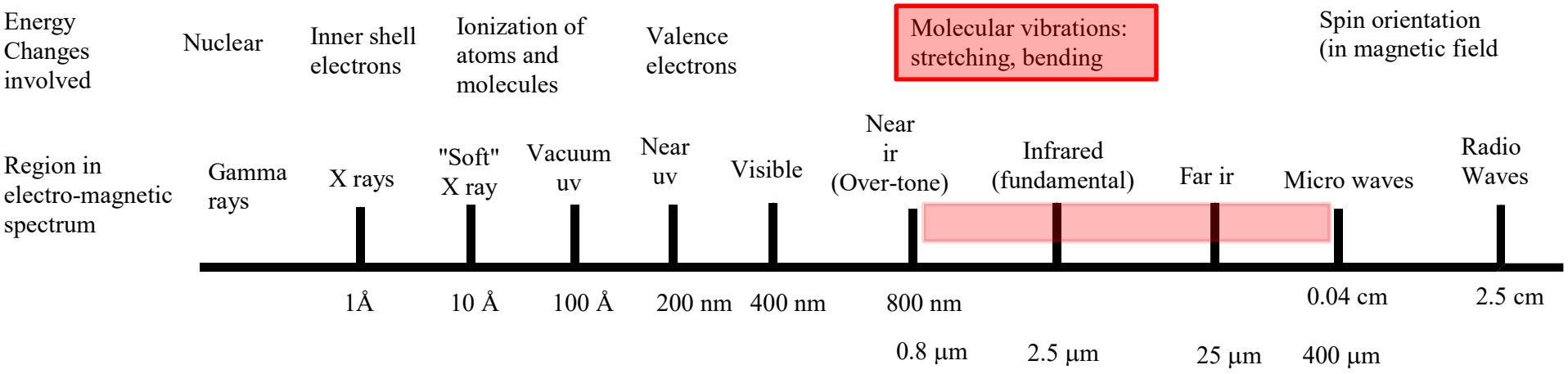
Infra-Red (IR)
&
Fourier Transform Infra-Red (FT-IR) Spectroscopy

Electromagnetic Spectrum: IR

- Far IR: 50 - 1000 μm
- Middle IR: 2.5 - 50 μm
- Near IR: 0.8 - 2.5 μm: 800 - 2500 nm
- Vibrational energy wavelength: 2.5 - 25 μm: 2.5×10^{-4} - 25×10^{-4} cm

✓ mostly 2.5 – 15 μm: 2.5×10^{-4} - 15×10^{-4} cm

- Vibrational energy wavenumber (frequency): 4000 - 400 cm^{-1}



$$cm^{-1} = \frac{1}{(\mu m)} \times 10{,}000 \quad \text{and} \quad \mu m = \frac{1}{(cm^{-1})} \times 10{,}000$$

Electromagnetic Spectrum Portions

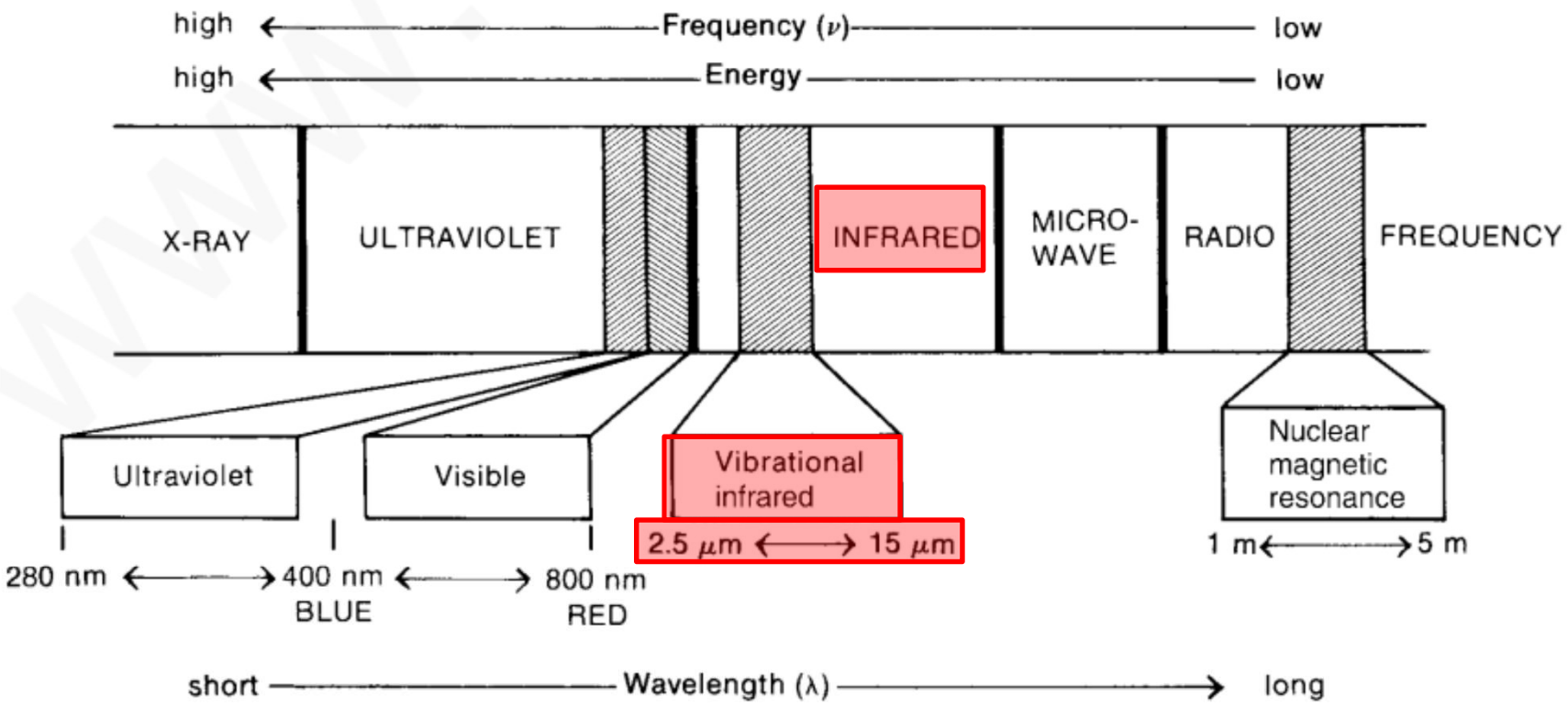


FIGURE 2.1 A portion of the electromagnetic spectrum showing the relationship of the vibrational infrared to other types of radiation.

Types of Energy in Electromagnetic Spectrum

TABLE 2.1
TYPES OF ENERGY TRANSITIONS IN EACH REGION OF THE ELECTROMAGNETIC SPECTRUM

Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

Interaction of IR & Matter

- Selected frequencies or energy of IR radiation is absorbed by atoms in bonds.
- Absorbed frequencies are close to natural vibrational frequencies of molecules & bonds in molecules.
- Bonds that have dipole moment that changes as a function of time are capable of absorption of IR radiation.
- Symmetric bonds do not absorb IR.
- No two molecules has the same IR absorption pattern or spectrum.
- Hence, IR spectrum is called as fingerprint of a compound.
- Simplest types or modes of vibrational motion in a molecule that is IR active, give rise to absorptions, are stretching & bending modes.

IR Approximate Regions Absorbed by Common Types of Bonds & Functional Groups

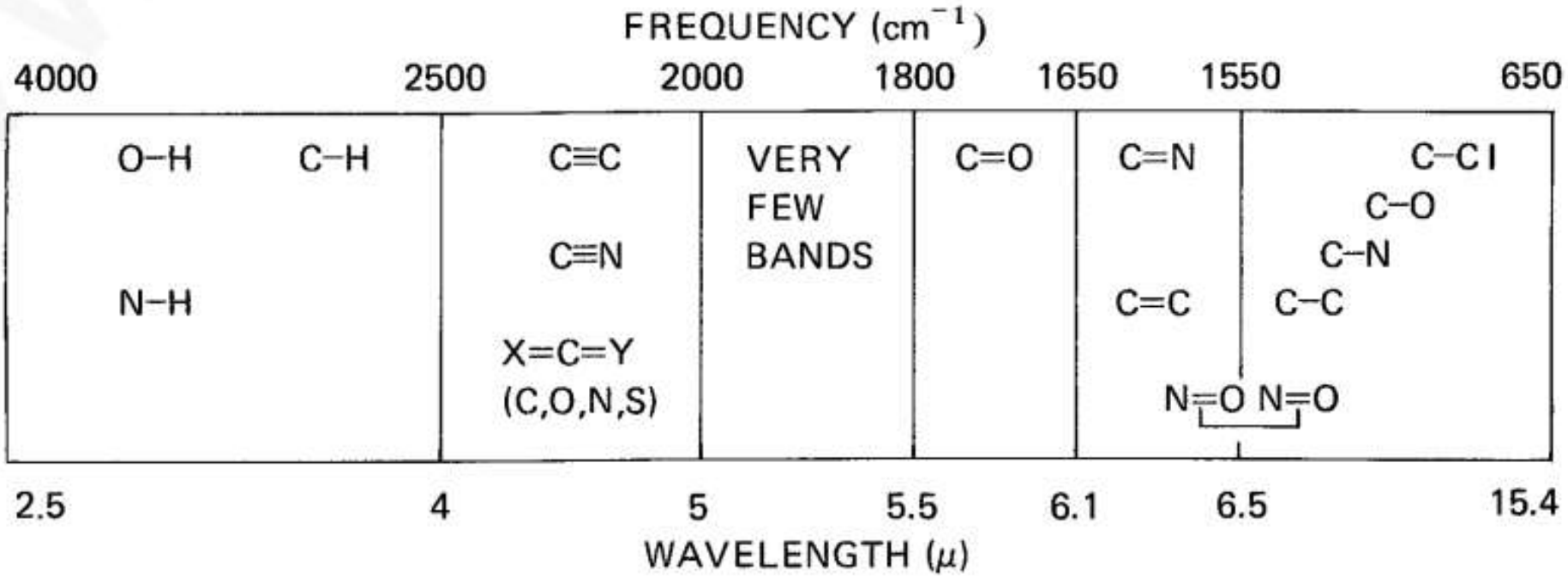


FIGURE 2.2 The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

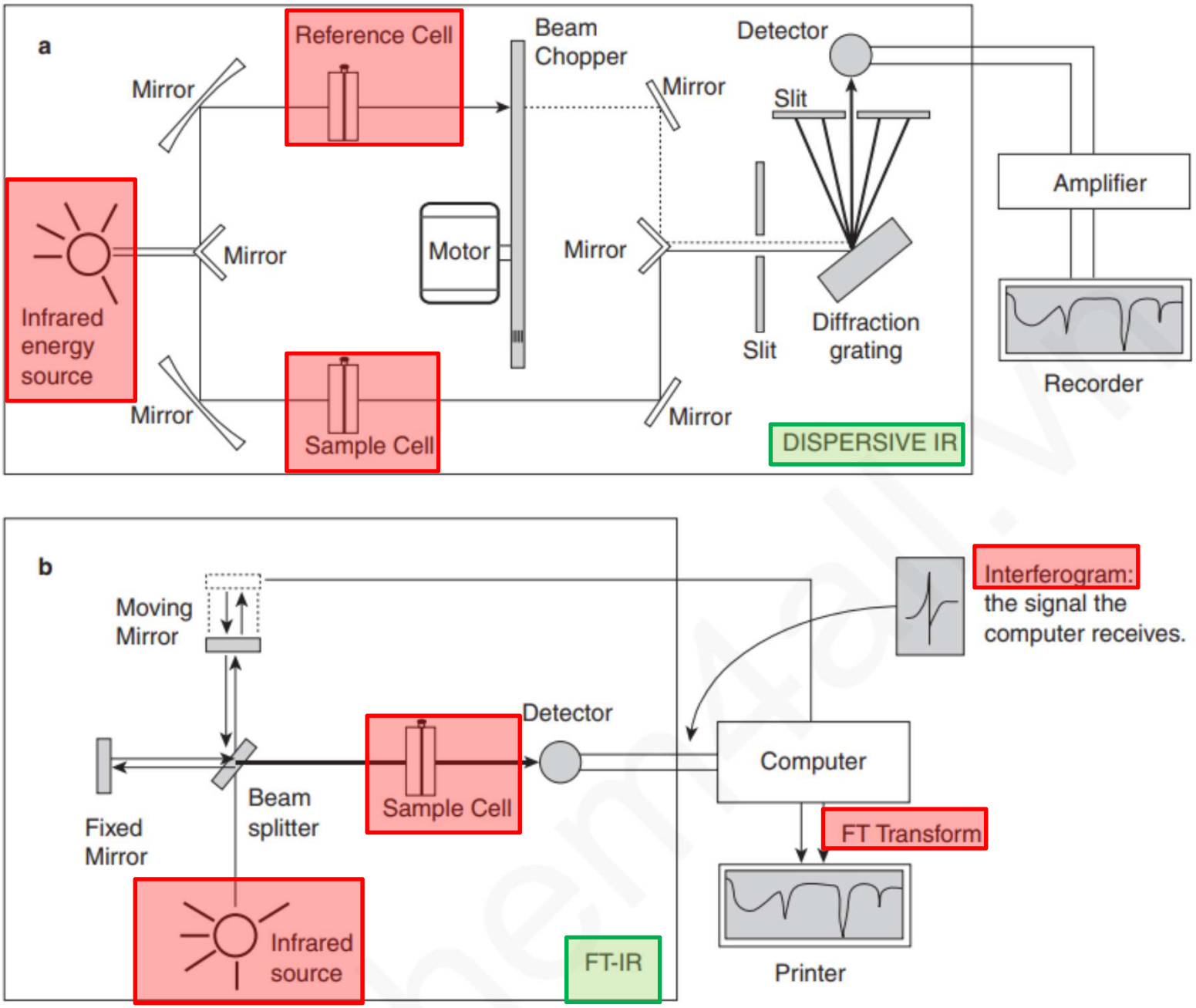
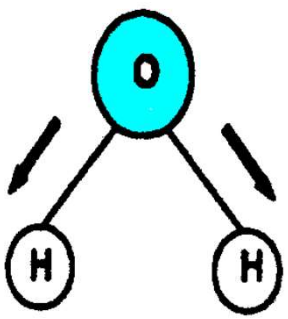


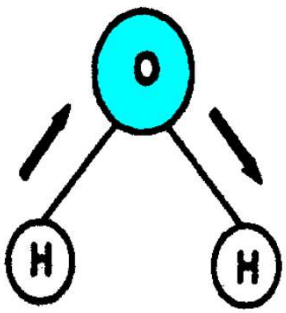
FIGURE 2.3 Schematic diagrams of (a) dispersive and (b) Fourier transform infrared spectrophotometers.

Stretching & Bending by IR Radiation

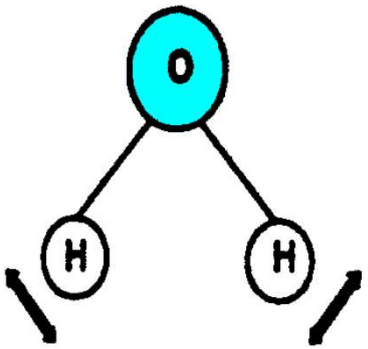
- The bonds between atoms in a molecule stretch & bend via absorbing infrared energy & creating the infrared spectrum.



Symmetric Stretch



Antisymmetric Stretch

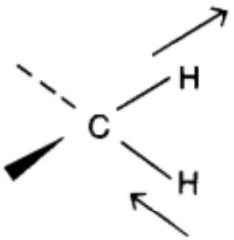


Bend

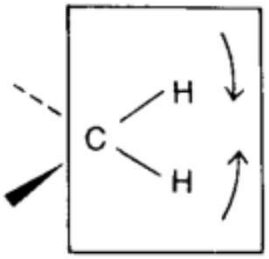
- A molecule such as H_2O will absorb infrared light when the vibration (stretch or bend) results in a molecular dipole moment change.

Types of Stretching & Bending in Molecules

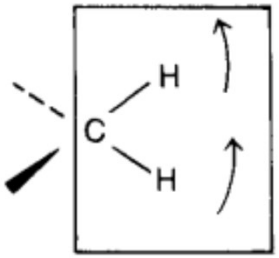
Symmetric stretch
(~2853 cm^{-1})



Asymmetric stretch
(~2926 cm^{-1})

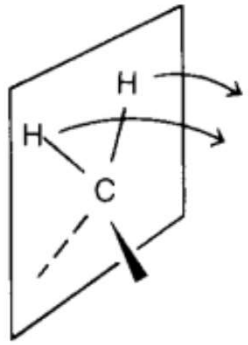


Scissoring
(~1450 cm^{-1})

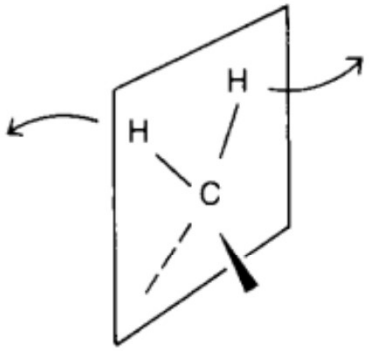


Rocking
(~720 cm^{-1})

IN-PLANE



Wagging
(~1250 cm^{-1})



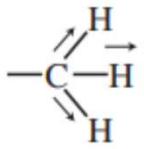
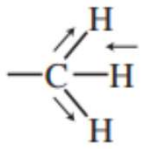
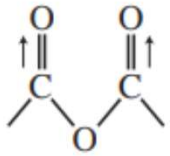
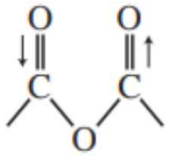
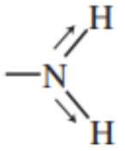
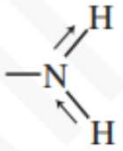
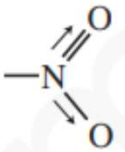
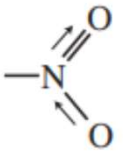
Twisting
(~1250 cm^{-1})

OUT-OF-PLANE

STRETCHING VIBRATIONS

BENDING VIBRATIONS

Symmetric & Asymmetric Stretches for a Couple of Functional Groups

	Symmetric Stretch	Asymmetric Stretch
Methyl		
	~2872 cm^{-1}	~2962 cm^{-1}
Anhydride		
	~1760 cm^{-1}	~1800 cm^{-1}
Amino		
	~3300 cm^{-1}	~3400 cm^{-1}
Nitro		
	~1350 cm^{-1}	~1550 cm^{-1}

Hook Law to Imagine Vibrational Energy

$$\bar{\nu}(\text{cm}^{-1}) = 4.12\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2}, \quad \text{where } M_1 \text{ and } M_2 \text{ are atomic weights}$$

K = force constant in dynes/cm (1 dyne = 1.020×10^{-3} g)

- K: force constant which is depended on atoms & bonds

Examples of Theoretical Calculations for Stretching Frequency of IR Absorption:

- Planck equation: E = h×υ
- -C=C-
- -C-H
- -C-D

TABLE 2.2
CALCULATION OF STRETCHING FREQUENCIES FOR DIFFERENT TYPES OF BONDS

C=C bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 10 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_C}{M_C + M_C} = \frac{(12)(12)}{12 + 12} = 6$$

$$\bar{\nu} = 4.12\sqrt{\frac{10 \times 10^5}{6}} = 1682 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{\nu} = 1650 \text{ cm}^{-1}$ (experimental)

C–H bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 5 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_H}{M_C + M_H} = \frac{(12)(1)}{12 + 1} = 0.923$$

$$\bar{\nu} = 4.12\sqrt{\frac{5 \times 10^5}{0.923}} = 3032 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{\nu} = 3000 \text{ cm}^{-1}$ (experimental)

C–D bond:

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 5 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_D}{M_C + M_D} = \frac{(12)(2)}{12 + 2} = 1.71$$

$$\bar{\nu} = 4.12\sqrt{\frac{5 \times 10^5}{1.71}} = 2228 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{\nu} = 2206 \text{ cm}^{-1}$ (experimental)

Applications of Infrared Analysis

- Qualitative control analysis, mostly:

✓ identification of organic solid, liquid or gas samples.

✓ distinguish of identical compounds: due to pattern of spectrum.

- structural elucidation: to identify structural information of compounds: by its molecular vibrations:

✓ based on the absorption wavelength/s & intensity of spectrum peaks.

- Quantitative control analysis, rarely:

✓ quantitation of organic solid, liquid or gas samples.

- Target analysts: powders, solids, gels, emulsions, pastes, pure liquids & solutions, polymers, pure & mixed gases.
- Applied for research, method development, quality control & assurance.
- Definitely, computer is applied for the mentioned applications.

Various Fields to Apply Infrared

- Pharmaceutical research
- Forensic investigations
- Polymer analysis
- Lubricant formulation and fuel additives
- Foods research
- Quality assurance & control
- Environmental & water quality analysis methods
- Biochemical & biomedical research
- Coatings & surfactants
- Etc.

Applications of IR Spectroscopy in Various Fields

- Quantitative fingerprint check for identification of raw material used in manufacture.
- Quantitative analysis of multicomponent in a sample.
- Characterization of components & excipients in the solid & semi-solid states of matters.
- Fingerprint test for films, coating & packing plastics
- Detection or determination of polymorphs of drugs
- Detection or determination of water content of drugs
- Detection of moisture as impurity: strong absorption band in 1940 cm^{-1}
- Distinguish of enantiomers in mixture comparing to pure enantiomers

- Reaction progress study in synthetic chemistry: due to functional groups