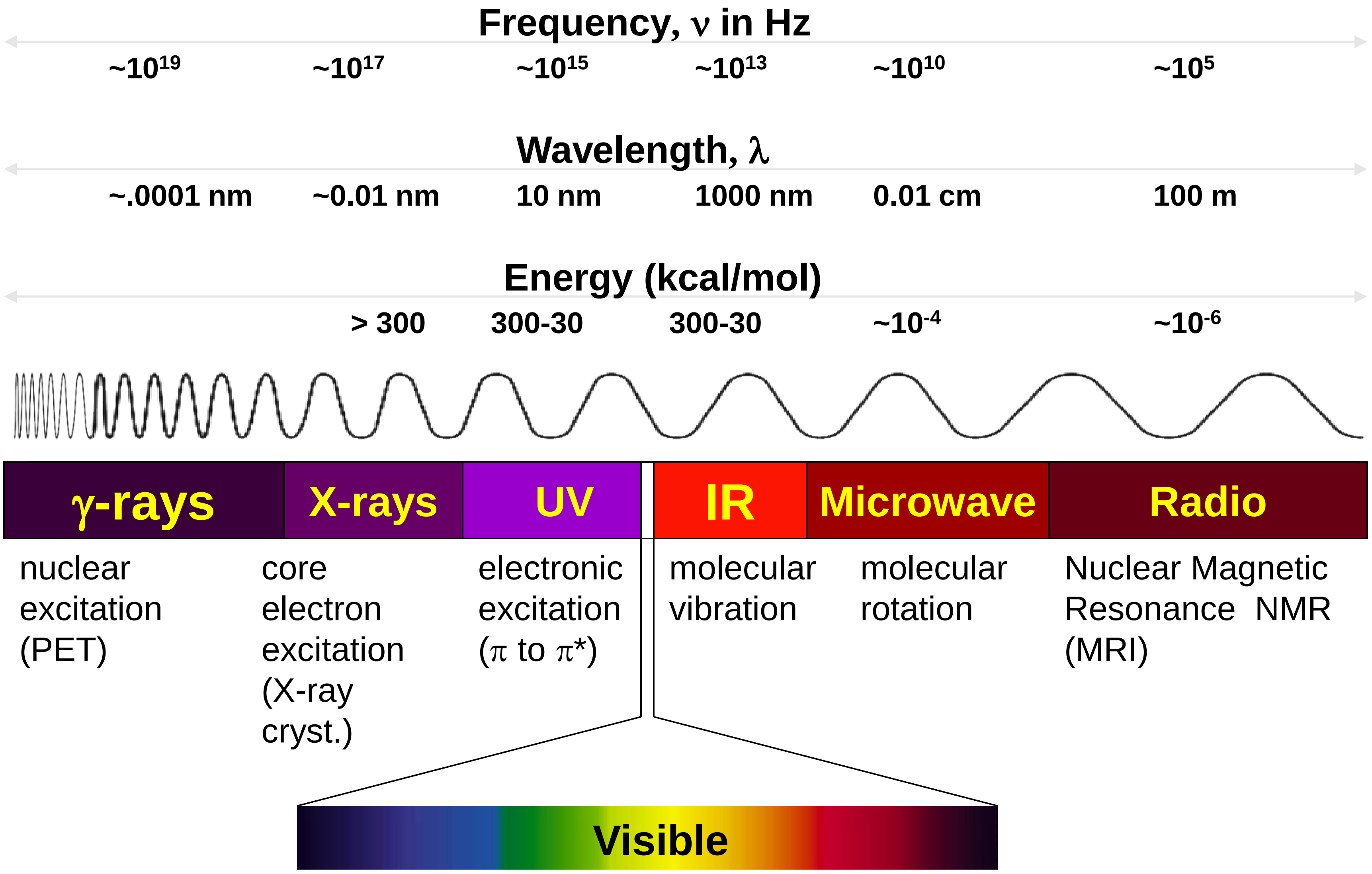
7. Because the atomic particles in matter also exhibit wave and particle properties (though opposite in how much) EM radiation can interact with matter in two ways:
   - Collision – particle-to-particle – energy is lost as heat and movement

   - Coupling – the wave property of the radiation matches the wave property of the particle and "couple" to the next higher quantum mechanical energy level

IR Spectroscopy

I. Introduction

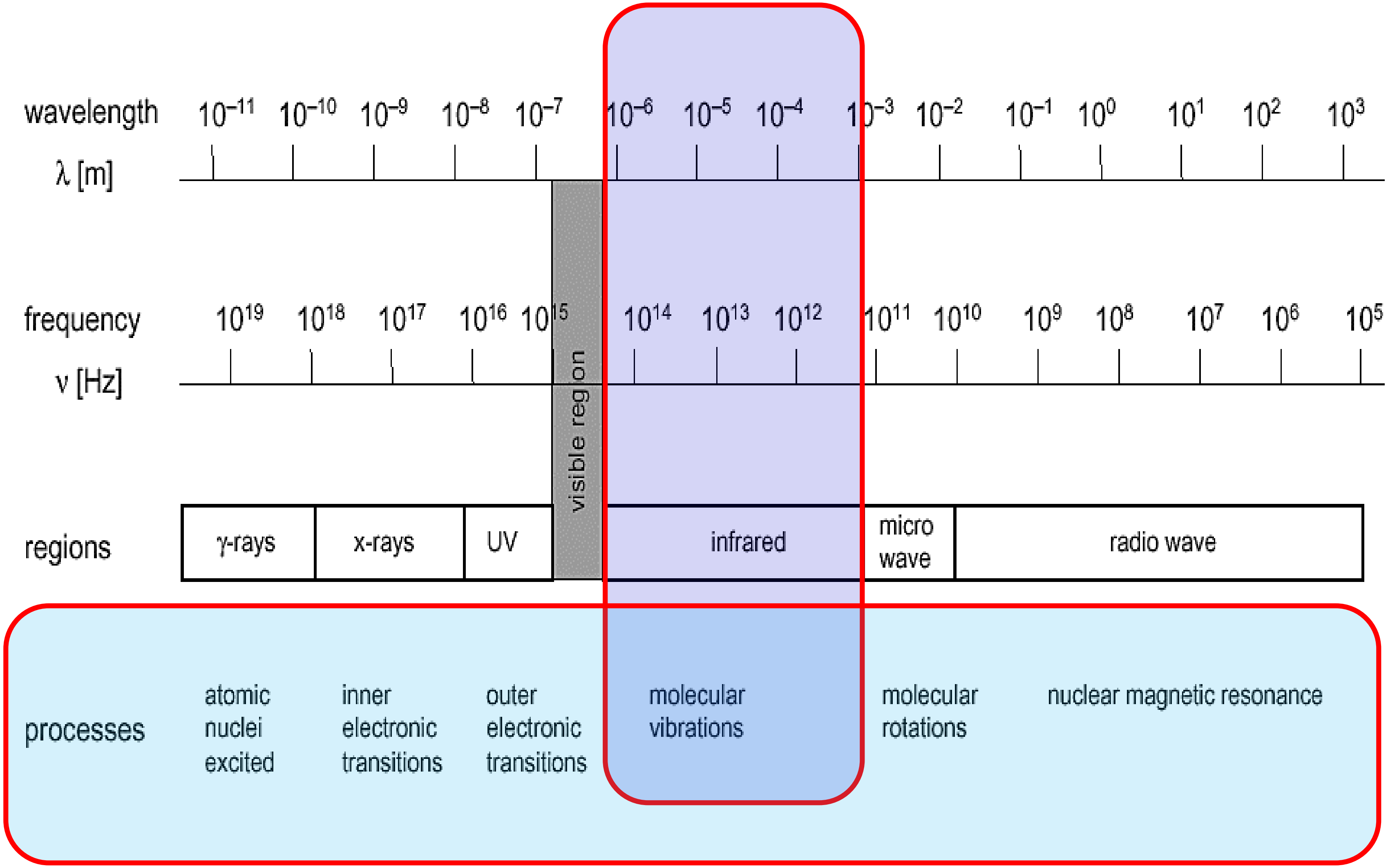
8. The entire electromagnetic spectrum:



	γ-rays	X-rays	UV	IR	Microwave	Radio
Frequency, ν in Hz	**$\sim 10^{19}$**	**$\sim 10^{17}$**	**$\sim 10^{15}$**	**$\sim 10^{13}$**	**$\sim 10^{10}$**	**$\sim 10^{5}$**
Wavelength, λ	**~.0001 nm**	**~0.01 nm**	**10 nm**	**1000 nm**	**0.01 cm**	**100 m**
Energy (kcal/mol)		**> 300**	**300-30**	**300-30**	**$\sim 10^{-4}$**	**$\sim 10^{-6}$**
	nuclear excitation (PET)	core electron excitation (X-ray cryst.)	electronic excitation (π to π*)	molecular vibration	molecular rotation	Nuclear Magnetic Resonance NMR (MRI)

Visible

The Electromagnetic Spectrum



IR Spectroscopy

I. Introduction

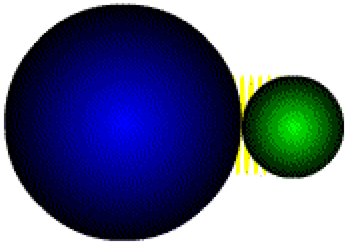
C. The IR Spectroscopic Process:

1. The quantum mechanical energy levels observed in IR spectroscopy are those of ***molecular vibrations.***

2. We perceive this vibration as heat.

3. When we say a ***covalent bond*** between two atoms is of a certain length, we are citing an average because the bond behaves as if it were a vibrating spring connecting the two atoms.

4. For a simple diatomic molecule, this model is easy to visualize:



Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

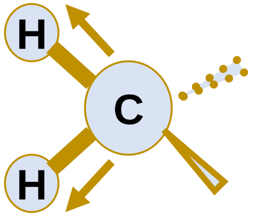
IR Spectroscopy

I. Introduction

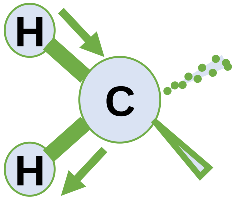
C. The IR Spectroscopic Process

5. There are two types of bond vibration:

- ***Stretch*** – Vibration or oscillation along the line of the bond

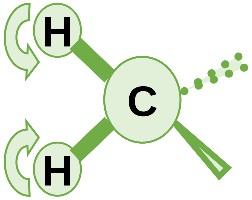


symmetric

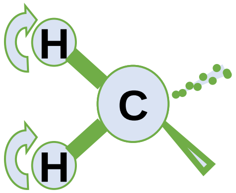


asymmetric

- ***Bend*** – Vibration or oscillation not along the line of the bond

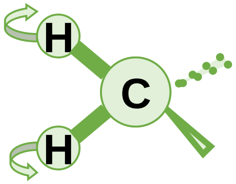


scissor

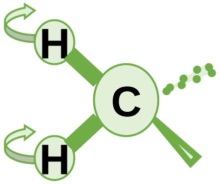


rock

in plane



twist

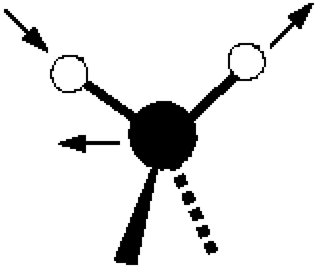


wag

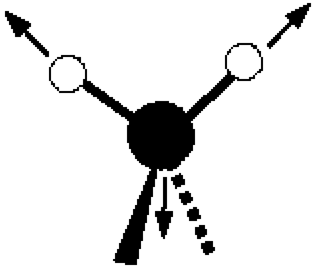
out of plane

Vibrational Modes for a CH_2 Group

stretching vibrations

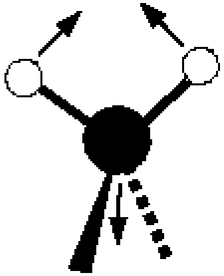


asymmetrical stretching
(ν_{as} CH_2)
2926 cm^{-1}

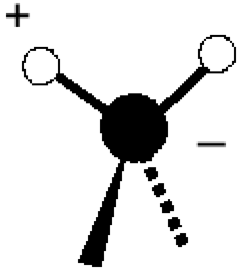


symmetrical stretching
(ν_s CH_2)
2853 cm^{-1}

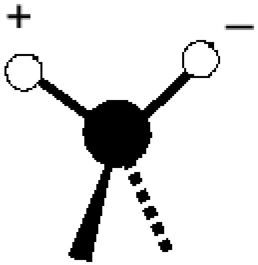
bending vibrations



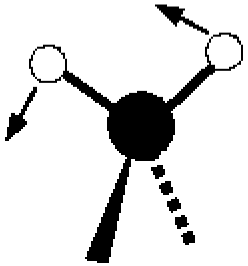
in-plane bending or scissoring
(δ_s CH_2)
1465 cm^{-1}



out-of-plane bending or wagging
(ω CH_2)
1465 cm^{-1}



out-of-plane bending or twisting
(τ CH_2)
1350-1150 cm^{-1}

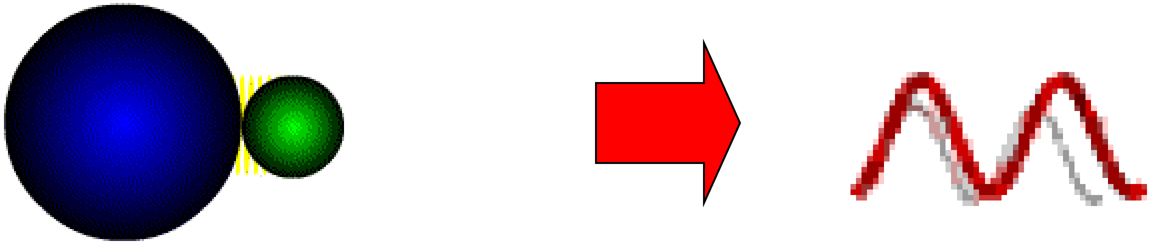


in-plane bending or rocking
(ρ CH_2)
720 cm^{-1}

IR Spectroscopy

C. The IR Spectroscopic Process

6. As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic field is produced



Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

7. The greater the dipole moment change through the vibration, the more intense the EM field that is generated.

Sample preparation techniques

Infrared spectra may be obtained for gases, liquids or solids (neat or in solution)

The preparation of samples for infrared spectrometry is often the most challenging task in obtaining an IR spectrum. Since almost all substances absorb IR radiation at some wave length, and solvents must be carefully chosen for the wavelength region and the sample of interest.

Gas samples

- A gas sample cell consists of a cylinder of glass or sometimes a metal. The cell is closed at both ends with an appropriate window materials (NaCl/KBr) and equipped with valves or stopcocks for introduction of the sample.

- Long pathlength (>10 cm) cells – used to study dilute (few molecules) or weakly absorbing samples.

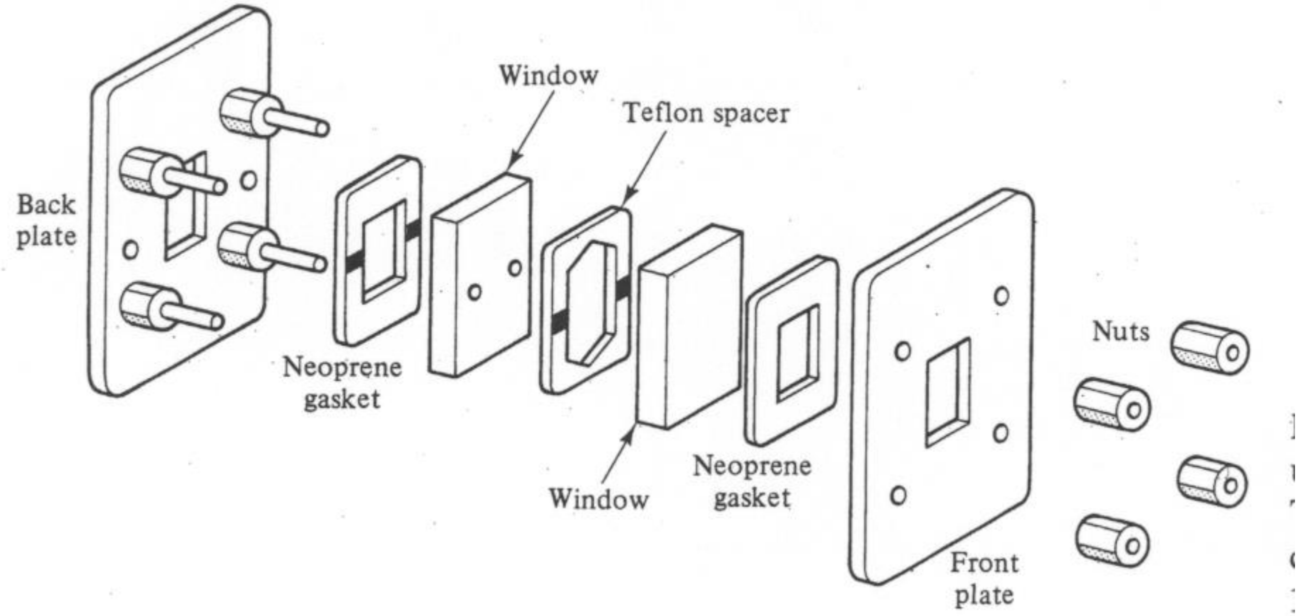
- Multipass cells – more compact and efficient instead of long-pathlength cells. Mirrors are used so that the beam makes several passes through the sample before exiting the cell. (Effective pathlength > 10 m).

- To resolve the rotational structure of the sample, the cells must be capable of being evacuated to measure the spectrum at reduced pressure.

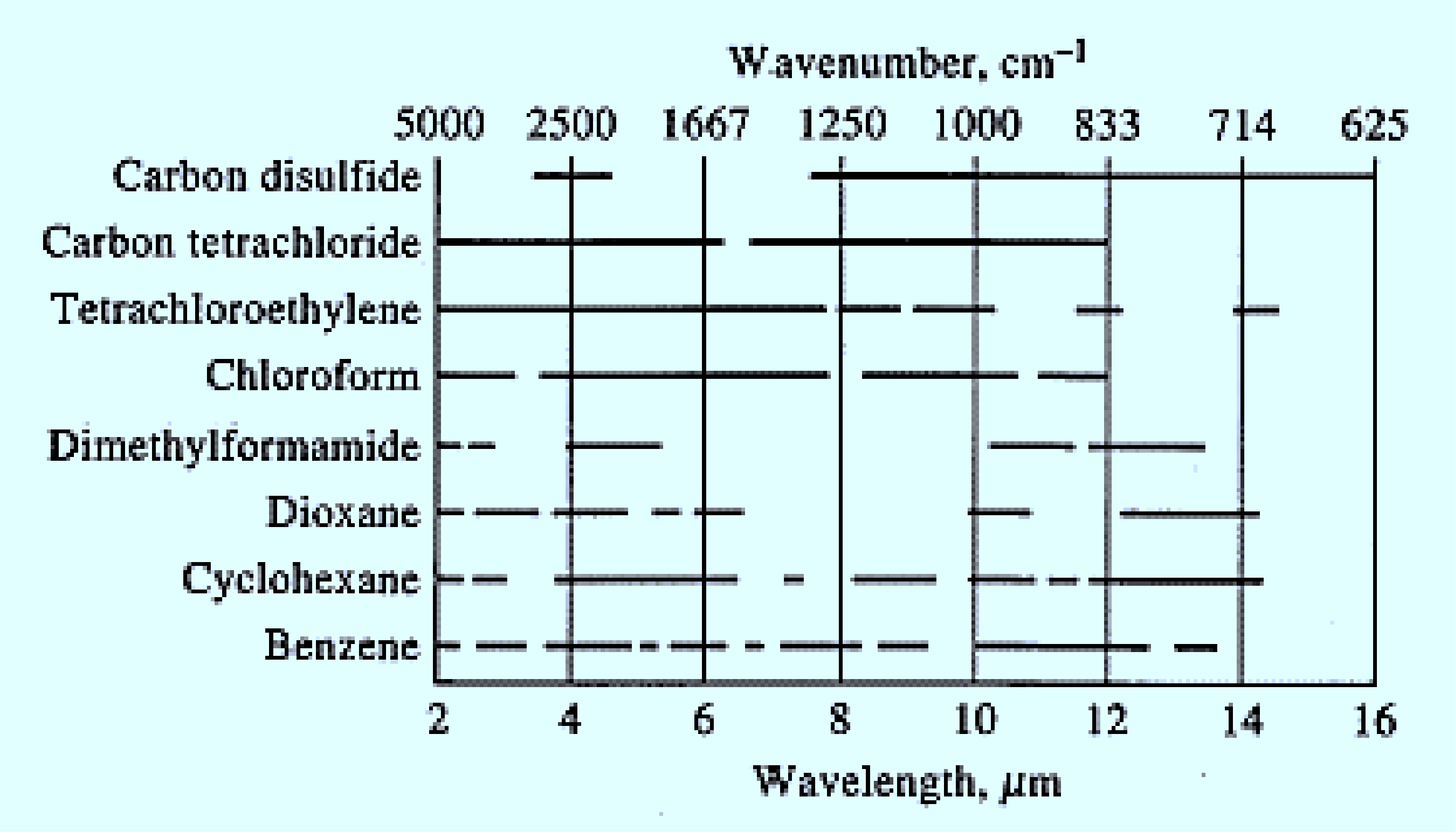
- For quantitative determinations with light molecules, the cell is sometimes pressurized in order to broaden the rotational structure and all simpler measurement.

Liquid samples

- Pure or soluted in transparent solvent – not water (attacks windows)
- The sample is most often in the form of liquid films (“sandwiched” between two NaCl plates)
- Adjustable pathlength (0.015 to 1 mm) – by Teflon spacer



Regions of transparency for common infrared solvents.



The horizontal lines indicate regions where solvent transmits at least 25% of the incident radiation in a 1-mm cell.

Solid samples

- Spectra of solids are obtained as:
  1. *Alkali halide discs (KBr)*
  2. *Mulls (e.g. Nujol, a highly refined mixture of saturated hydrocarbons).*
  3. *Films (solvent or melt casting).*

Alkali halide discs:.

1. A milligram or less of the fine ground sample mixed with about 100 mg of dry KBr powder in a mortar or ball mill.
2. The mixture compressed in a die to form transparent disc.

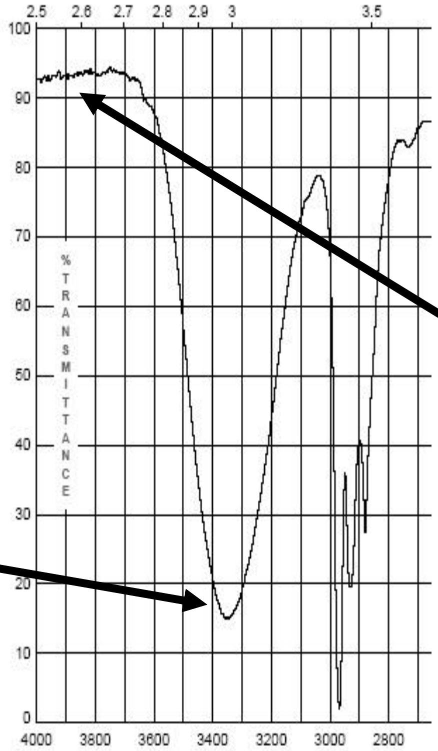
Mulls

1. Grinding a few milligrams of the powdered sample with a mortar or with pulverizing equipment. A few drops of the mineral oil added (grinding continued to form a smooth paste).
2. The IR of the paste can be obtained as the liquid sample.

IR Spectroscopy

D. The IR Spectrum

1. Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds



The y-axis on an IR spectrum is in units of % transmittance

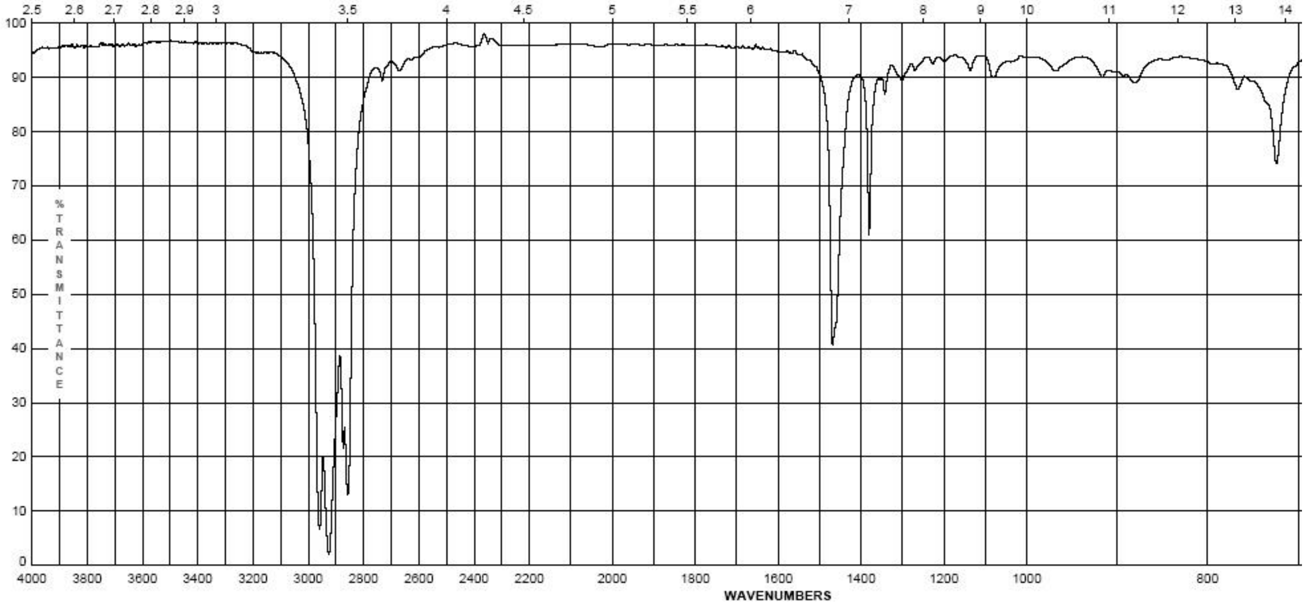
In regions where the EM field of an osc. bond interacts with IR light of the same ν – transmittance is low hence IR light is absorbed.

In regions where no osc. bond is interacting with IR light, transmittance nears 100%

IR Spectroscopy

D. The IR Spectrum

2. The x-axis of the IR spectrum is in units of wavenumbers, $\bar{\nu}$, which is the number of waves per centimeter in units of cm^{-1} (Remember $E = h\nu$ or $E = hc/\lambda$)



IR Spectroscopy

D. The IR Spectrum

3. This unit is used rather than wavelength (microns) because wavenumbers are directly proportional to the energy of transition being observed.

   High frequencies and high wavenumbers equate higher energy

   is quicker to understand than Short wavelengths equate higher energy.

4. This unit is used rather than frequency as the numbers are more "real" than the exponential units of frequency

5. IR spectra are observed for the mid-infrared: wavelengths: 2.5 - 50 μm, wavenumbers: 4000 - 200 cm^{-1}

6. The peaks are Gaussian distributions of the average energy of a transition

IR Spectroscopy

D. The IR Spectrum

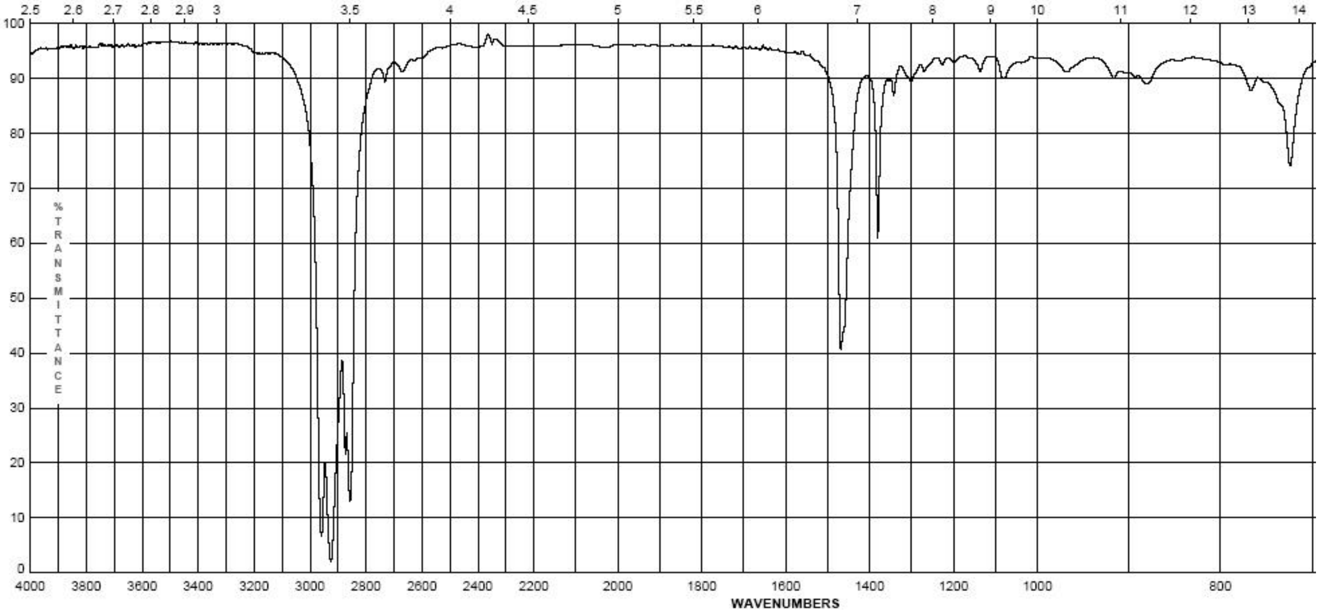
7. In general:

Lighter atoms will allow the oscillation to be faster – *higher energy*

This is especially true of bonds to hydrogen – C-H, N-H and O-H

Stronger bonds will have higher energy oscillations

Triple bonds > double bonds > single bonds in energy



Energy/ν of oscillation

IR Spectroscopy

E. The IR Spectrum – The detection of different bonds

7. As opposed to chromatography or other spectroscopic methods, the area of a IR band (or peak) is not ***directly*** proportional to concentration of the functional group producing the peak

8. The intensity of an IR band is affected by two primary factors:

   Whether the vibration is one of stretching or bending

   Electronegativity difference of the atoms involved in the bond

   - For both effects, the greater the change in dipole moment in a given vibration or bend, the larger the peak.

   - The greater the difference in electronegativity between the atoms involved in bonding, the larger the dipole moment

   - Typically, stretching will change dipole moment more than bending

IR Spectroscopy

E. The IR Spectrum – The detection of different bonds

9. It is important to make note of peak intensities to show the effect of these factors:

- ***Strong (s)*** – peak is tall, transmittance is low (0-35 %)
- ***Medium (m)*** – peak is mid-height (75-35%)
- ***Weak* (w)** – peak is short, transmittance is high (90-75%)
- **** Broad (br)*** – if the Gaussian distribution is abnormally broad *(*this is more for describing a bond that spans many energies)*

Exact transmittance values are rarely recorded

II. Infrared Group Analysis

A. General

1. The primary use of the IR is to ***detect functional groups.***

2. Because the IR looks at the interaction of the EM spectrum with actual bonds, it provides a unique qualitative probe into the functionality of a molecule, as functional groups are merely different configurations of different types of bonds.

3. Since most “types” of bonds in covalent molecules have roughly the same energy, i.e., C=C and C=O bonds, C-H and N-H bonds they show up in similar regions of the IR spectrum.

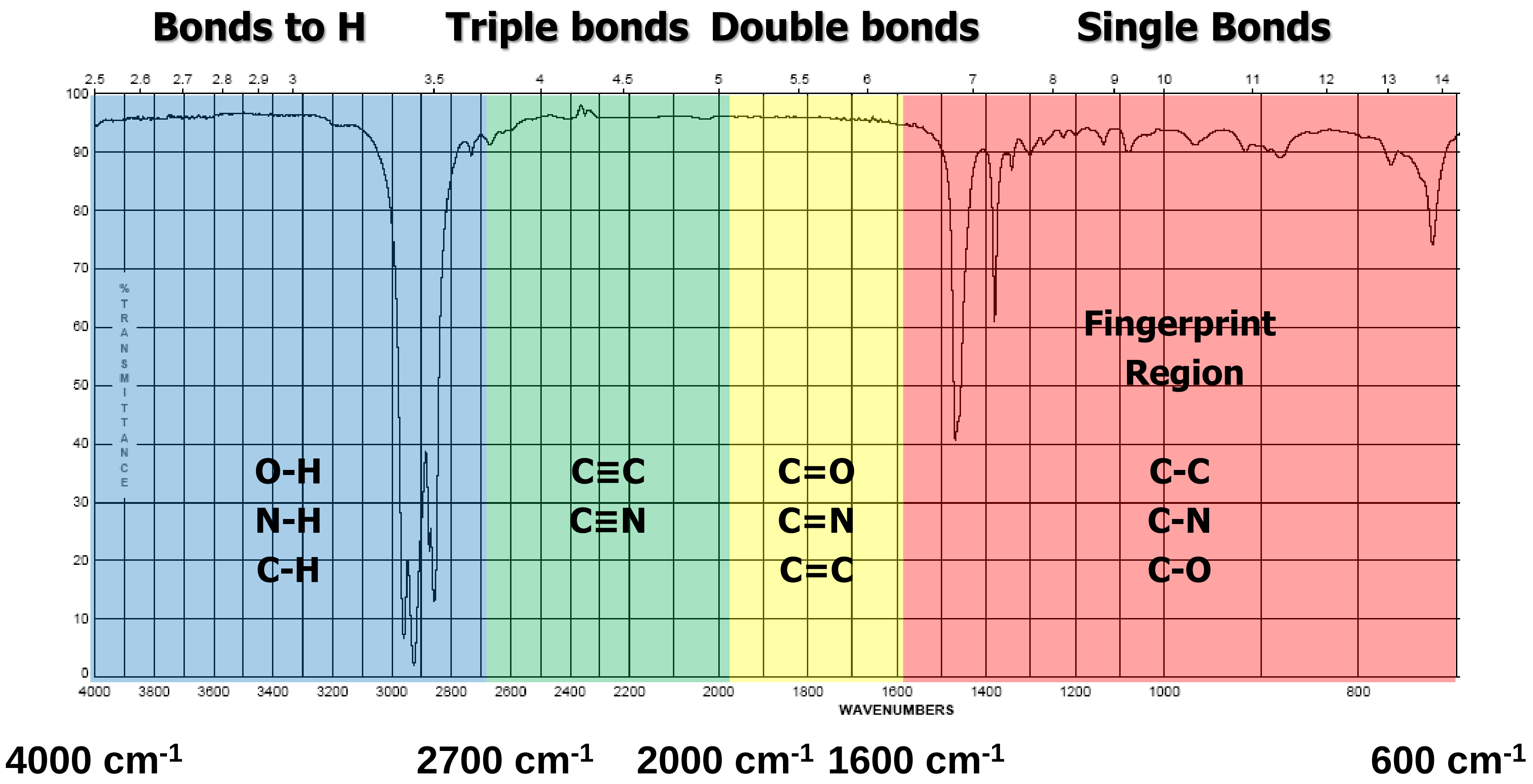
4. Remember all organic functional groups are made of multiple bonds and therefore show up as multiple IR bands (peaks)

Infrared Spectroscopy

II. Infrared Group Analysis

A. General

5. The four primary regions of the IR spectrum



Infrared Spectroscopy

1. **Alkanes** – combination of C-C and C-H bonds
    - C-C stretches and bends 1360-1470 cm^{-1}
    - CH_2-CH_2 bond 1450-1470 cm^{-1}
    - CH_2-CH_3 bond 1360-1390 cm^{-1}
    - C-H of (CH_3) between 2800-3000 cm^{-1}
    - **(w= weak, m= moderate, and s= strong peaks)**

Octane