Introduction to Spectroscopy and Introduction to Infra-Red Spectroscopy

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Introduction

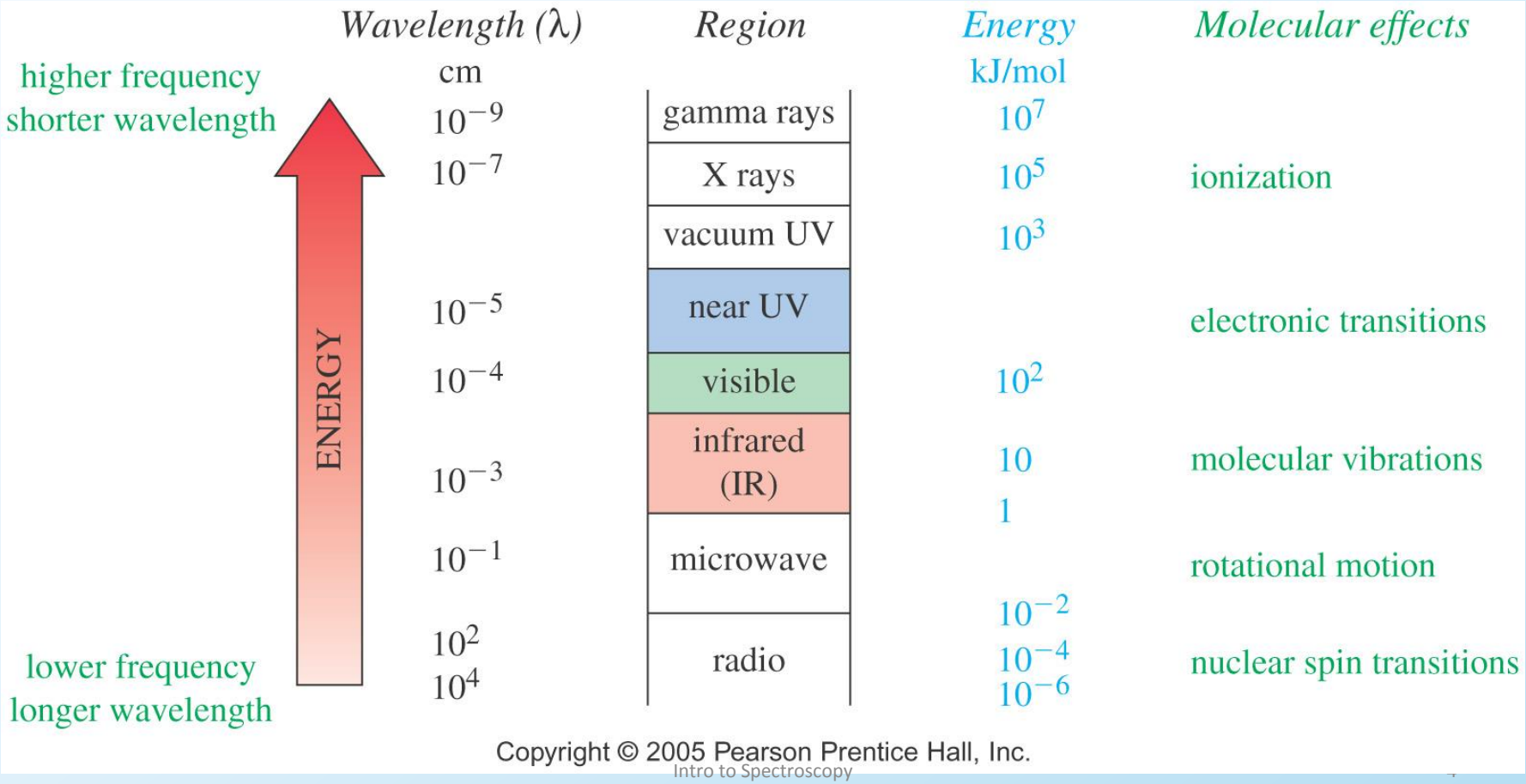
- Spectroscopy is an analytical technique which helps determine structure.
- It destroys little or no sample.
- The amount of light absorbed by the sample is measured as wavelength is varied.

Types of Spectroscopy

- Ultraviolet (UV) spectroscopy uses electron transitions to determine bonding patterns.
- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.
- Mass spectrometry (MS) fragments the molecule and measures the masses.
- Nuclear magnetic resonance (NMR) spectroscopy detects signals from hydrogen atoms and can be used to distinguish isomers.

Electromagnetic Spectrum

- Examples: X rays, microwaves, radio waves, visible light, IR, and UV.
- Frequency and wavelength are inversely proportional.
- $c = \lambda \nu$, where c is the speed of light.
- Energy per photon = $h \nu$, where h is Planck's constant, 6.62×10^{-37} kJ•sec.

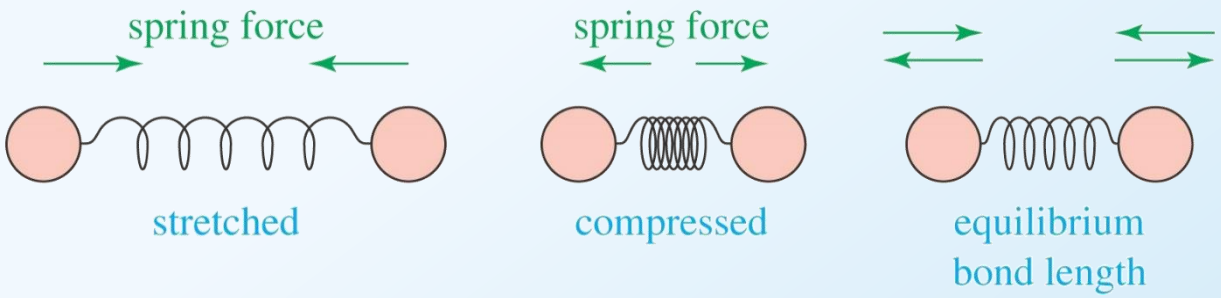


The IR Region

- 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.

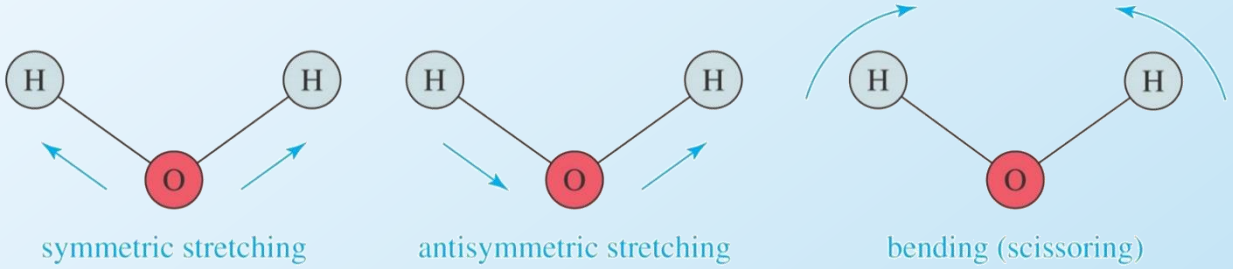
Molecular Vibrations

Covalent bonds vibrate at only certain allowable frequencies.



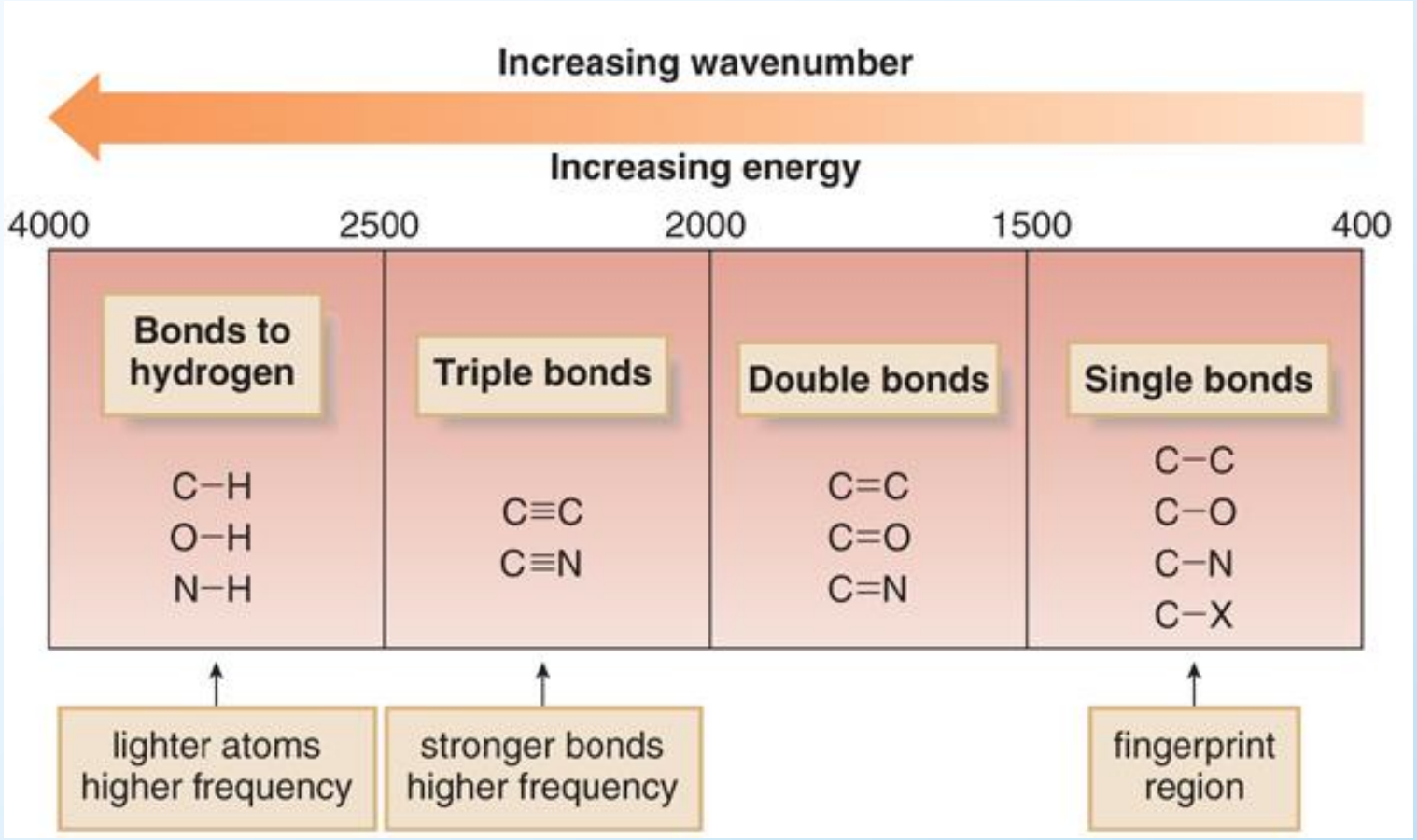
Vibrational Modes

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.



Stretching Frequencies

- Frequency decreases with increasing atomic mass.
- Frequency increases with increasing bond energy.

TABLE 12-1 Bond Stretching Frequencies.

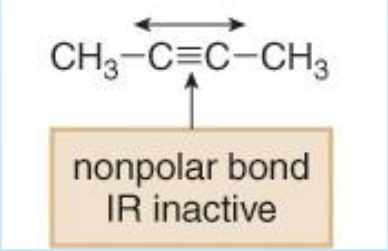
Bond	Bond Energy [kJ (kcal)]	Stretching Frequency (cm^{-1})
Frequency decreases with increasing atomic mass		
C—H ↓ heavier atoms	420 (100) <note these are trs>	3000 ↓ $\bar{\nu}$ decreases
C—D	420 (100)	2100
C—C	350 (83)	1200
Frequency increases with bond energy		
C—C	350 (83)	1200
C=C	611 (146) ↓ stronger bond	1660 ↓ $\bar{\nu}$ increases
C≡C	840 (200)	2200

Fingerprint of Molecule

- Whole-molecule vibrations and bending vibrations are also quantized.
- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Simple stretching: 1600-3500 cm^{-1}.
- Complex vibrations: 600-1400 cm^{-1}, called the "fingerprint region."

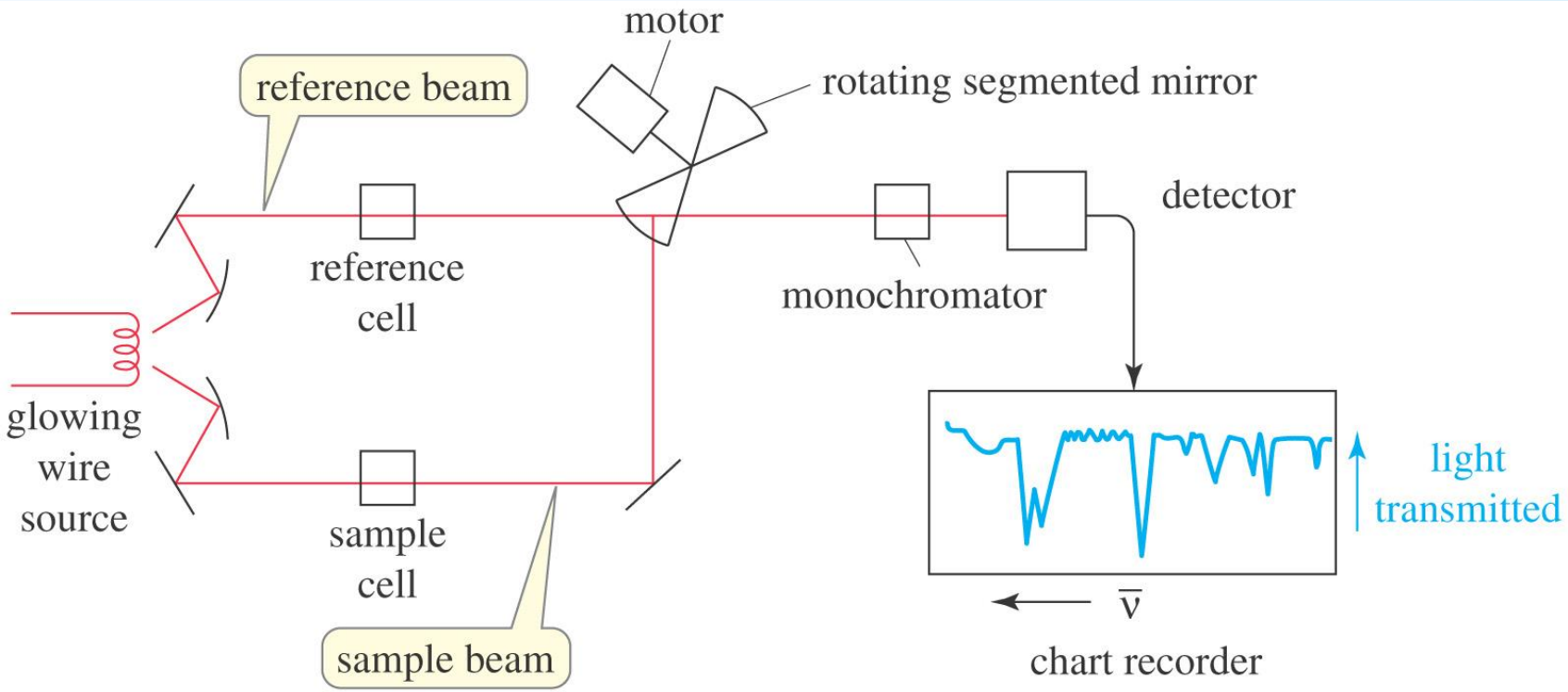
IR-Active and Inactive

- A polar bond is usually IR-active.



- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.

An Infrared Spectrometer

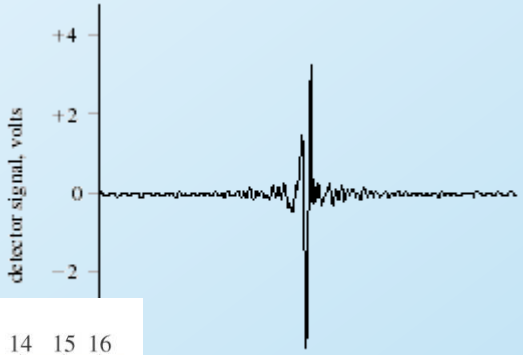


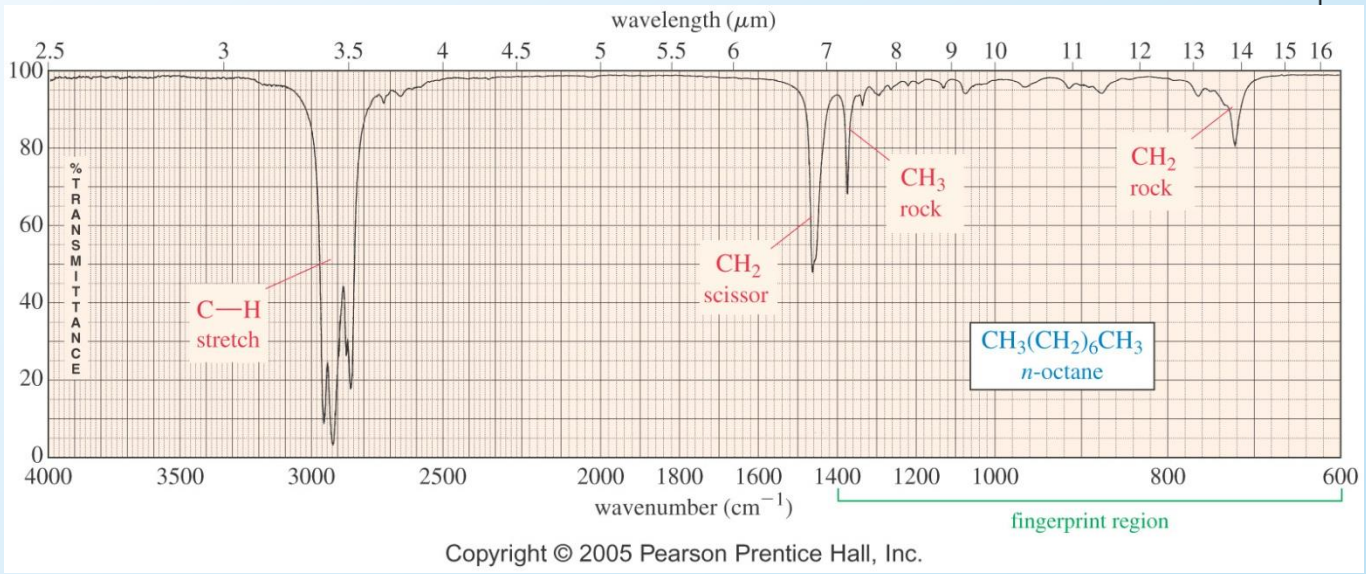
Sample Preparation: for solids – a pellet in KBr.
For liquids between salt plates. KBr and NaCl are IR inactive.
Sample is lost during analysis.

FT-IR Spectrometer

- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1-2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated.

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.