

Infrared Spectroscopy

- IR radiation has lower energy than UV and visible radiation.
- IR radiation is associated with molecular vibrations.

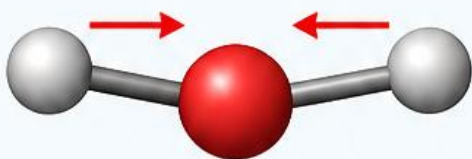
Vibrational transitions of molecules

Two types

1. Stretching

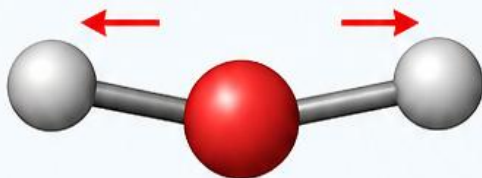
(change in bond length)

Symmetric stretching



Both bonds stretch and compress together.

Asymmetric stretching



One bond stretches while the other compresses.

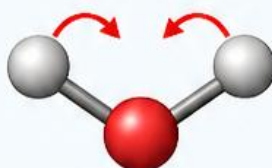
2. Bending

(change in bond angle)

In-plane bending

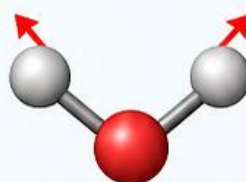
(vibration in the plane of the molecule)

Scissoring



Angle decreases and increases in the plane.

Rocking

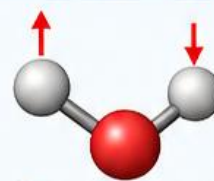


Both atoms move in the same direction in the plane.

Out-of-plane bending

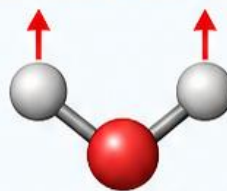
(vibration out of the plane of the molecule)

Twisting



One atom moves above the plane and the other below the plane.

Wagging



Both atoms move in the same direction above or below the plane.

Vibrational transitions are low-energy transitions.

These energy levels correspond to energies of electromagnetic radiation in the IR region of the spectrum.

Wavenumber and Vibrational Frequency

- Wavenumber is used in an IR spectrum rather than wavelength (λ).
- An IR spectrum is presented as percent transmission versus wavenumber.

Calculation of vibrational frequency

The vibrational frequency of a bond can be calculated with the help of Hooke's law, which correlates frequency with bond strength and atomic masses.

Vibrational frequency of a chemical bond (Hooke's law)

Dependence on bond strength and mass

$$\nu \propto \sqrt{\frac{\text{bond strength}}{\text{mass}}}$$

Vibrational frequency increases with increasing bond strength (stronger bond).

Vibrational frequency decreases with increasing mass (heavier atoms).

Mathematical expression for vibrational frequency

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{m_1 m_2 (m_1 + m_2)}}$$

Where,

ν = frequency (vibrational frequency) (s^{-1} or cm^{-1})

k = force constant of the bond (N m^{-1})

m_1, m_2 = masses of the two atoms involved in the bond (kg or atomic mass units, amu)

$m_1 m_2 / (m_1 + m_2)$ = reduced mass (often written as μ)

c = speed of light ($2.998 \times 10^{10} \text{ cm s}^{-1}$)

Bond strength and mass effect on vibrational frequency (IR spectroscopy)

Vibrational frequency (ν) of a bond is given by Hooke's law:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{m_1 m_2 (m_1 + m_2)}}$$

Where,

- ν = frequency (vibrational frequency) (s^{-1} or cm^{-1})
 k = force constant of the bond (N m^{-1})
 m_1, m_2 = masses of the two atoms involved in the bond (kg or amu)
 $m_1 m_2 / (m_1 + m_2)$ = reduced mass (often written as μ)
 c = speed of light ($2.998 \times 10^{10} \text{ cm s}^{-1}$)

Effect of bond strength and mass

Bond strength (k)

Vibrational frequency increases with increasing bond strength (stronger bond).



Mass (m)

Vibrational frequency decreases with increasing mass (heavier atoms).



Comparison of some common bonds

Bond strength	Mass	Approximate trend in IR frequency (ν)
C—C	lower	lower ν
C=C	lower	higher ν
C≡C	lower	even higher ν

Examples of bonds

Bond	Force constant (k)
C—H	high
N—H	high
O—H	high
F—H	high

All these must absorb at higher ν (wavenumber) in series order on the basis of reduced mass.

Modes of Vibration and Instrumentation

1 Number of fundamental vibrational modes

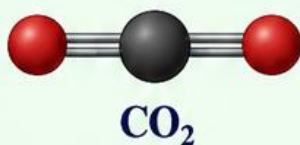
The theory of molecular vibrations predicts that a **non-linear molecule** containing n atoms has $3n - 6$ fundamental vibrational modes.

For CO_2 :

$$(3 \times 3) - 6 = 3$$

vibrational modes

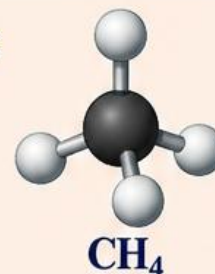
(as written in the original notes).



For methane (CH_4):

$$(5 \times 3) - 6 = 9$$

vibrational modes

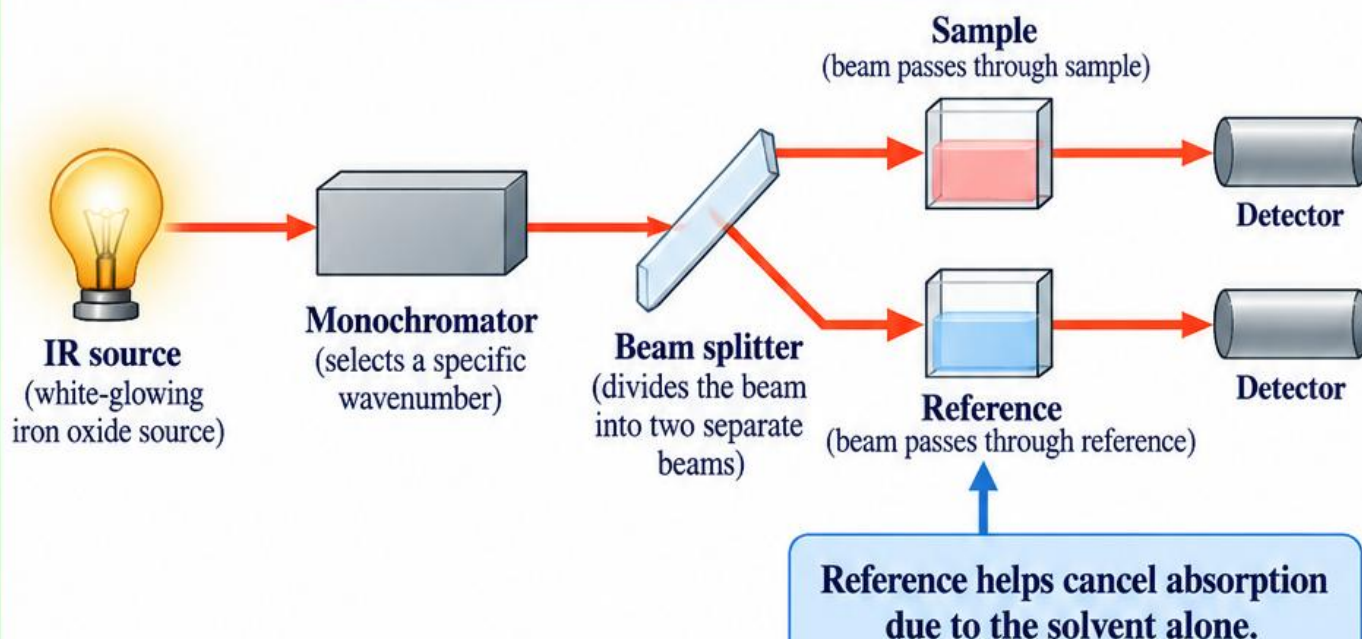


The original notes use the $3n - 6$ expression for CO_2 .
The calculation is preserved as written.

2 Instrumentation

- The most common source of IR light in the notes is a **white-glowing iron oxide source**.
- The beam passes through a **monochromator** and is split into **two separate beams**.

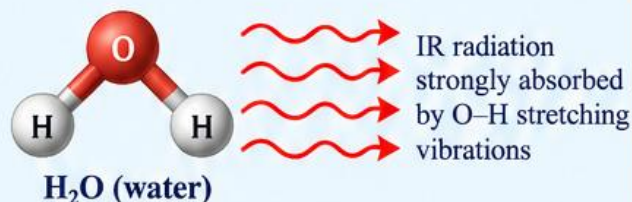
Optical path in an IR spectrometer



Instrumentation and Applications of IR Spectroscopy

Note

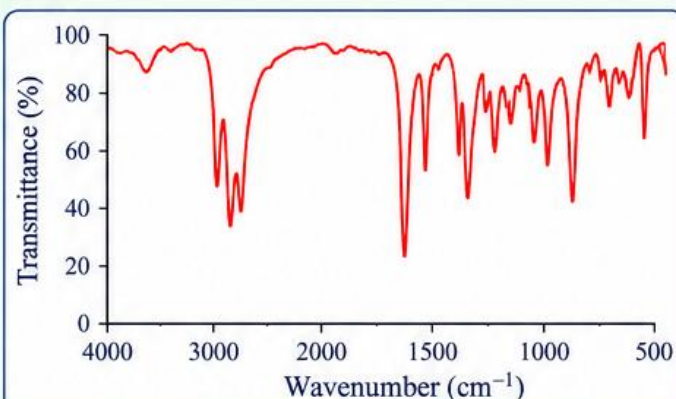
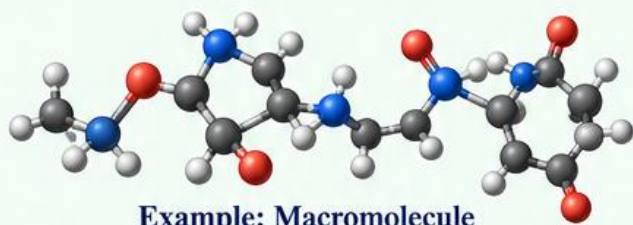
Aqueous solutions cannot generally be used for routine IR spectra because water (O–H) absorbs IR radiation strongly.



Applications

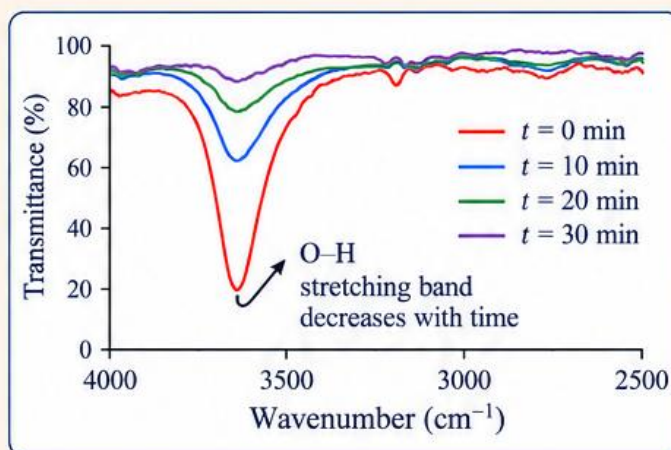
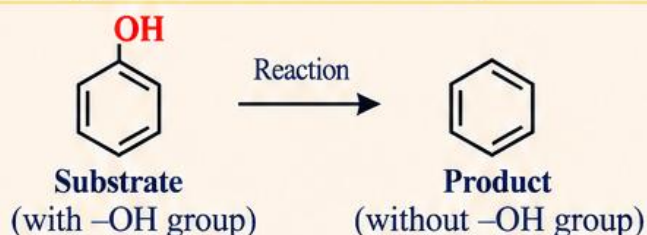
1 Identification of compounds

Macromolecules possess a large number of atoms and therefore a large number of fundamental vibrations.



2 Rate of reactions

If the substrate possesses an –OH group and the product does not, the reaction rate can be measured by following the rate of disappearance of O–H stretching vibrations.



3 Study of conformation

IR spectroscopy can be used to study molecular conformation, including characteristic vibrational bands of biological macromolecules.

