SEMESTER - V
19U5CRCHE8 : PHYSICAL CHEMISTRY II

Vibrational Spectroscopy

Dr. Jinu George

Department of Chemistry

Sacred Heart College

Infrared (IR) Spectroscopy

•IR deals with the interaction of infrared radiation with matter. The IR spectrum of a compound can provide important information about its chemical nature and molecular structure.

•Most commonly, the spectrum is obtained by measuring the *absorption* of IR radiation, although infrared emission and reflection are also used.

•Widely applied in the analysis of organic materials, also useful for polyatomic inorganic molecules and for organometallic compounds.
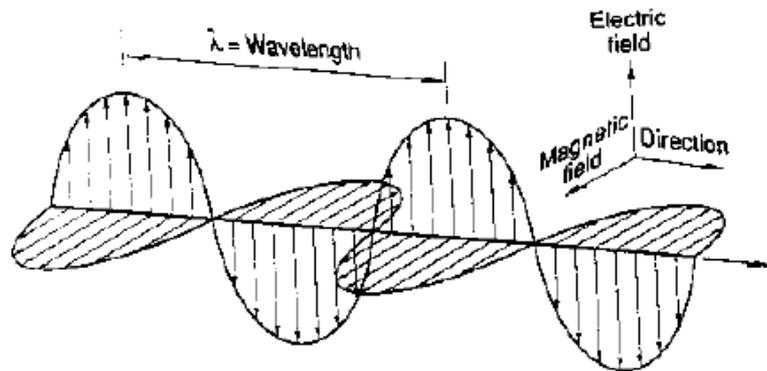
Overview

1. **Electromagnetic radiation**

2. **Vibrations**

3. **Principle of IR experiment**

4. **IR spectrum**

5. **Types of vibration**

6. **CGF/Fingerprint regions**

7. **IR activity of vibrations**

Electromagnetic Radiation

The propagation of electromagnetic radiation in a vacuum is constant for all regions of the spectrum (= velocity of light):

$$c = \lambda \times \nu$$

$1\,\text{Å} = 10^{-10}\,\text{m} \quad 1\,\text{nm} = 10^{-9}\,\text{m} \quad 1\,\mu\text{m} = 10^{-6}\,\text{m}$

Another unit commonly used is the wavenumber, which is linear with energy:

$$\bar{\nu}\,(\text{cm}^{-1}) = \frac{1}{\lambda} = \frac{\nu}{c}$$
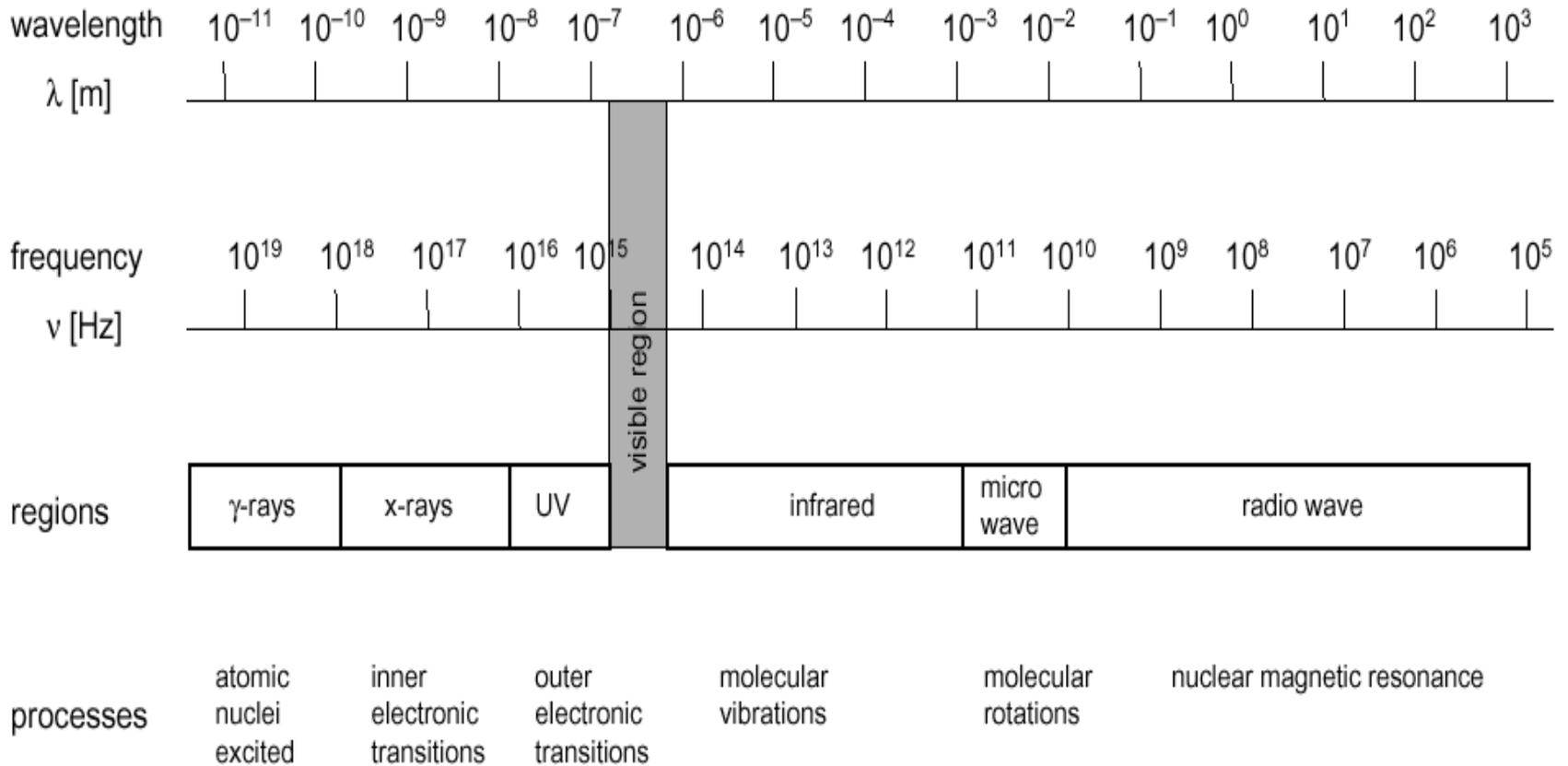
Work by Einstein, Planck and Bohr indicated that electromagnetic radiation can be regarded as a stream of particles or quanta, for which the energy is given by the *Bohr equatio*n:

$$\Delta E = h \cdot \nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \bar{\nu}$$

$h = 6.626 \times 10^{-34}\,\text{Js}$
$c = 2.997925 \times 10^{8}\,\text{ms}^{-1}$

The Electromagnetic Spectrum

wavelength λ [m]	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}

frequency ν [Hz]	10^{19}	10^{18}	10^{17}	10^{16}	10^{15}	10^{14}	10^{13}	10^{12}	10^{11}	10^{10}	10^{9}	10^{8}	10^{7}	10^{6}	10^{5}

visible region

regions	γ-rays	x-rays	UV		infrared	micro wave	radio wave

processes	atomic nuclei excited	inner electronic transitions	outer electronic transitions	molecular vibrations	molecular rotations	nuclear magnetic resonance

Infrared region

LIMIT OF RED LIGHT: 800 nm, 0.8 μm, 12500 cm^{-1}

NEAR INFRARED: 0.8 -2.5 μm, 12500 - 4000 cm^{-1}

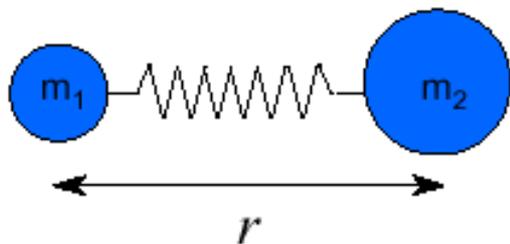**MID INFRARED**: 2.5 - 50 μm, 4000 - 200 cm^{-1}

FAR INFRARED: 50 - 1000 μm, 200 - 10 cm^{-1}

Divisions arise because of different optical materials and instrumentation.

Vibrational spectra (I): Harmonic oscillator model

• Infrared radiation in the range from 10,000 – 100 cm $^{-1}$ is absorbed and converted by an organic molecule into energy of molecular vibration

$\longrightarrow$ this absorption is quantized:

Hooke's law

$$F = -f \cdot \Delta r \qquad f: \text{ force constant}$$

A simple harmonic oscillator is a mechanical system consisting of a point mass connected to a massless spring. The mass is under action of a restoring force proportional to the displacement of particle from its equilibrium position and the force constant f (also k in followings) of the spring.

• The vibrational energy V(r) can be calculated using the (classical) model of the harmonic oscillator:

$$V(r) = \frac{1}{2} k \cdot \Delta r^2 = 2\pi^2 \cdot \mu \mathbf{v}_{osc} \Delta r^2 \qquad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad \text{(reduced mass)}$$

• Using this potential energy function in the Schrödinger equation, the vibrational frequency can be calculated:

$$\mathbf{v}_{osc} = \frac{1}{2\pi} \cdot \sqrt{\frac{f}{\mu}}$$

The vibrational frequency is increasing with:

• increasing force constant f = increasing bond strength

• decreasing atomic mass

• Example: $f_{c\equiv c} > f_{c=c} > f_{c\text{-}c}$

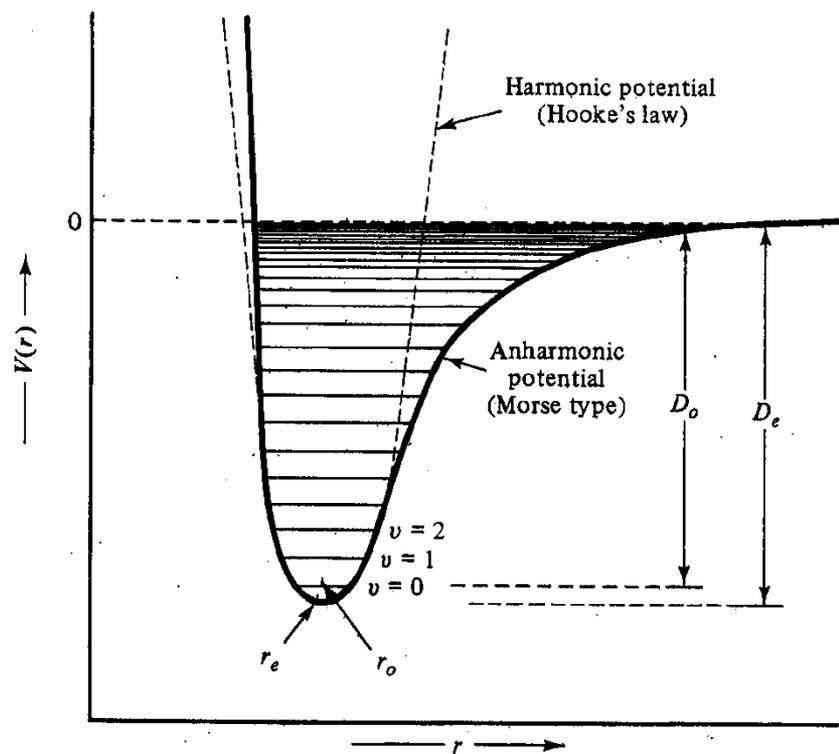# Vibrational spectra (II): Anharmonic oscillator model

FIGURE 12-1 The harmonic (Hooke's law) and anharmonic (Morse-type) potentials for a diatomic molecule. Here D_e is the dissociation energy relative to the minimum of the potential curve and D_0 is the measured dissociation energy relative to the zero-point vibrational energy.

The actual potential energy of vibrations fits the parabolic function fairly well only near the equilibrium internuclear distance. The Morse potential function more closely resembles the potential energy of vibrations in a molecule for all internuclear distances-anharmonic oscillator model.
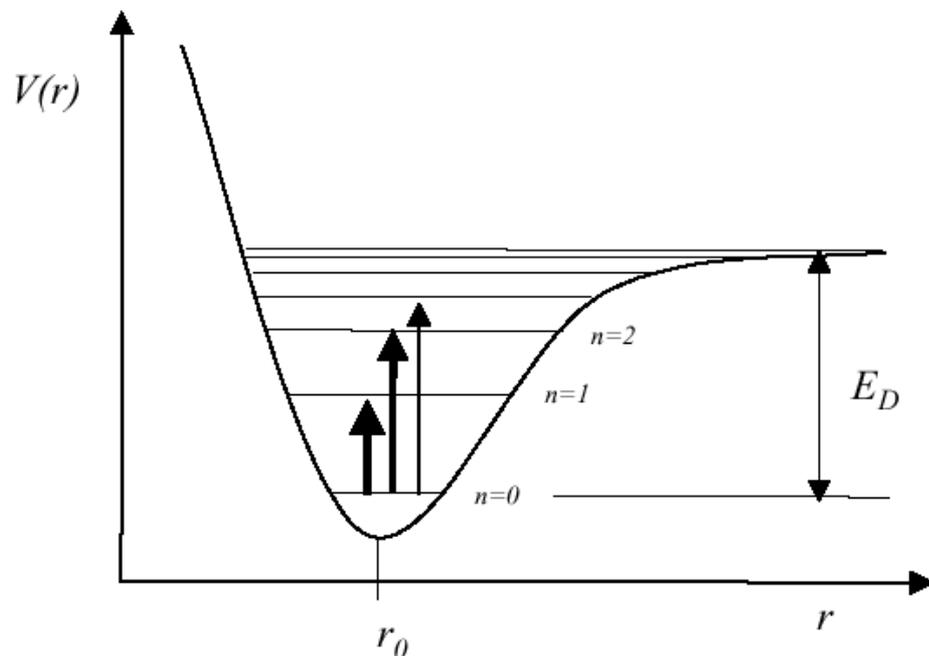
- The energy difference between the transition from *n* to *n+1* corresponds to the energy of the absorbed light quantum

- The difference between two adjacent energy levels gets smaller with increasing *n* until dissociation of the molecule occurs (Dissociation energy E_D)

Note:

Weaker transitions called "*overtones*" are sometimes observed. These correspond to $\Delta \upsilon = 2$ or 3, and their frequencies are less than two or three times the fundamental frequency ($\Delta \upsilon = 1$) because of anharmonicity.

Typical energy spacings for vibrational levels are on the order of 10^{-20} J. from the Bolzmann distribution, it can be shown that at room temperature typically 1% or less of the molecules are in excited states in the absence of external radiation. Thus most absorption transitions observed at room temperature are from the $\upsilon = 0$ to the $\upsilon = 1$ level.

Equations for vibrational spectroscopy[a]

Harmonic oscillator model

Potential energy: $V = \frac{1}{2}kq^2$ $\hspace{4cm}$ (12-4)

Energy levels: $E_v = \bar{\nu}(v + \frac{1}{2})$ in cm^{-1} for $v = 0, 1, 2, \ldots$ $\hspace{1cm}$ (12-5)

$\hspace{3cm} E_v = h\nu(v + \frac{1}{2})$ in J (ergs)

Wavenumber or frequency: $\bar{\nu} = \dfrac{\nu}{c} = \dfrac{(k/\mu)^{1/2}}{2\pi c}$; typically, $\bar{\nu} = 200$ to 3500 cm^{-1}

$$\nu = \frac{(k/\mu)^{1/2}}{2\pi} \hspace{4cm} (12\text{-}6)$$

Reduced mass: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ $\hspace{4cm}$ (12-7)

Anharmonic oscillator model

Morse potential energy: $V = \bar{D}_e |1 - e^{-\beta q}|^2$ $\hspace{3cm}$ (12-8)

Energy levels: $E_v = \bar{\nu}(v + \frac{1}{2}) - \bar{\nu}\bar{\chi}_e(v + \frac{1}{2})^2$ for $v = 0, 1, 2, \ldots$ $\hspace{1cm}$ (12-9)

Rotational-vibration transitions

$E_{vJ} = \bar{\nu}(v + \frac{1}{2}) + \bar{B}_v J(J + 1)$ for $v = 0, 1, 2, \ldots$ and $J = 0, 1, 2, \ldots$ $\hspace{0.5cm}$ (12-10)

[a]k, Force constant (N m^{-1})(typically, 200 to 2000); $q = r - r_e$, change in internuclear distance from its equilibrium value (cm); r, internuclear distance (cm); r_e, equilibrium internuclear distance (cm); v, vibrational quantum number, $0, 1, 2, \ldots$; β, molecular constant (cm^{-1}); $\bar{\chi}_e$, anharmonicity constant (dimensionless): typically, 0.002 to 0.02; $\bar{D}_e$, dissociation energy (cm^{-1}); $\bar{B}_v$, rotational constant dependent on v (cm^{-1}).

Molecular vibrations

• How many vibrations are possible (=fundamental vibrations)?

A molecule has as many degrees of freedom as the total degree of freedom of its individual atoms. Each atom has three degrees of freedom (corresponding to the Cartesian coordinates), thus in an N-atom molecule there will be 3N degree of freedom.

In molecules, movements of the atoms are constrained by interactions through chemical bonds.

Translation - the movement of the entire molecule while the positions of the atoms relative to each other remain fixed: 3 degrees of translational freedom.

Rotational transitions – interatomic distances remain constant but the entire molecule rotates with respect to three mutually perpendicular axes: 3 rotational freedom (nonlinear), 2 rotational freedom (linear).

Vibrations – relative positions of the atoms change while the average position and orientation of the molecule remain fixed.
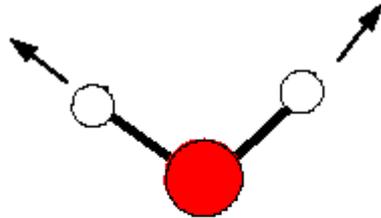
Fundamental Vibrations

Degrees of freedom	linear	non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N–5$	$3N–6$
Total	$3N$	$3N$

N = number of atoms in molecule

Vibration Types

• There are two different types of vibrational modes:

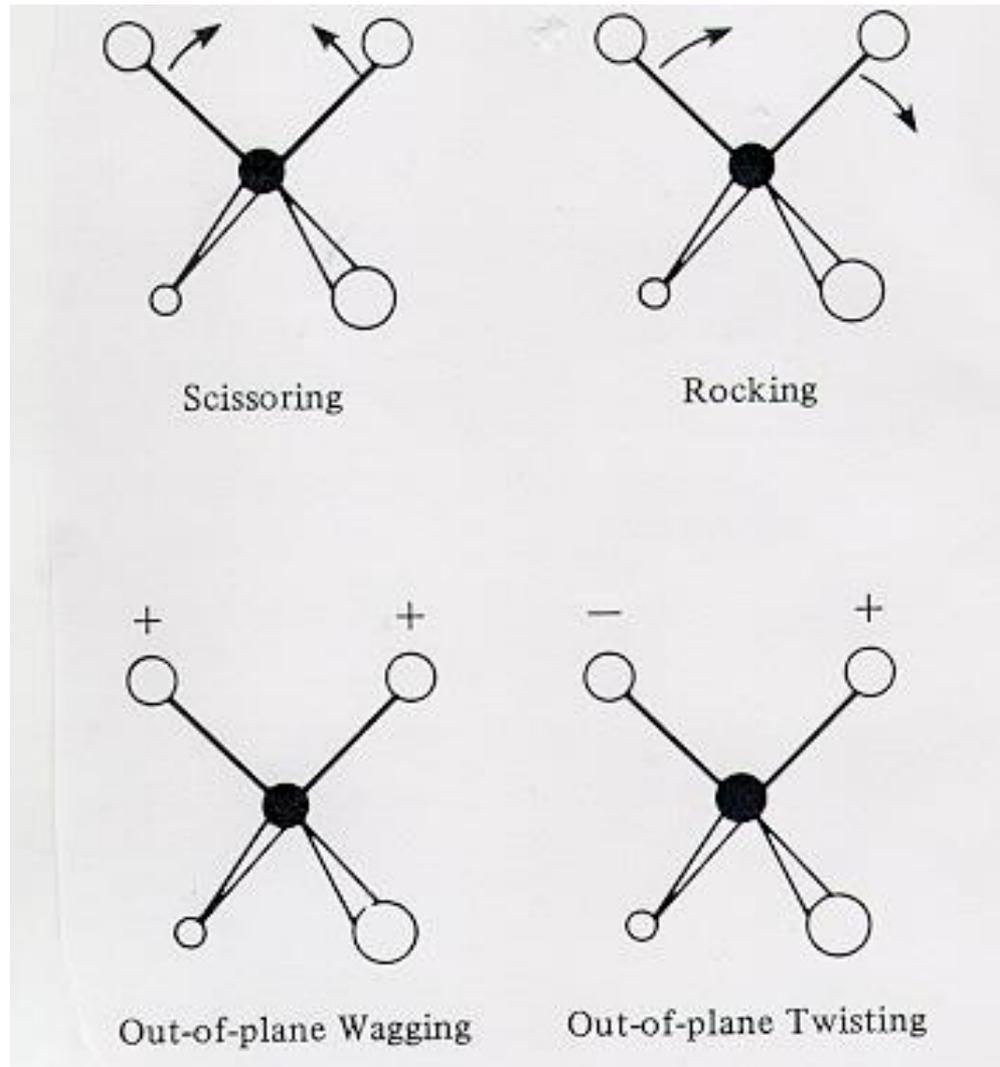Vibrations can either involve a change in bond length (stretching) or bond angle (bending)

Stretching
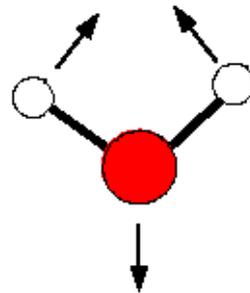
Bending

The bending vibrations are often subdivided into *scissoring, rocking, wagging, and twisting*.

Scissoring   Rocking

Out-of-plane Wagging   Out-of-plane Twisting

Selection Rules

The energy associated with a quantum of light may be transferred to the molecule if work can be performed on the molecule in the form of displacement of charge.

Selection rule:

A molecule will absorb infrared radiation if the change in vibrational states is associated with a change in the dipole moment (μ) of the molecule.

$$\mu = q\mathbf{r}$$

q: electrical charge, **r**: directed distance of that charge from some defined origin of coordinates from the molecule.

Dipole moment is greater when electronegativity difference between the atoms in a bond is greater. Some electronegativity values are:

H 2.2; C 2.55; N 3.04; O 3.44; F 3.98; P 2.19; S 2.58; Cl 3.16

• Vibrations which do not change the dipole moment are *Infrared Inactive* (homonuclear diatomics).

Why not 3N-6/3N-5 bands in IR spectrum?

- The theoretical number of fundamental vibrations (absorption frequencies) will seldom be observed

–> overtones (multiples of a given frequency), combination (sum of two other vibrations) or difference (the difference of two other vibrations) tones increase the number of bands

–> the following effects will reduce the number of theoretical bands:

- frequencies which fall outside the measured spectral region (400-4000 cm $^{-1}$)
- bands which are too weak
- bands are too close and coalesce
- occurrence of a degenerate band from several absorptions of the same frequency
- lack of change in molecular dipole
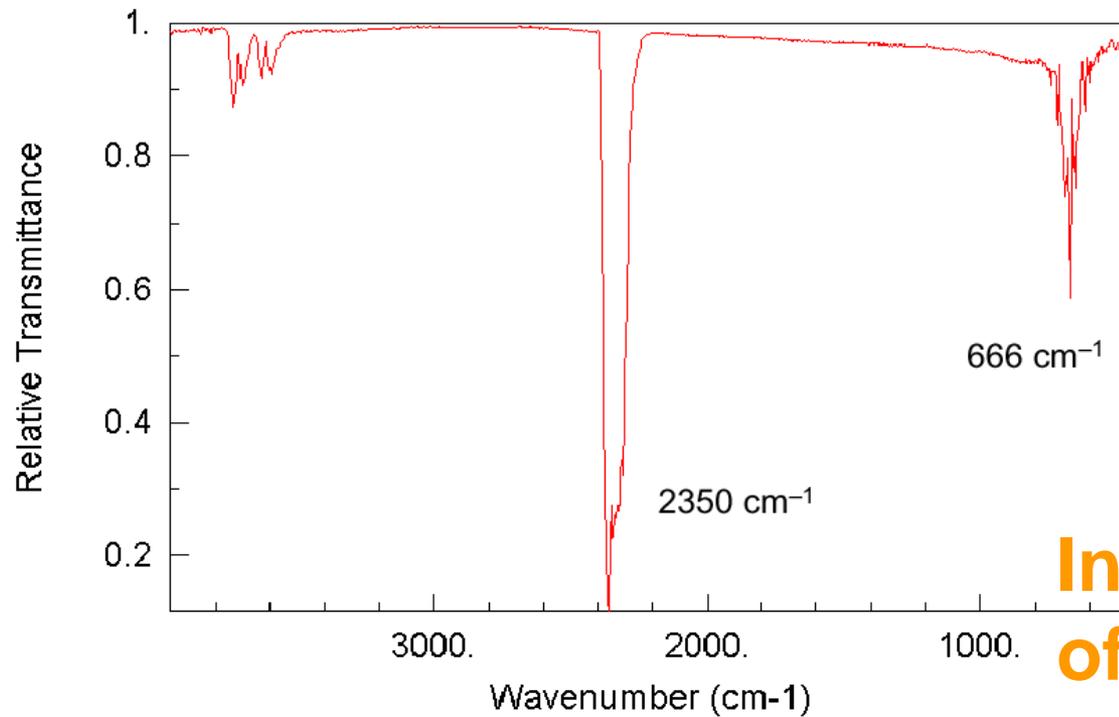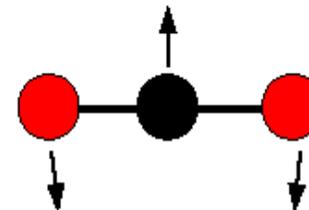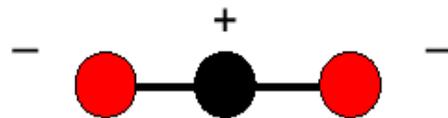
Infrared Spectrum of Carbon Dioxide

666 cm⁻¹

2350 cm⁻¹

Example: CO₂

symmetrical stretching
1340 cm⁻¹
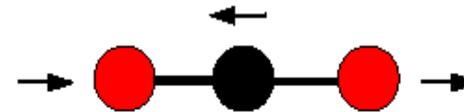
asymmetrical stretching
2350 cm⁻¹
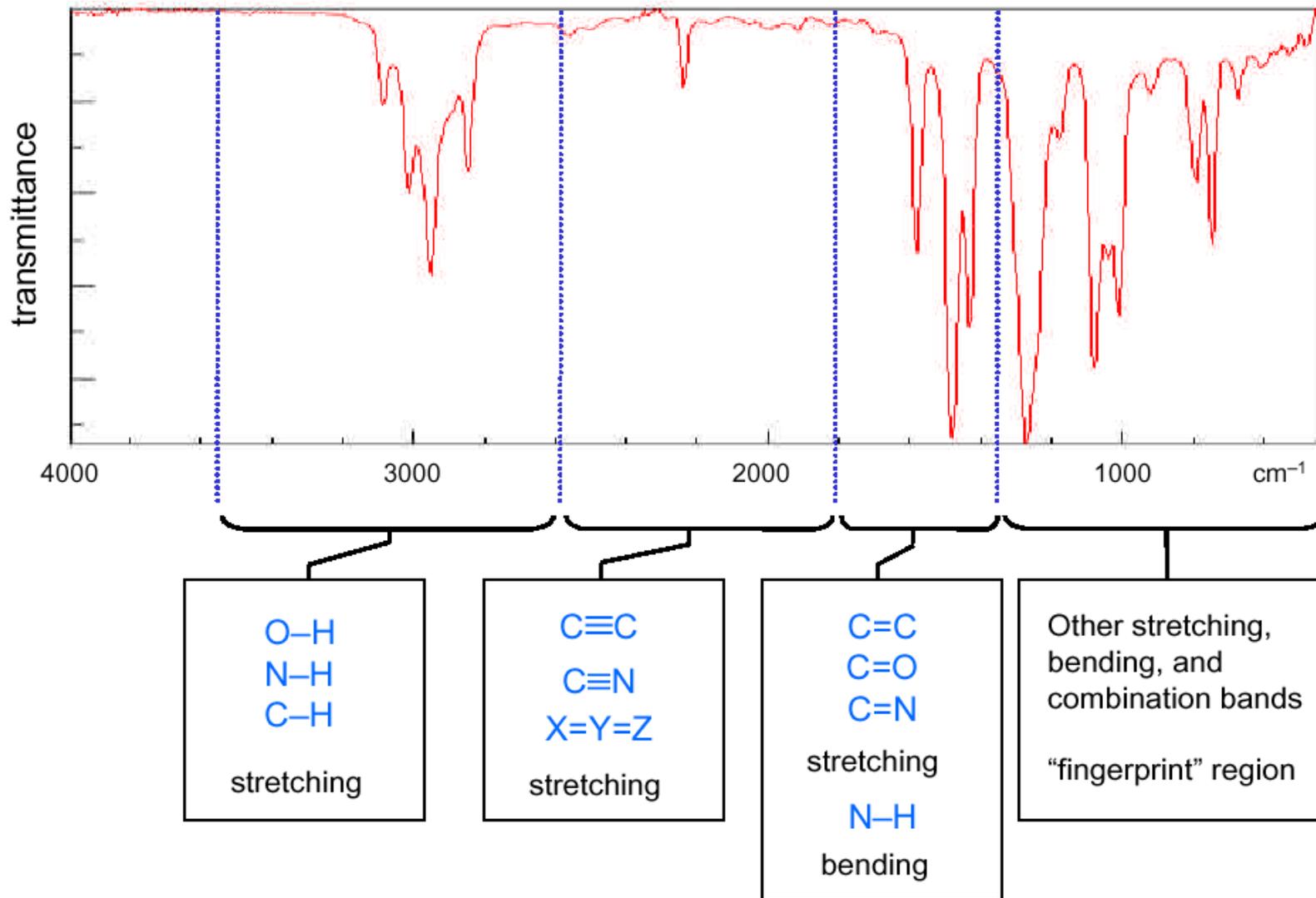
scissoring bending
666 cm⁻¹

scissoring bending
666 cm⁻¹

Absorption Regions

Irtutord.exe

Group frequencies

With certain functional or structural groups, it has been found that their vibrational frequencies are nearly independent of the rest of the molecule – group frequencies.

Carbonyl group   1650 to 1740 cm^{-1} various aldehydes and ketones

For many groups involving only two atoms, the approximate frequency of the fundamental vibration can be calculated from a simple *harmonic oscillator model*.

Calculations show that for most groups of interest, characteristic frequencies of stretching vibrations should lie in the region 4000 to 1000 cm^{-1}. In practical, the region from 4000 to 1300 cm^{-1} is often called the **group frequency region**.

The presence of various group vibrations in the IR spectrum is of great assistance in identifying the absorbing molecule.

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 $\left(\diagup C{=}C \diagdown^{H} \right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡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
C=C	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

Fingerprint region

In the region from $\approx$ 1300 to 400 cm^{-1}, vibrational frequencies are affected by the entire molecule, as the broader ranges for group absorptions in the figure below – **fingerprint region**.

Absorption in this fingerprint region is characteristic of the molecule as a whole. This region finds widespread use for identification purpose by comparison with library spectra.
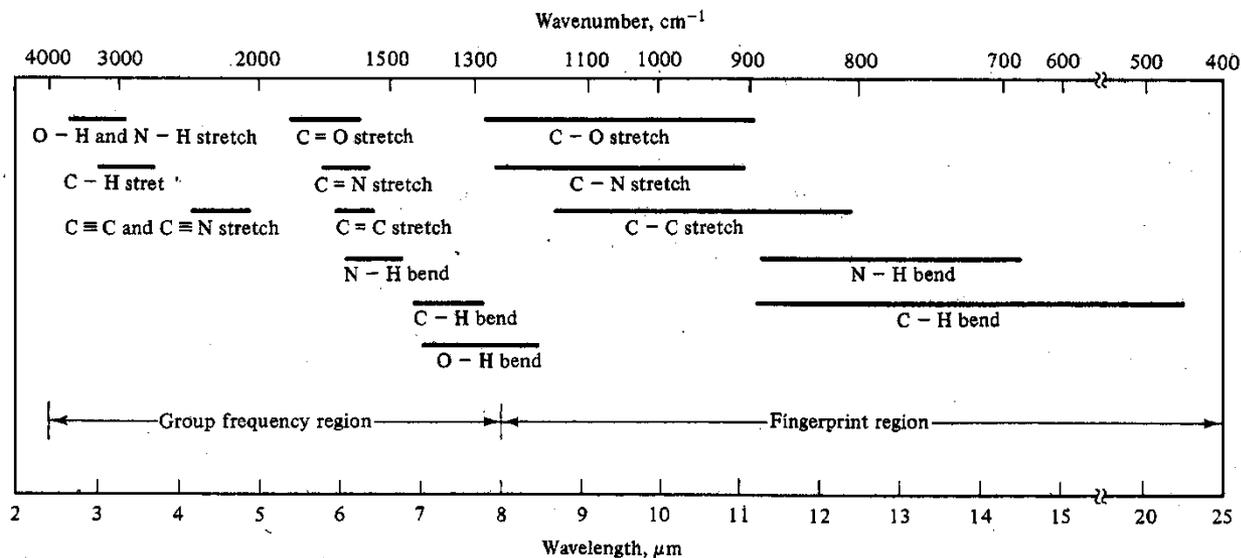

FIGURE 14-3 Frequencies of various group vibrations in the group frequency region and in the fingerprint region.

Main uses of IR spectroscopy:

1. Fundamental chemistry

Determination of molecular structure/geometry.

e.g. Determination of bond lengths, bond angles of gaseous molecules

2. Qualitative analysis – simple, fast, nondestructive

Monitoring trace gases: NDIR.Rapid, simultaneous analysis of GC, moisture, N in soil. Analysis of fragments left at the scene of a crime

Quantitative determination of hydrocarbons on filters, in air, or in water