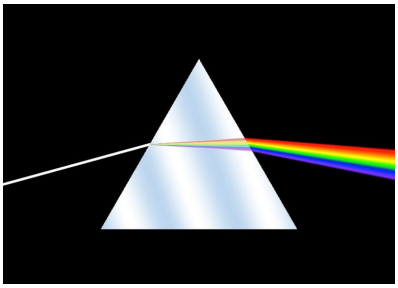
Introduction to Spectroscopy



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What is spectroscopy?

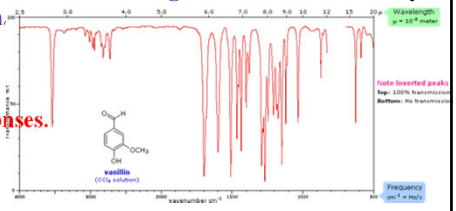
- Studying the properties of matter through its interaction with different frequency components of the electromagnetic spectrum.
- The study of the interaction between radiation and matter as a function of wavelength λ.
- Interaction with particle radiation or a response of a material to an alternating 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?

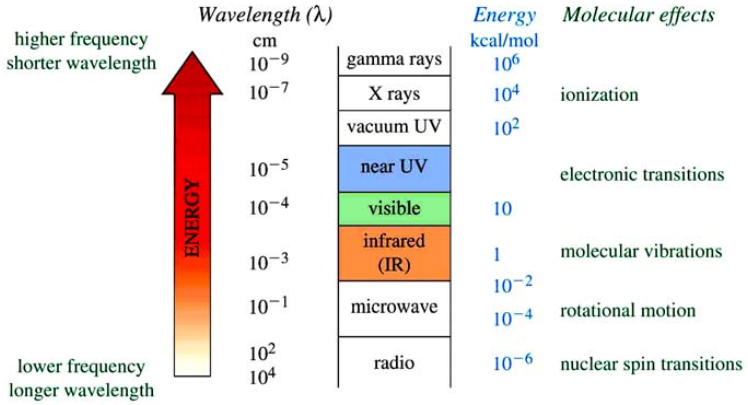
- Fluorescence Spectroscopy.
- X-ray spectroscopy and crystallography
- Flame spectroscopy
  a) Atomic emission spectroscopy
  b) Atomic absorption spectroscopy
  c) Atomic fluorescence spectroscopy
- Plasma emission spectroscopy
- Spark or arc emission spectroscopy
- **IR spectroscopy**
- **UV-Vis Spectroscopy**
- 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



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

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

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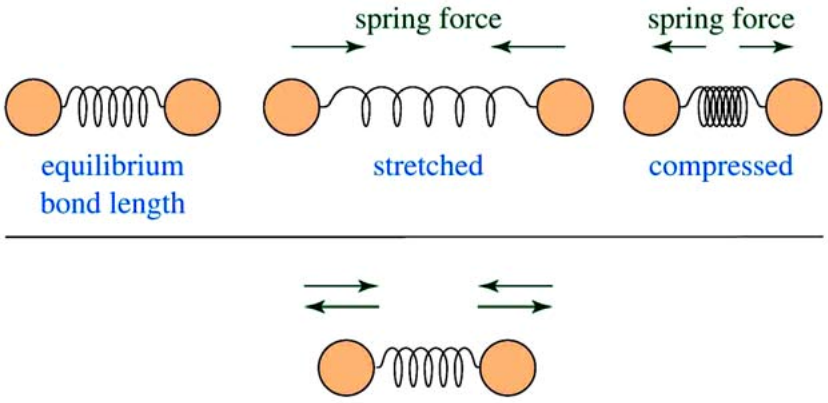
- **Infrared radiation is largely thermal energy.**
- **It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms.**

Specific bonds respond to (absorb) specific frequencies



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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

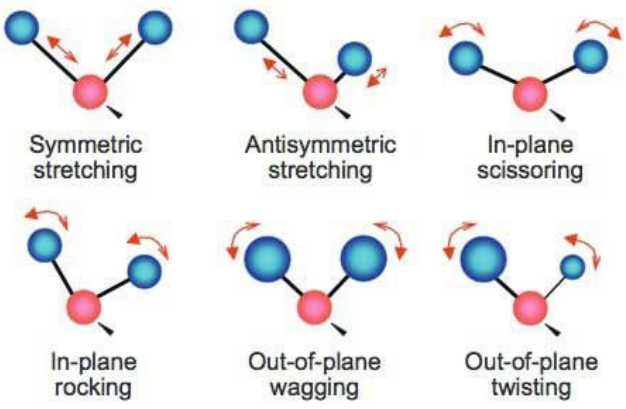
Bending Vibrations:

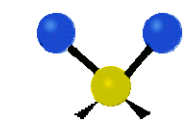
g) Scissoring

h) Rocking

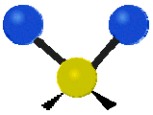
i) Wagging

j) Twisting

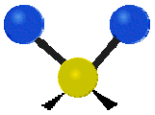




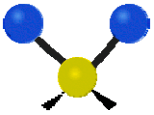
Symmetric stretching



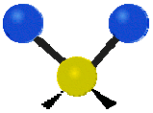
Asymmetric stretching



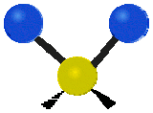
Scissoring



Rocking

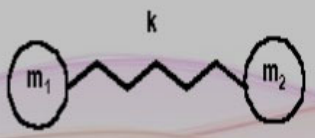


Twisting



Wagging

Hooke's law



$$\bar{\upsilon} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

$\bar{\upsilon}$ = frequency

μ = reduced mass

K = force constant (in dynes/cm)

m = atomic masses of atom 1 & 2

Hooke's law of elasticity is an approximation which states that the extension of a spring is in direct proportion with the load added to it as long as this load does not exceed the elastic limit.

Used to calculate approximate position of band

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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

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

which is derived from Hooke's Law for vibrating springs. The **reduced mass** μ 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, μ) 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}

← Increasing K

The C−H stretch occurs at about 3000 cm^{-1}. As the atom bonded to carbon increases in mass, the reduced mass (μ) 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}

→ Increasing μ

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}

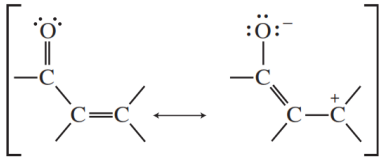
Hybridization affects the force constant K, also. Bonds are stronger in the order $sp > sp^2 > sp^3$, and the observed frequencies of C−H vibration illustrate this nicely.

sp	sp^2	sp^3
≡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

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

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.

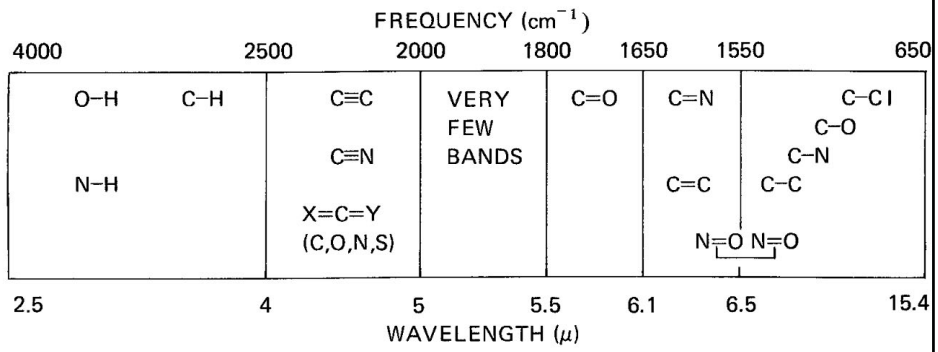


FIGURE 2.2 The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

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

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

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

c = velocity of light = 3×10^{10} cm/sec

K = force constant in dynes/cm

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$, masses of atoms in grams,

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

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

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

Solved Problems

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)

Solved Problems

C–D bond:

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

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

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

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

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

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.

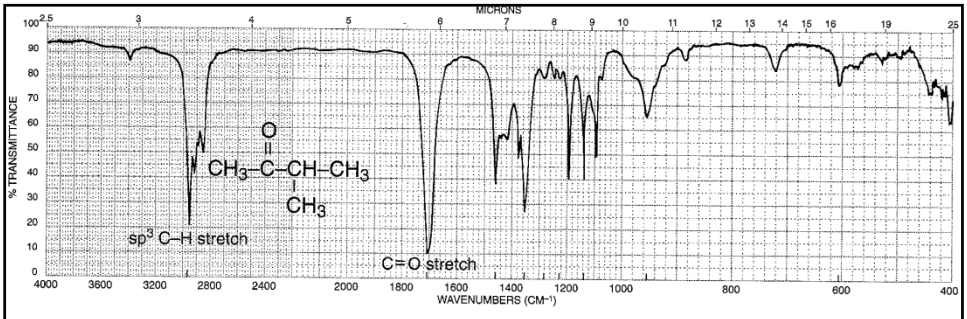
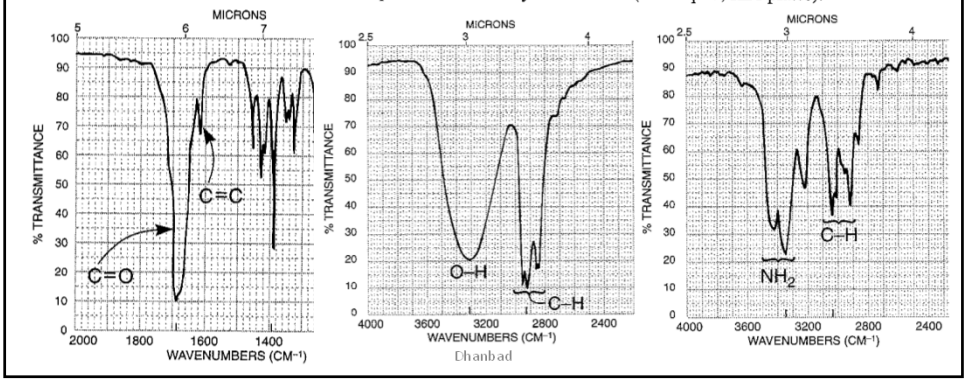


FIGURE 2.4 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).



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 (ν_1 and ν_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*, ν. Hence new hands may appear at 2ν, 3ν, 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.