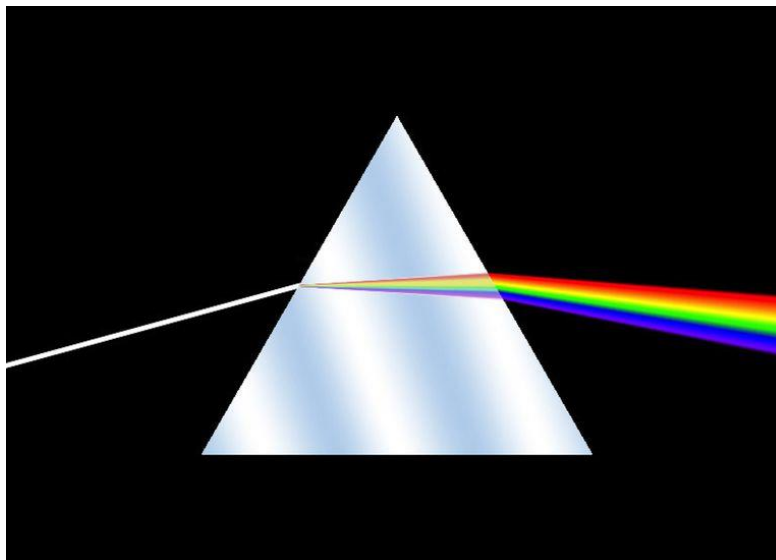# Introduction to Spectroscopy



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# ☐ What is spectroscopy?

➢ **Studying the properties of matter through its interaction with different frequency components of the electromagnetic spectrum.**

➢ **The study of the interaction between radiation and matter as a function of wavelength λ.**

➢ **Interaction with particle radiation or a response of a material to an alternating field or varying frequency ν.**

➢ **Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis.**

# ☐ Goals:

➢ **Understand how light interacts with matter and how you can use this to *quantitatively understand your sample*.**

➢ **Understand spectroscopy the way you understand other common tools of measurement like the watch or the ruler.**

➢ **See that *spectroscopy is a set of tools* that you can put together in different ways to *understand systems → solve chemical problems*.**

# ❑ What is Spectrum?

➤ **The data that is obtained from spectroscopy is called a spectrum.**

➤ A **spectrum** is a **plot of the intensity** of **energy detected** versus **the wavelength (or mass or momentum or frequency, etc.) of the energy.**

➤ A **plot** of the **response** as a **function** of **wavelength** or more commonly **frequency** is referred as a **spectrum.**

# ❑ What is Spectrometry?

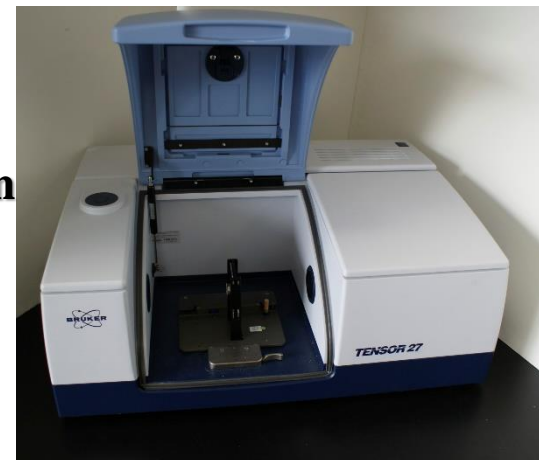➤ **It is the measurement of these responses.**

# ❑ What is spectrometer?

➤ **An instrument which performs such measurement.**
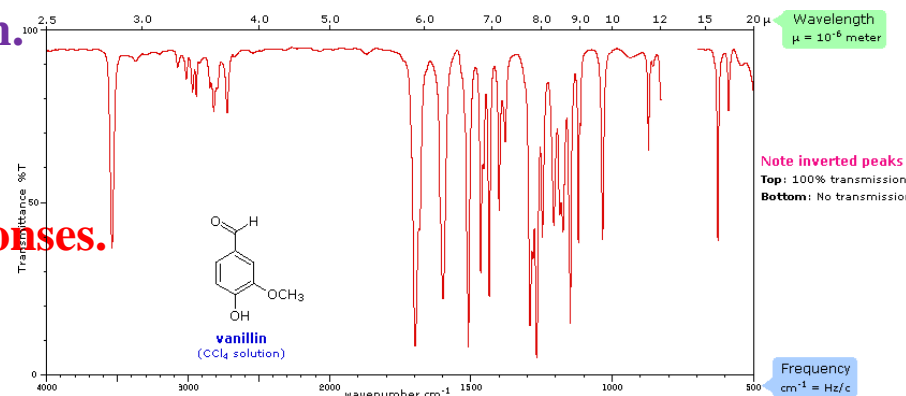
**Reference Books**
1. **Introduction to Spectroscopy, 3rd Edn, Pavia & Lampman**
2. **Organic Spectroscopy – P S Kalsi**

# ❑ Common types?

➢ **Fluorescence Spectroscopy.**

➢ **X-ray spectroscopy and crystallography**

➢ **Flame spectroscopy**

  a) **Atomic emission spectroscopy**

  b) **Atomic absorption spectroscopy**

  c) **Atomic fluorescence spectroscopy**

➢ **Plasma emission spectroscopy**

➢ **Spark or arc emission spectroscopy**

➢ **IR spectroscopy**

➢ **UV-Vis Spectroscopy**

➢ **Raman Spectroscopy**

➢ **NMR spectroscopy**

➢ **EPR Spectroscopy**

➢ **Photo thermal spectroscopy**

➢ **Thermal infra-red spectroscopy**
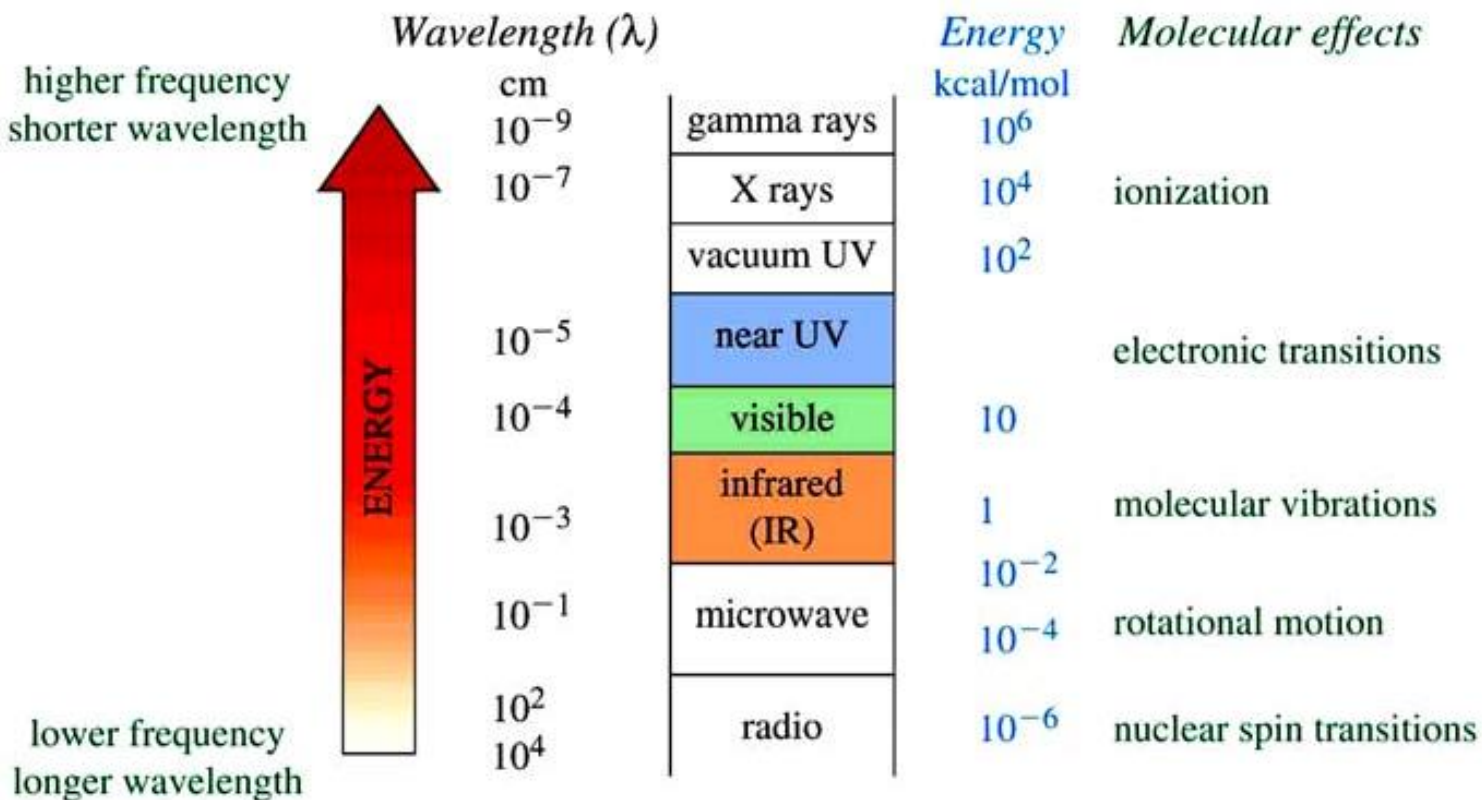
➢ **Mass Spectroscopy**

# ❏Infra-red spectroscopy

➢ **The important parameters associated with electromagnetic radiation are: Energy (E): Energy is directly proportional to frequency, and inversely proportional to wavelength, as indicated by the equation below.**

➢ **Frequency (ν)**
➢ **Wavelength (λ)**                    $E = h\nu$

## EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



| Wavelength (λ) | | Energy | Molecular effects |
|---|---|---|---|
| higher frequency shorter wavelength | cm | kcal/mol | |
| | $10^{-9}$ | gamma rays | $10^{6}$ | |
| | $10^{-7}$ | X rays | $10^{4}$ | ionization |
| | | vacuum UV | $10^{2}$ | |
| | $10^{-5}$ | near UV | | electronic transitions |
| | $10^{-4}$ | visible | $10$ | |
| | $10^{-3}$ | infrared (IR) | $1$ | molecular vibrations |
| | | | $10^{-2}$ | |
| | $10^{-1}$ | microwave | $10^{-4}$ | rotational motion |
| | $10^{2}$ $10^{4}$ | radio | $10^{-6}$ | nuclear spin transitions |

lower frequency longer wavelength

ENERGY

# **Applications of IR Spectroscopy**

- To establish the identity of two compounds (comparative study)

- To determine the structure of a new compound from its functional groups

- To determine the nature of contaminants in a sample

- For quantitative analysis of a component in the overall mixture

- For the quantitative analysis of contaminants in given sample

- Some advanced physical properties of the materials

# IR REGION

From application and instrumentation point of view infrared region is subdivided into

| Region | Wave length (m) | Wave number(cm$^{-1}$) |
|---|---|---|
| Near infrared | 0.75-2.5 | 14000-4000 |
| Mid infrared | 2.5-50 | 4000-400 |
| Far infrared | 50-300 | 400-40 |

```
                Mid IR
            (4000-40 cm⁻¹)


   Functional group     Finger Print/Single
        region             bond region
    (4000-1400 cm⁻¹)      (1400-40cm⁻¹)
```

Mid IR (4000-40 cm$^{-1}$)

Functional group region (4000-1400 cm$^{-1}$)

Finger Print/Single bond region (1400-40cm$^{-1}$)

➤ Stretching vibrations occurs in F.G. region
➤ Bending vibrations occurs in F.P. region

❑ **Infrared radiation is largely thermal energy.**

❑ **It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms.**

**Specific bonds respond to (absorb) specific frequencies**
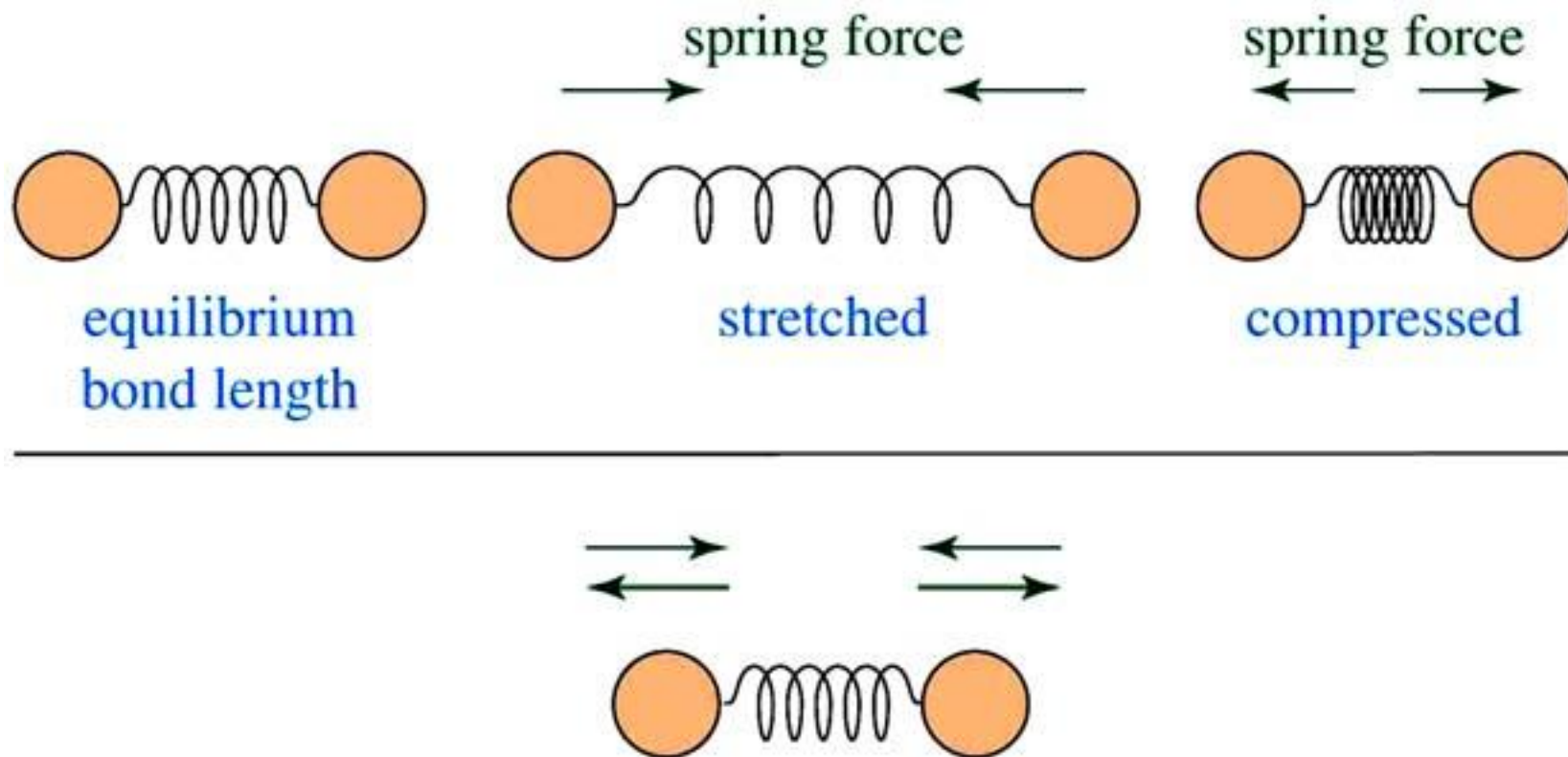
# Types of vibrations in a molecule

Two fundaments types:

       1- Stretching

       2- Bending

## Stretching:

The distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

## Bending:

The position of the atoms changes with respect to the original bond axis.

**Essential criteria for a molecule to be IR active**:
- Only those vibration modes are **IR active** that involve *a change in dipolemoment, during vibration*.
- $H_2, N_2, O_2, Br_2, Cl_2, I_2$ etc and IR inactive, while **CO, NO, CO_2**, etc are **IR active**

## Stretching Vibrations:

c) Symmetric stretch

d) Asymmetric stretch

## Bending Vibrations:

g) Scissoring

h) Rocking

i) Wagging

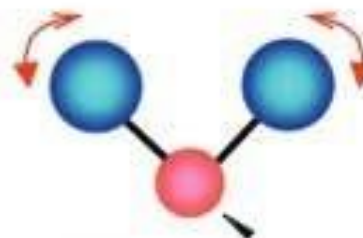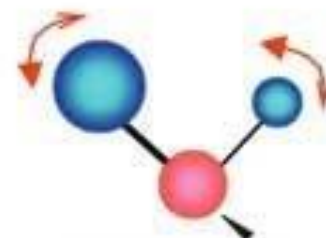j) Twisting
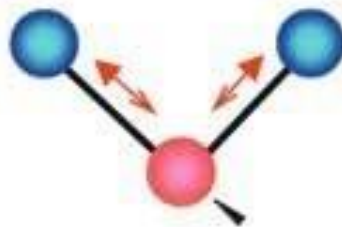


Symmetric stretching
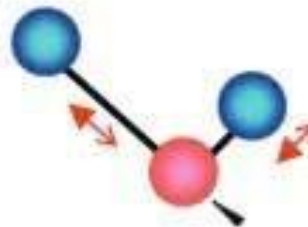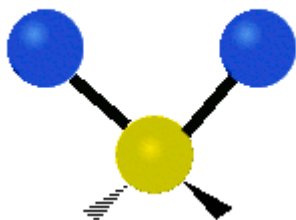
Antisymmetric stretching
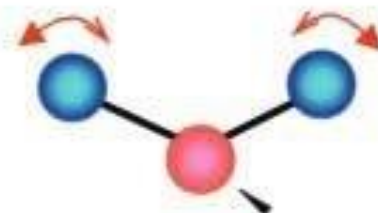
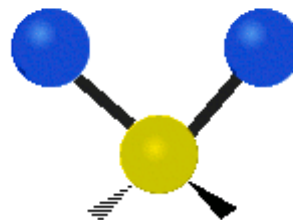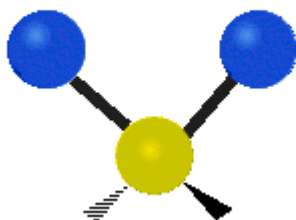In-plane scissoring
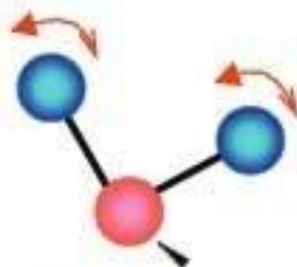
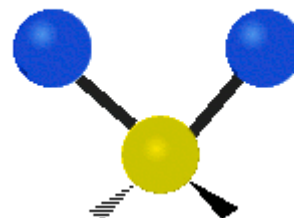In-plane rocking

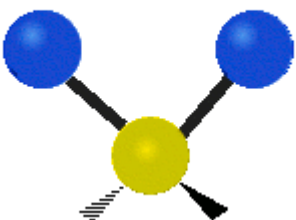Out-of-plane wagging

Out-of-plane twisting
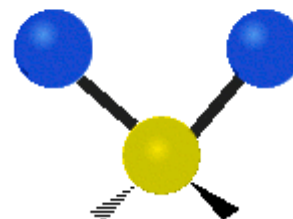
**Symmetric stretching**

**Asymmetric stretching**

**Scissoring**

**Rocking**

**Twisting**

**Wagging**

# Hooke's Law

$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$\bar{v}$ = wave number, in $cm^{-1}$, corresponding to the vibrational frequency of the bond

c = speed of light in $cms^{-1}$

K = force constant in $dynescm^{-1}$ ( a measure of bond strength. The stronger the bond, the larger the K.)

$\mu$ = reduced mass in $gatom^{-1}$

atom 1                                                                                          atom 2

mass = $m_1$ g                                                                              mass = $m_2$ g

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

which for a harmonic oscillator is determined by the force constant $K$ of the spring, or its stiffness, and the masses ($m_1$ and $m_2$) of the two bonded atoms. The natural frequency of vibration of a bond is given by the equation

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

which is derived from Hooke's Law for vibrating springs. The **reduced mass** $\mu$ of the system is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$K$ is a constant that varies from one bond to another. As a first approximation, the force constants for triple bonds are three times those of single bonds, whereas the force constants for double bonds are twice those of single bonds.

Two things should be noticeable immediately. One is that stronger bonds have a larger force constant $K$ and vibrate at higher frequencies than weaker bonds. The second is that bonds between atoms of higher masses (larger reduced mass, $\mu$) vibrate at lower frequencies than bonds between lighter atoms.

In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration (higher wavenumbers):

| C≡C | C=C | C−C |
|---|---|---|
| 2150 cm⁻¹ | 1650 cm⁻¹ | 1200 cm⁻¹ |

$$\longleftarrow$$
Increasing $K$
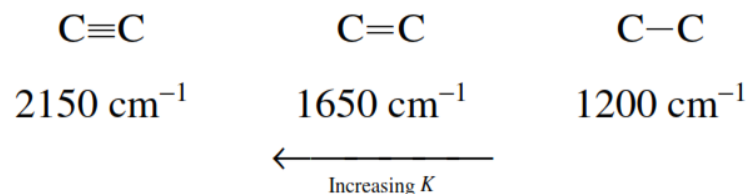
The C−H stretch occurs at about 3000 cm$^{-1}$. As the atom bonded to carbon increases in mass, the reduced mass ($\mu$) increases, and the frequency of vibration decreases (wavenumbers get smaller):

| C−H | C−C | C−O | C−Cl | C−Br | C−I |
|---|---|---|---|---|---|
| 3000 cm$^{-1}$ | 1200 cm$^{-1}$ | 1100 cm$^{-1}$ | 750 cm$^{-1}$ | 600 cm$^{-1}$ | 500 cm$^{-1}$ |

$\longrightarrow$

Increasing $\mu$

Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant $K$.

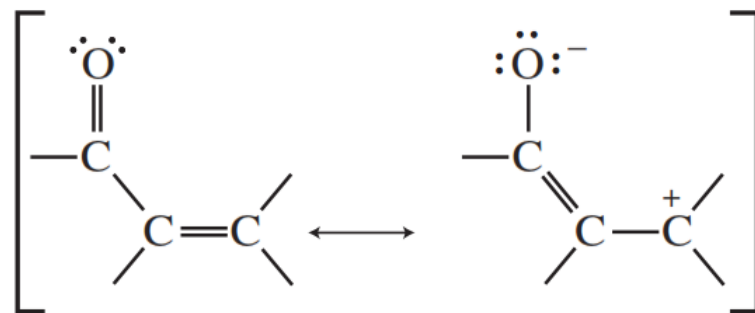| C−H stretching | C−H bending |
|---|---|
| ~3000 cm$^{-1}$ | ~1340 cm$^{-1}$ |

Hybridization affects the force constant $K$, also. Bonds are stronger in the order $sp > sp^2 > sp^3$, and the observed frequencies of C−H vibration illustrate this nicely.

| $sp$ | $sp^2$ | $sp^3$ |
|---|---|---|
| $\equiv$C−H | $=$C−H | −C−H |
| 3300 cm$^{-1}$ | 3100 cm$^{-1}$ | 2900 cm$^{-1}$ |

*Wavelength* in **μm** and *wavenumber* in **cm⁻¹** can be interconverted using the following expression

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

Resonance also affects the strength and length of a bond and hence its force constant $K$. Thus, whereas a normal ketone has its C=O stretching vibration at $1715\ cm^{-1}$, a ketone that is conjugated with a C=C double bond absorbs at a lower frequency, near 1675 to $1680\ cm^{-1}$. That is because resonance lengthens the C=O bond distance and gives it more single-bond character:



Resonance has the effect of reducing the force constant $K$, and the absorption moves to a lower frequency.
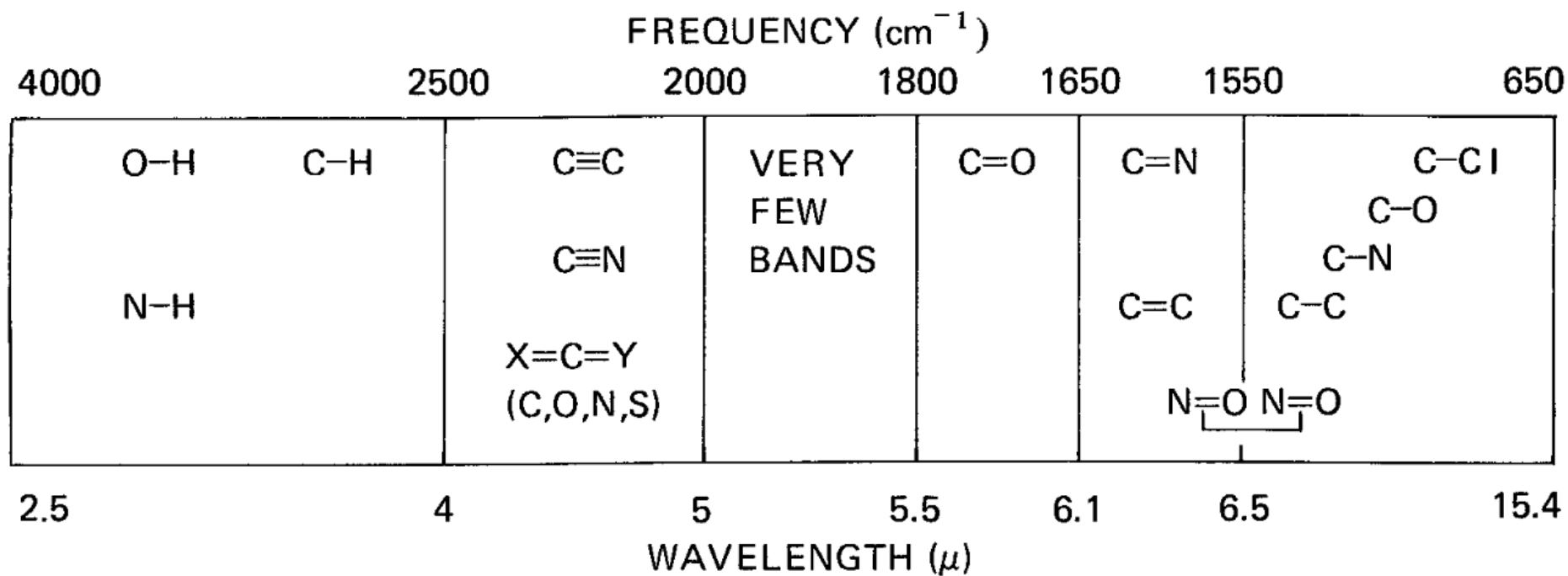
**FIGURE 2.2** The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

The Hooke's Law expression given earlier may be transformed into a very useful equation as follows:

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{v}$ = frequency in cm$^{-1}$

$c$ = velocity of light = $3 \times 10^{10}$ cm/sec

$K$ = force constant in dynes/cm

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \text{masses of atoms in grams,}$$

$$\text{or} \quad \frac{M_1 M_2}{(M_1 + M_2)(6.02 \times 10^{23})}, \quad \text{masses of atoms in amu}$$

Removing Avogadro's number ($6.02 \times 10^{23}$) from the denominator of the reduced mass expression ($\mu$) by taking its square root, we obtain the expression

$$\bar{v} = \frac{7.76 \times 10^{11}}{2\pi c} \sqrt{\frac{K}{\mu}}$$

# Solved Problems

C=C bond:

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

$$K = 10 \times 10^5 \text{ dynes/cm}$$

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

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

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

C−H bond:

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

$$K = 5 \times 10^5 \text{ dynes/cm}$$

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

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

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

# Solved Problems

C−D bond:

$$\overline{v} = 4.12\sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ dynes/cm}$$

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

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

$$\overline{v} = 2206 \text{ cm}^{-1} \text{ (experimental)}$$

**Q:** Why **IR** spectra is always reported in **wavenumbers** (cm⁻¹) and not in **wavelength** (μm)?

**Ans:** The reason is, if reported in **wavelength (μm)** the mid-**IR** range comes in the range 25 μm to 2.5 μm which is equivalent to 400 to 4000cm⁻¹ when reported in **wavenumbers (cm⁻¹)**. The reporting in **wavenumber** gives **better resolution** and make identification of the spectral bands easier.
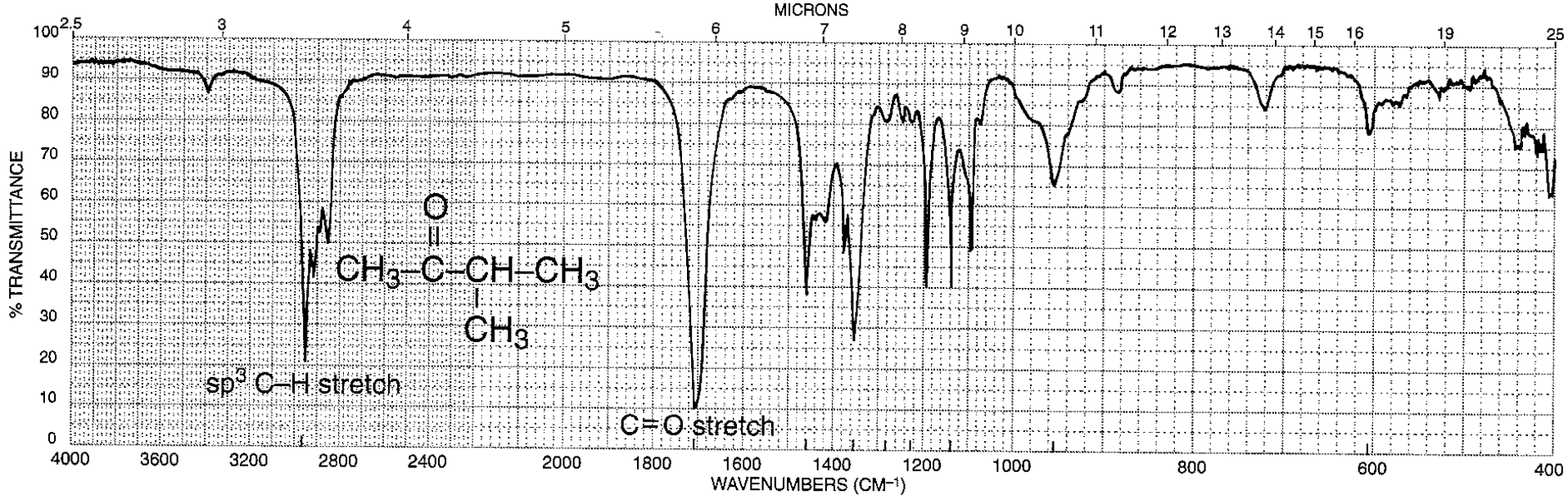
**FIGURE 2.4** The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).
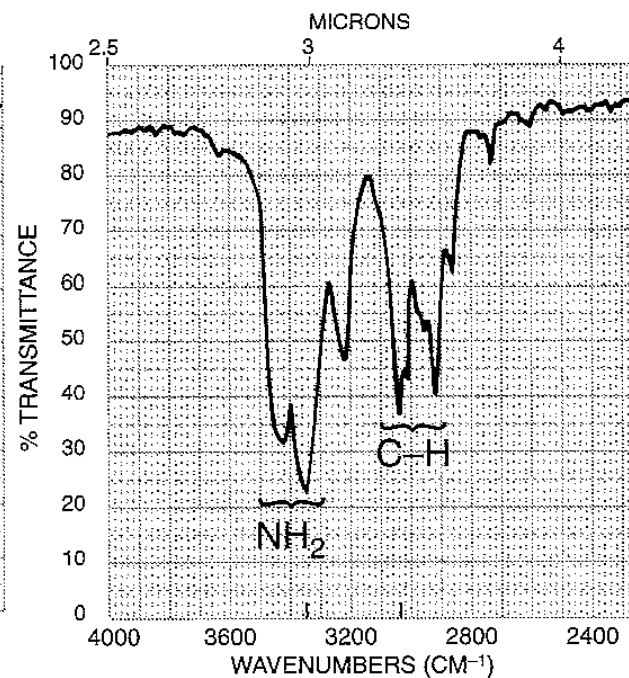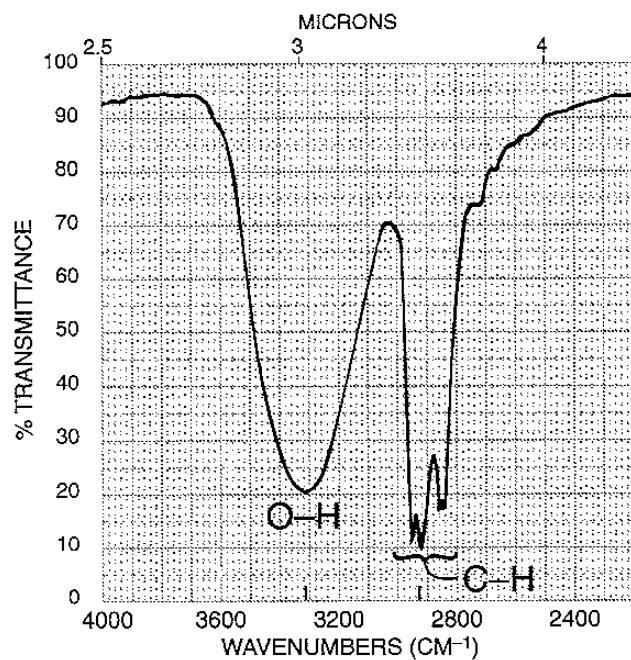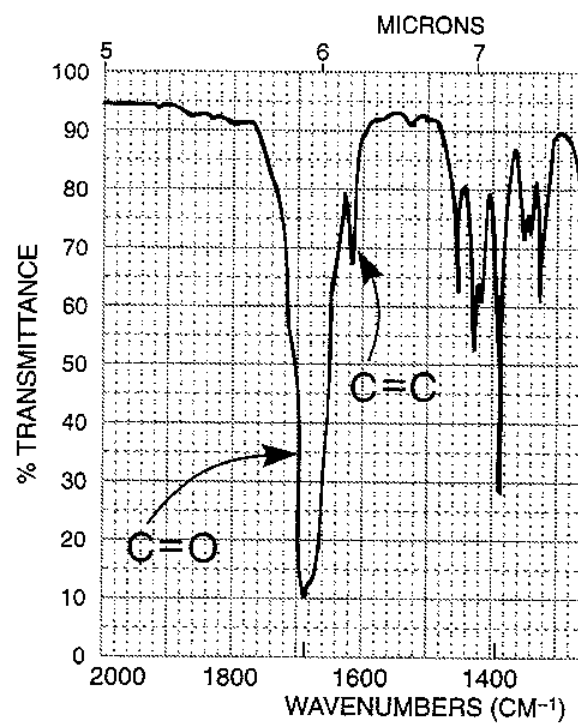
# Curio-city

**Q**: Why there are so many small and medium bands in IR spectra of even compounds with simple structure?

**Ans**: The reason is presence of Overtones, combination bands and difference bands.

**Q**: What are combination bands, Overtones and difference bands

**Ans:** Some times two vibrations of different values ($\nu_1$ and $\nu_2$) couple to give a new band whose frequency is $\nu_1 + \nu_2$. These bands are called combination bands.

During vibrational excitation from ground states to excited states some times excitation to higher energy states are also possible which are integral multiples of *fundamental vibration*, $\nu$. Hence new hands may appear at $2\nu$, $3\nu$, etc. These bands are called Overtones

Some times coupling of two different bands leads to new bands which are difference between the frequencies of either bands. $\nu_3 = \nu_1 - \nu_2$. These bands are called difference bands.

**Q**: Why the bands are **not sharp, but rather broad**?

**Ans:** This is because, some times, rotational frequencies couple with vibrational frequency, creating additional fine structure due to small transitions.