Infra-Red Spectroscopy
2 – Theory and Instrumentation

Dr. Sapna Gupta

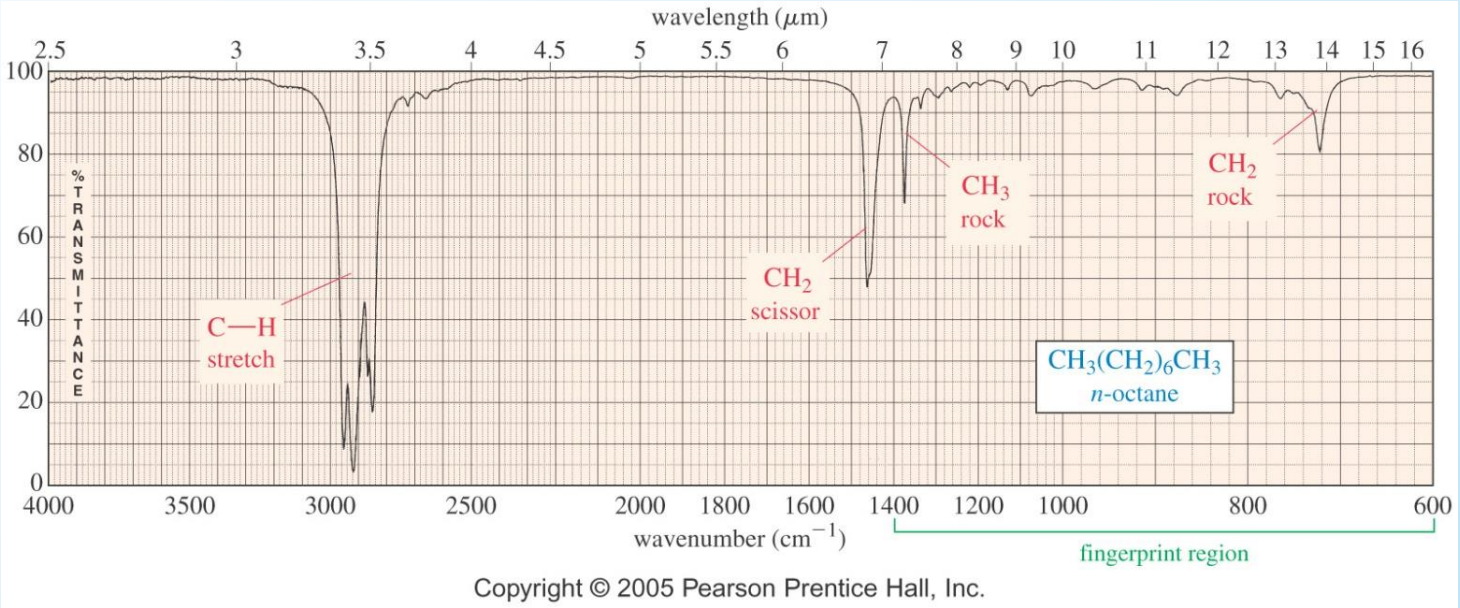
Introduction to Infra Red Spectroscopy

Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group in a compound.

- IR is just below red in the visible region.
- Wavelengths usually 2.5-25 μm.
- More common units are wavenumbers, or cm^{-1}, the reciprocal of the wavelength in centimeters.
- Wavenumbers are proportional to frequency and energy.

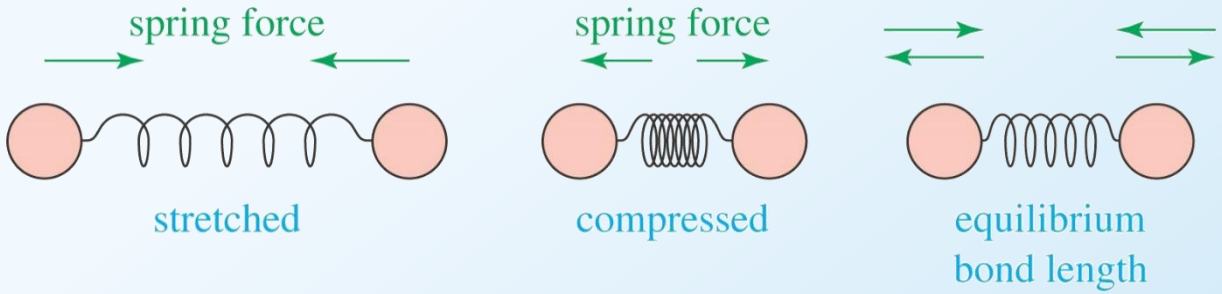
IR Spectrum – A First Look

- IR spectrum is graph of signals that look like hanging peaks.
- The x-axis is wavenumber cm^{-1} and y-axis is % transmittance.
- Not each peak can be analyzed, however some key peaks can give a good idea of what the functional group in the compound can be.



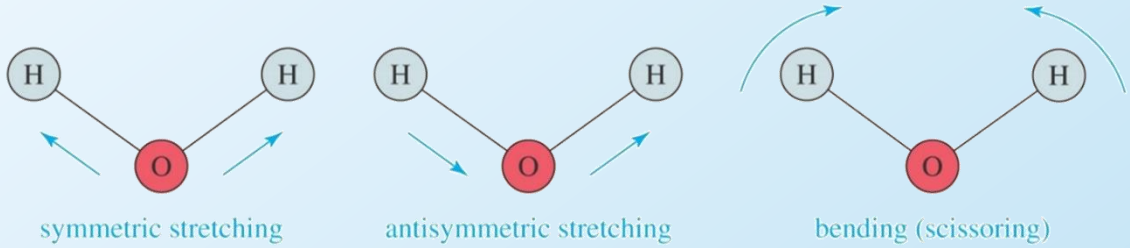
Theory - IR Spectroscopy

Molecular vibrations (stretching and bending) occur when covalent bonds are exposed to Infra red radiation. These vibrations occur at certain allowable frequencies.



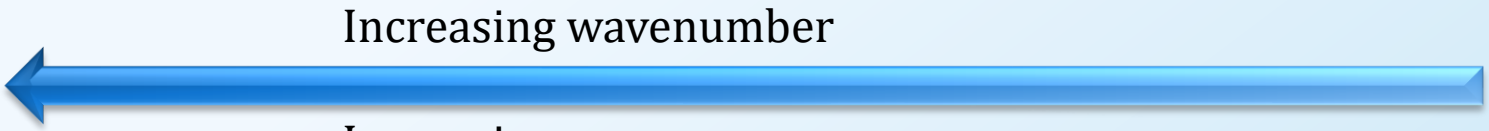
Vibrational Modes

Nonlinear molecule with *n* atoms usually has 3*n* - 6 fundamental vibrational modes.



IR Absorptions

Bonds absorb in four predictable regions of an IR spectrum.



4000	2500	2000	1500	400

Bonds to Hydrogen	Triple bonds	Double bonds	Single bonds
C - H O - H N - H	C ≡ C C ≡ N	C = C C = O C = N	C - C C - O C - N C - X
Lighter atoms Higher frequency	Stronger bonds Higher frequency		Fingerprint region

Stretching Frequencies

How the atoms are connected determines how much energy is required to vibrate that bond. Energy is directly related to wavenumber.

- Frequency decreases with increasing atomic mass. This means lighter atoms connected stretch at higher energy for example C-H > C-C.
- Frequency increases with increasing bond energy. Triple bonds stretch at a higher frequency than double than single bonds. Triple bonds need much more energy in order to show a signal in IR.

Bonds	Frequency cm^{-1}
C - H C - D C - C ↓ *Heavier atoms*	3000 2100 1200 ↓ $\overline{\nu}$ *Decreases with increasing atomic mass*
C – C C = C C ≡ C ↓ *Stronger bond*	1200 1660 2200 ↓ $\overline{\nu}$ *Increases with stronger bond (increasing bond energy)*

IR - Fingerprint of Molecule

IR spectrum is the fingerprint of a molecule. No two molecules will give exactly the same IR spectrum (except enantiomers).

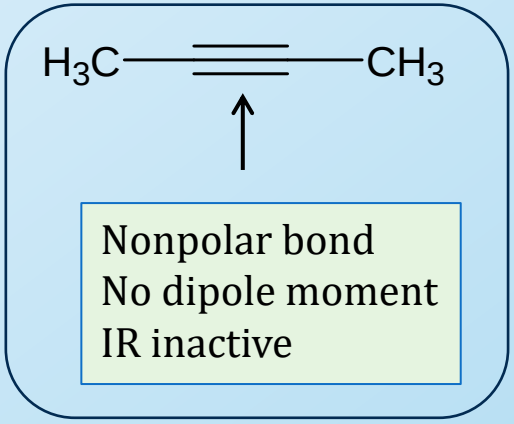
There are two main regions of IR:

- Simple stretching: 1600-3500 cm^{-1}.
- Complex vibrations: 600-1400 cm^{-1}, called the "fingerprint region."

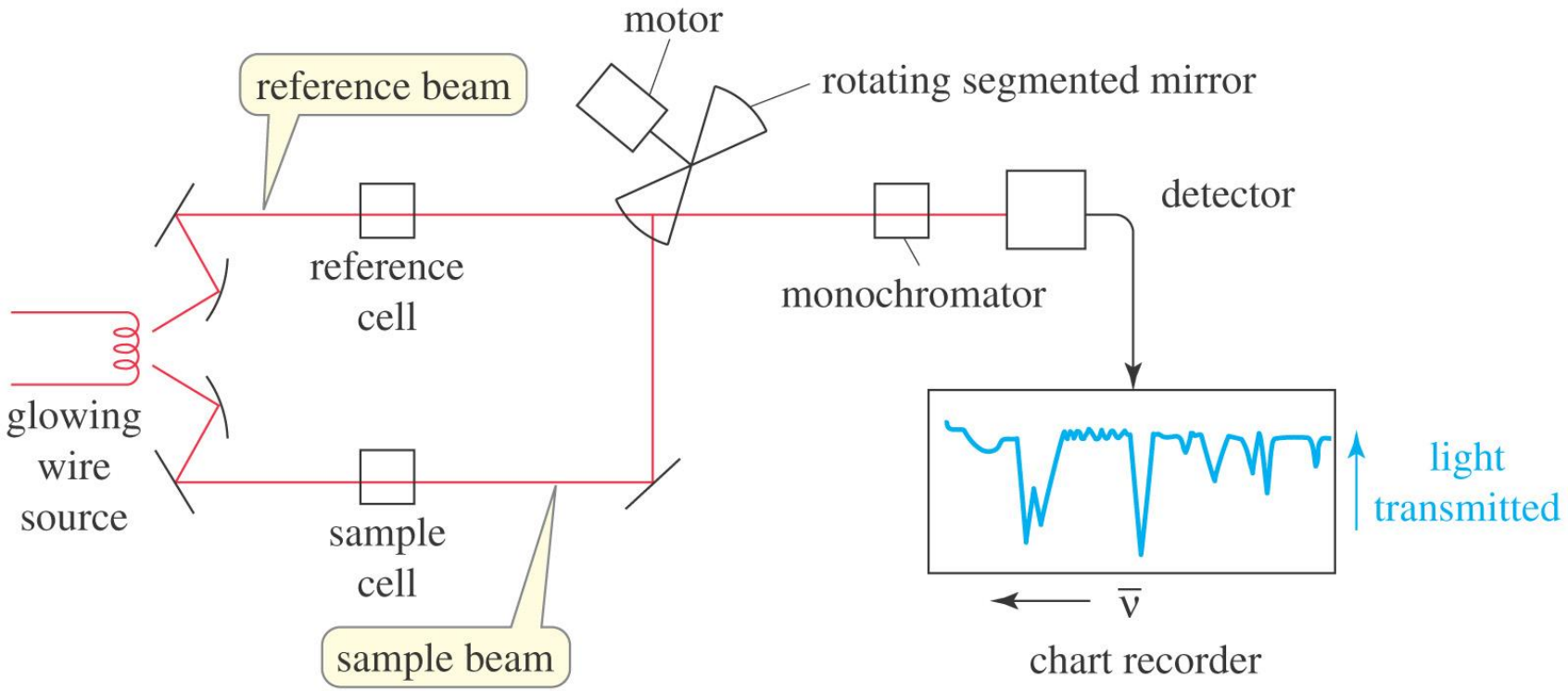
The fingerprint region is complex to interpret and can give much more information about a compound.

IR-Active and Inactive

- A polar bond is usually IR-active.
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.



Instrumentation - Infrared Spectrometer



Sample Preparation

New instruments don't generally need any special preparation. The neat sample liquid or solid can be placed on the sample holder to analyze the sample. Sometimes the solids may need to be pressed into a pellet to analyze them. (*Samples don't have to be dissolved in any solvent*).

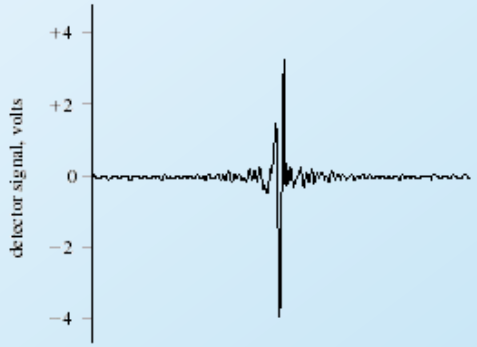
Older instrumentations may require salt plates for liquids to be placed between salt plates. And solids are mixed with KBr and NaCl and pressed into a pellet (about 2 cm in diameter). The salt plates and slats used are IR inactive.

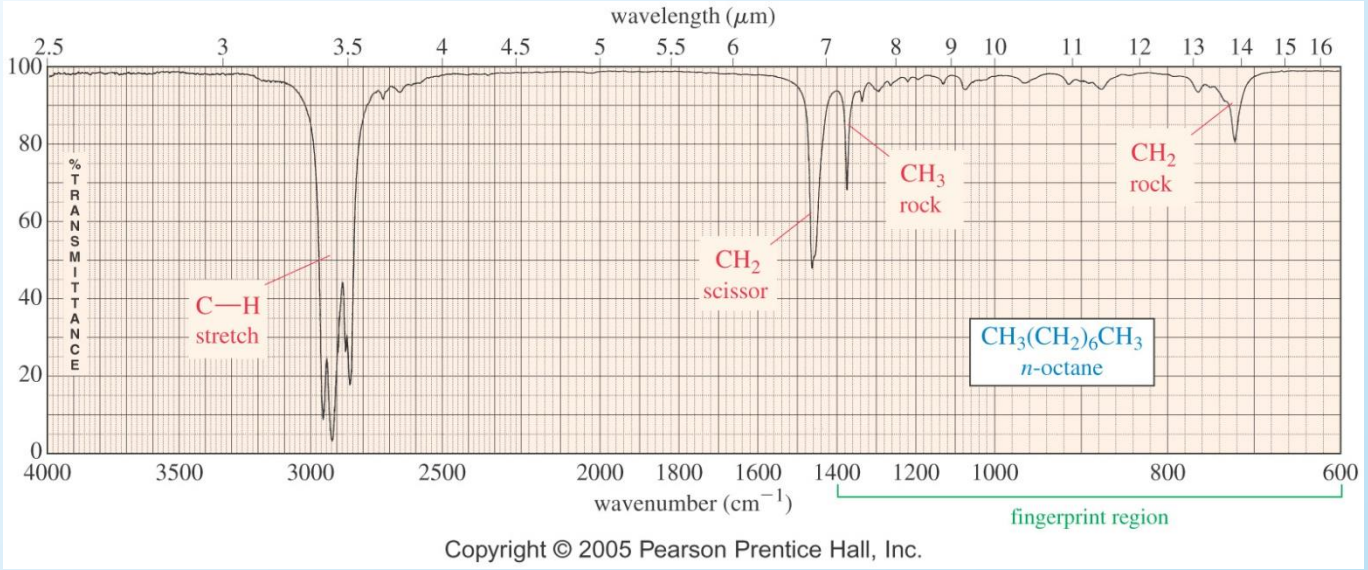
In the newer machines samples can be recovered but is generally not. In the older machines sample is lost during analysis.

FT-IR Spectrometer

"Fourier Transform" part of FT-IR refers to the mathematical technique used to convert the raw data collected from the instrument into a useful spectrum. This transformation simplifies the data and makes it easier to interpret the spectrum. This increases sensitivity, uses less energy, works faster and has a laser to maintain calibration.

The interferogram at the right displays the interference pattern and contains all of the spectrum information.





Key Concepts

- Know the basics of electromagnetic spectrum.
- Know how IR works
- Be able to predict the relationship between energy and bond length and atomic weight.