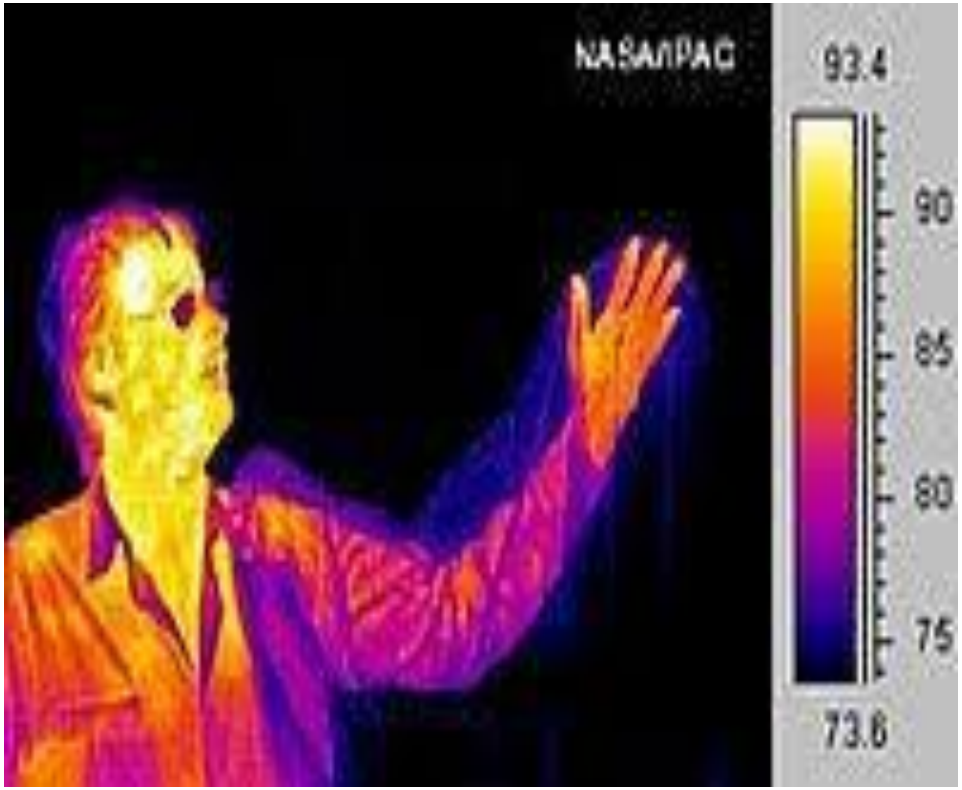
Infrared Spectroscopy



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Objective and Outcome

- Objective:

  To make students aware about Infrared spectroscopy and its application in pharmaceutical industry

- Outcome :

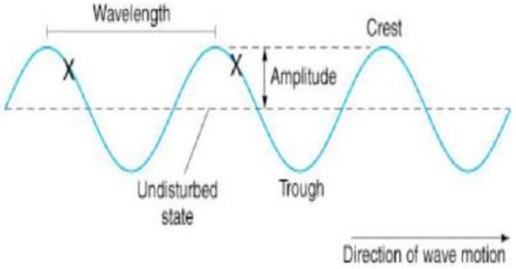
  Students should be able to understand and explain the interaction of matter with EMR of IR range and its applications in pharmaceutical industry.

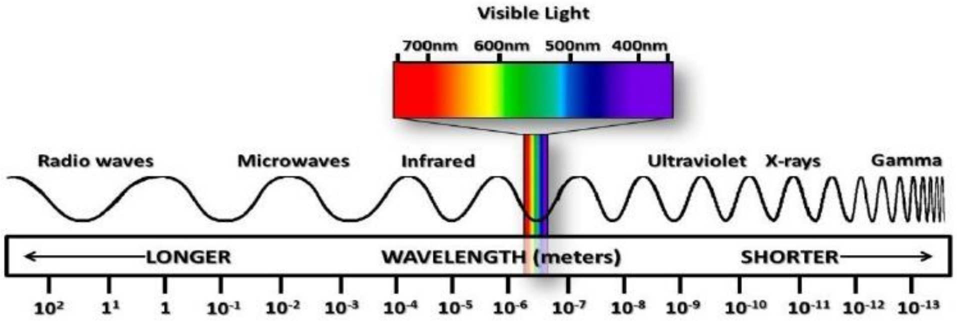
Contents:

- Introduction :
- Theory of IR absorption spectroscopy (modes of vibration of atoms in polyatomic molecules, stretching and bending vibration)
- Interpretation of IR spectra, quantitative analysis, routine maintenance,
- Dispersive and FT-IR instrumentation
- Application to pharmaceuticals.

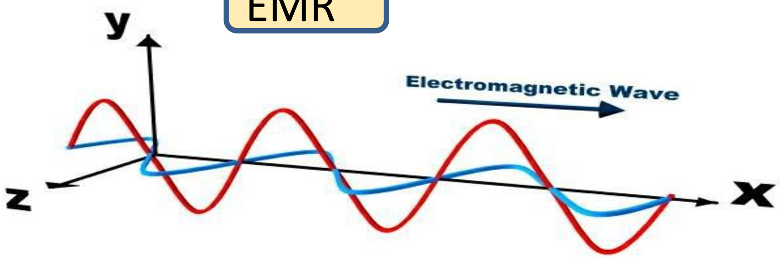
Introduction:

Spectroscopy : Interaction of EMR with matter



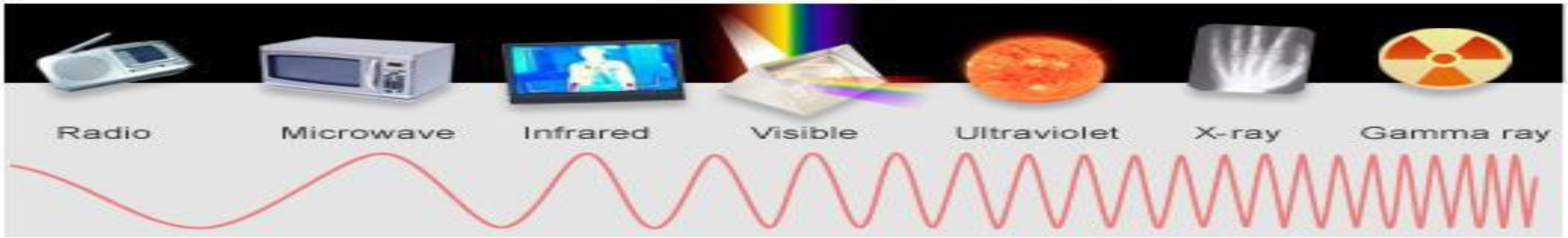


EMR

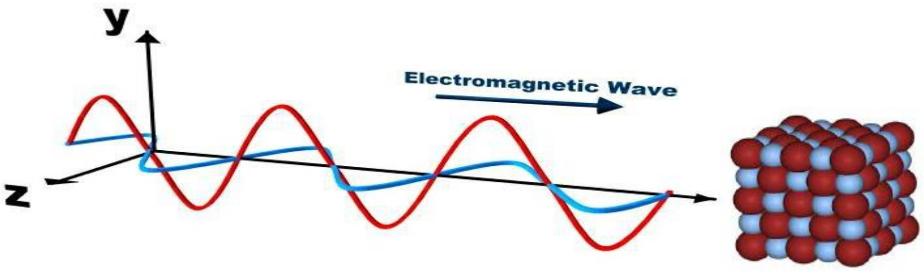


Matter:

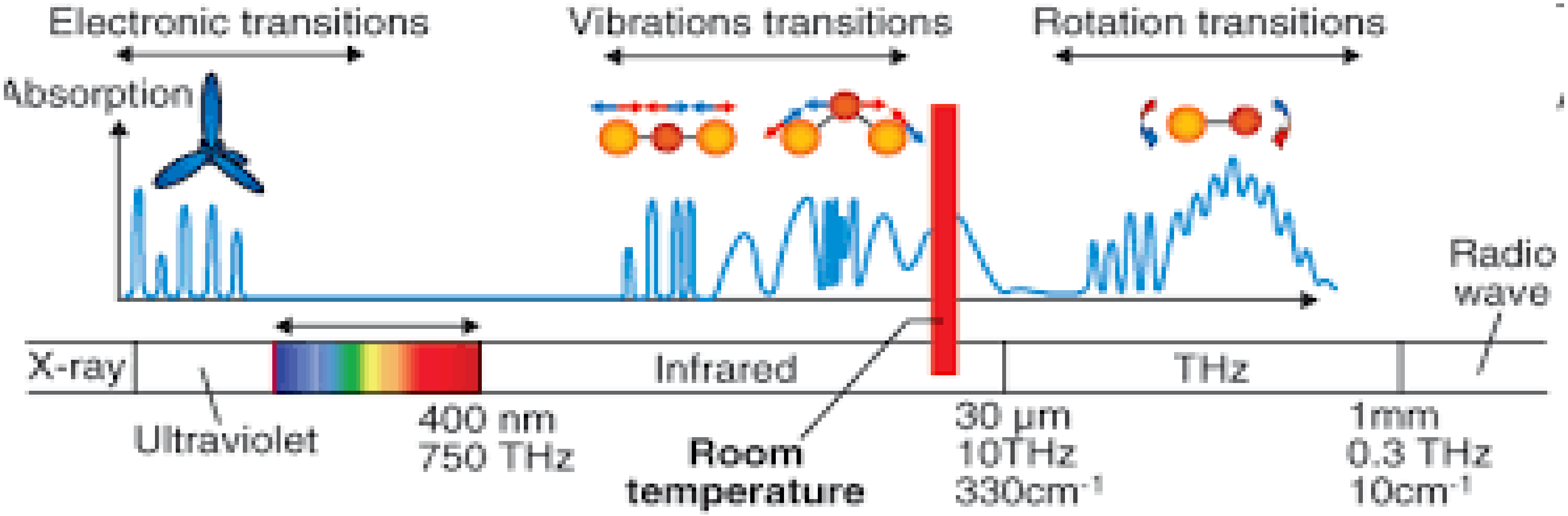
Solid or liquid or Gas



Interaction of EMR with matter

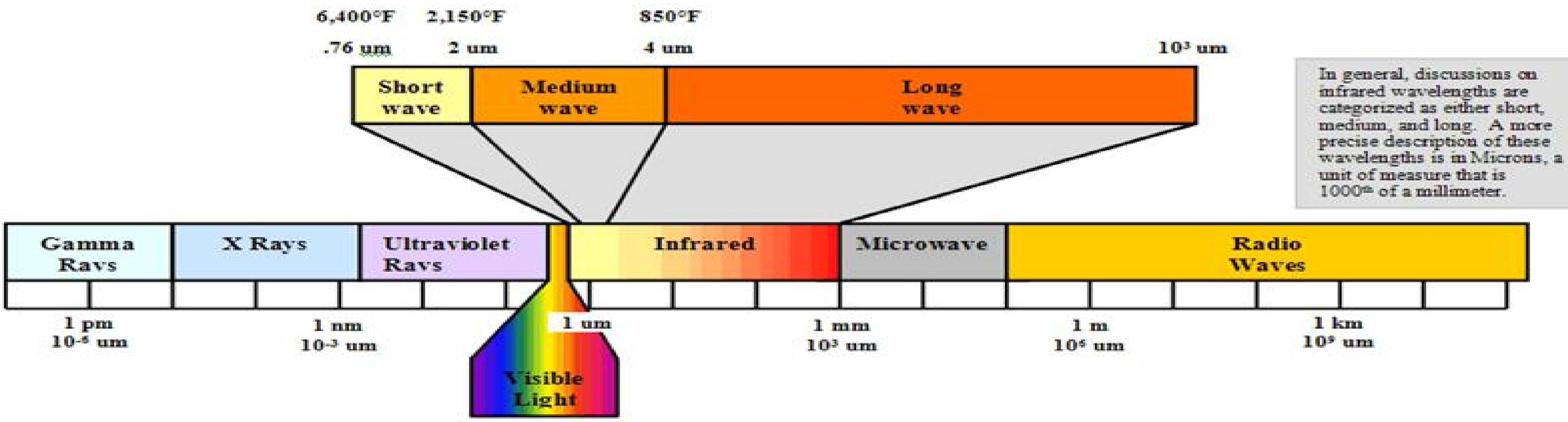


Energy of molecule
=
Electronic energy
+
Vibrational energy
+
Rotational energy

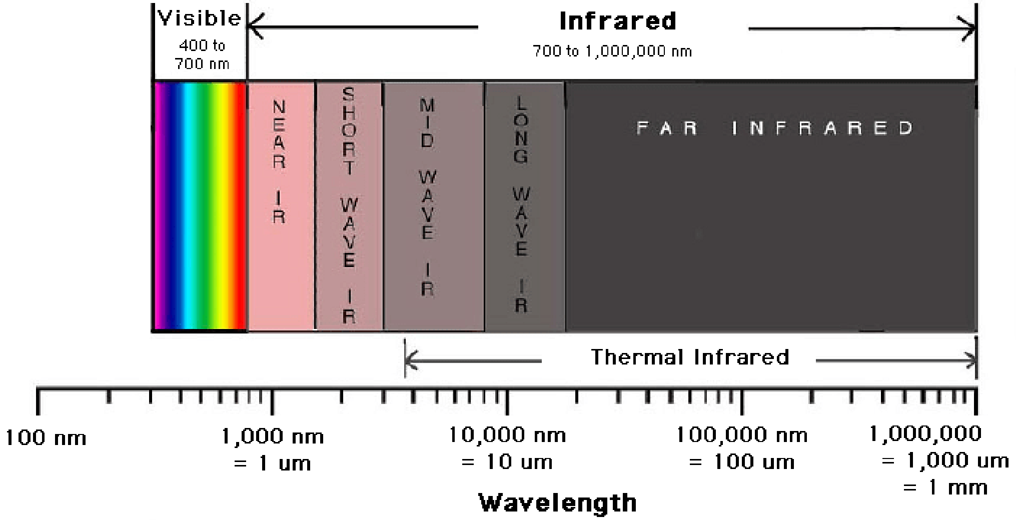


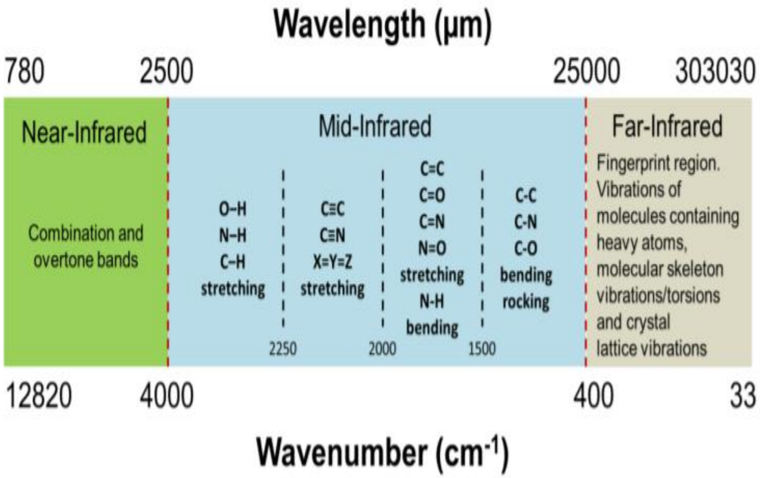
I.R. spectroscopy is referred as rotational and vibration spectroscopy

Infrared ray as EMR



In general, discussions on infrared wavelengths are categorized as either short, medium, and long. A more precise description of these wavelengths is in Microns, a unit of measure that is 1000^{th} of a millimeter.





FUNCTIONAL GROUP REGION

4000 cm^{-1} - 1300 cm^{-1}

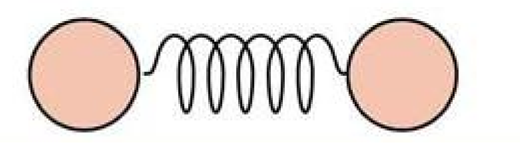
FINGERPRINT REGION

1300 cm^{-1} - 400 cm^{-1}

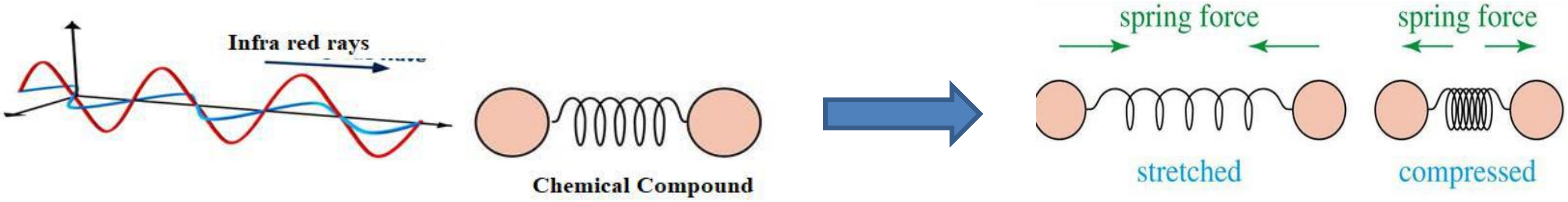
I.R. Spectroscopy : Principle

- Molecules are made up of atoms linked by chemical bonds

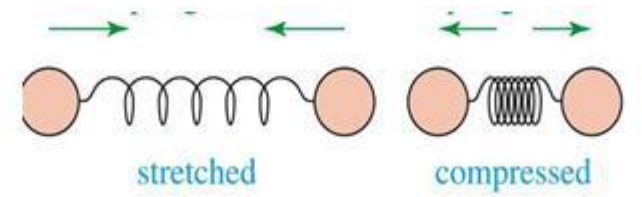
- The movement of atoms and the chemical bonds like spring and balls (vibration) • This characteristic vibration are called Natural frequency of vibration.



- When energy in the form of infrared radiation is applied then it causes the vibration between the atoms of the molecules



Applied infrared frequency = Natural frequency of vibration



Absorption of IR radiation takes place

Peak is observed

Different functional groups absorb characteristic frequencies of IR radiation. Hence gives the characteristic peak value.

Criteria for a compound to absorb IR radiation:

1. Correct wavelength of radiation

Criteria for a compound to absorb IR radiation

2. Change in dipole moment

Symmetrical stretch

Asymmetrical stretch

In plane bending

Out of plane bending

No change in dipole moment therefore IR inactive

There is change in polarisability therefore Raman active

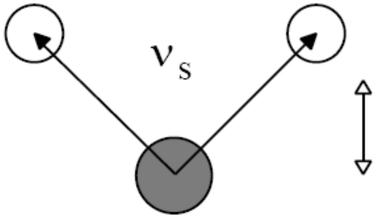
There is change in dipole moment therefore IR active but Raman inactive

The deformation vibrations of CO_2 are degenerate and appear at the same region (666 cm^{-1}) in the IR spectrum of CO_2. There is no change in polarisability therefore these vibrations are Raman inactive.

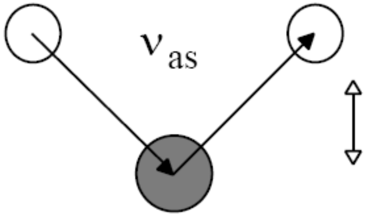
Molecular Vibrations and its types

Bond Stretching

symmetric

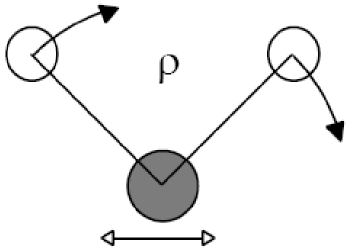


asymmetric

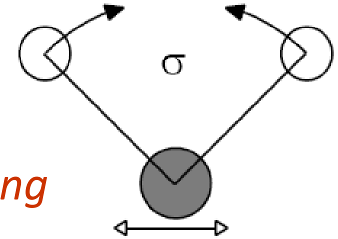


Bond Bending

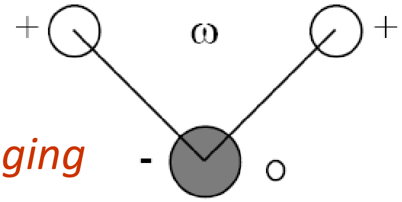
In-plane rocking



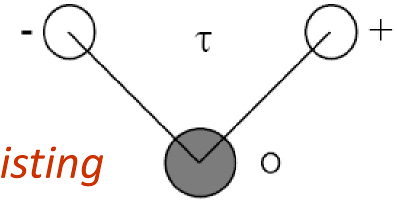
In-plane scissoring



Out-of-plane wagging

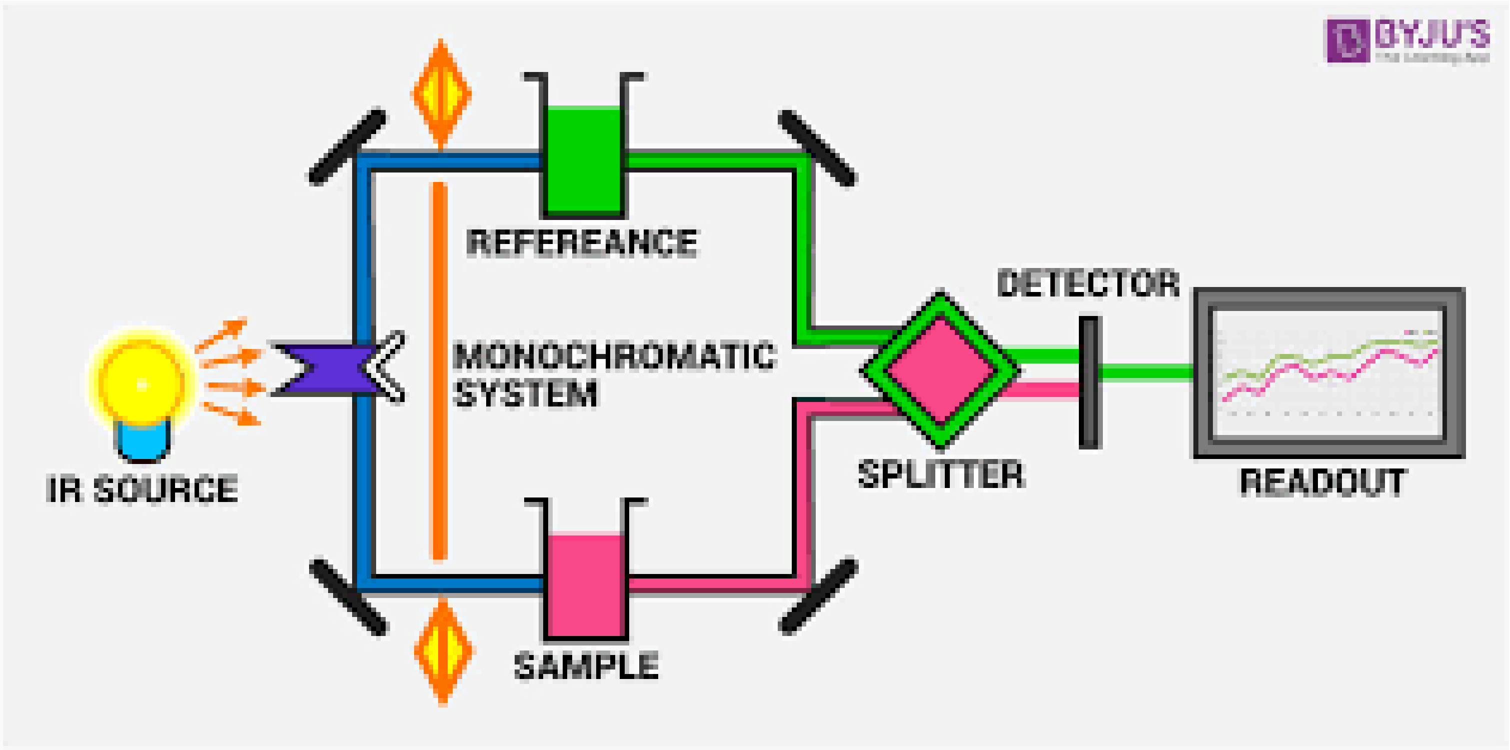


Out-of-plane twisting



Diatomic and polyatomic molecular vibrations

INSTRUMENTATION



Fourier Transfer IR (FTIR)

Principle:

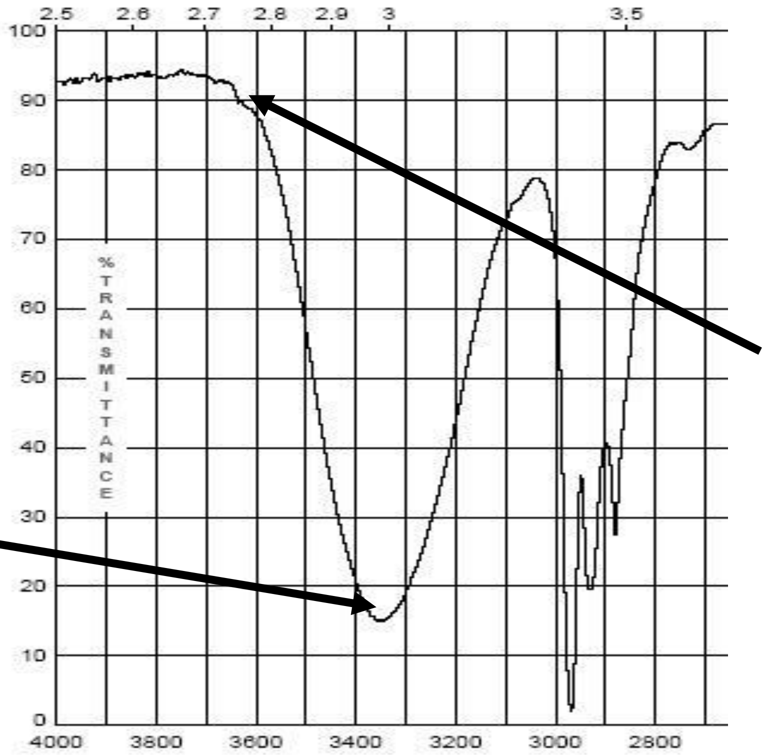
1) Light from source is split by central mirror into 2 beams of equal intensity
2) Beams go to two other mirrors, reflected by central mirror, recombine and pass through sample to detector
3) two side mirrors. One fixed and other movable
    - a) move second mirror, light in two-paths travel different distances before recombined
    - b) constructive & destructive interference
    - c) as mirror is moved, get a change in signal

Working of FTIR

Interpretation of I.R. Spectrum

1. Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds

The y-axis on an IR spectrum is in units of % transmittance

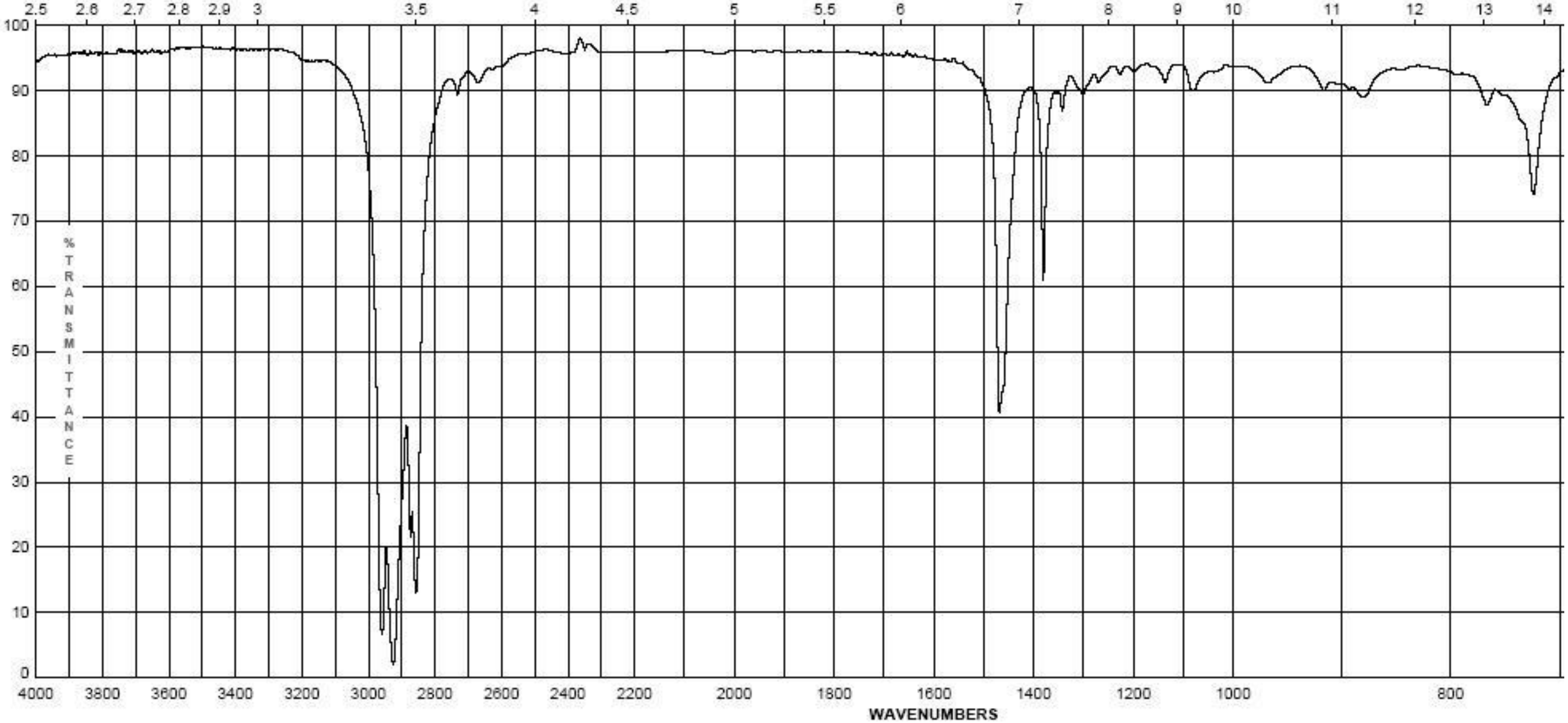


In regions where the EM field of an osc. bond interacts with IR light of the same ν – transmittance is low (light is absorbed)

In regions where no osc. bond is interacting with IR light, transmittance nears 100%

Interpretation of IR Spectra

2. The x-axis of the IR spectrum is in units of wave numbers, n, which is the number of waves per centimeter in units of cm^{-1} (Remember $E = hn$ or $E = hc/l$)



Interpretation of IR Spectrum

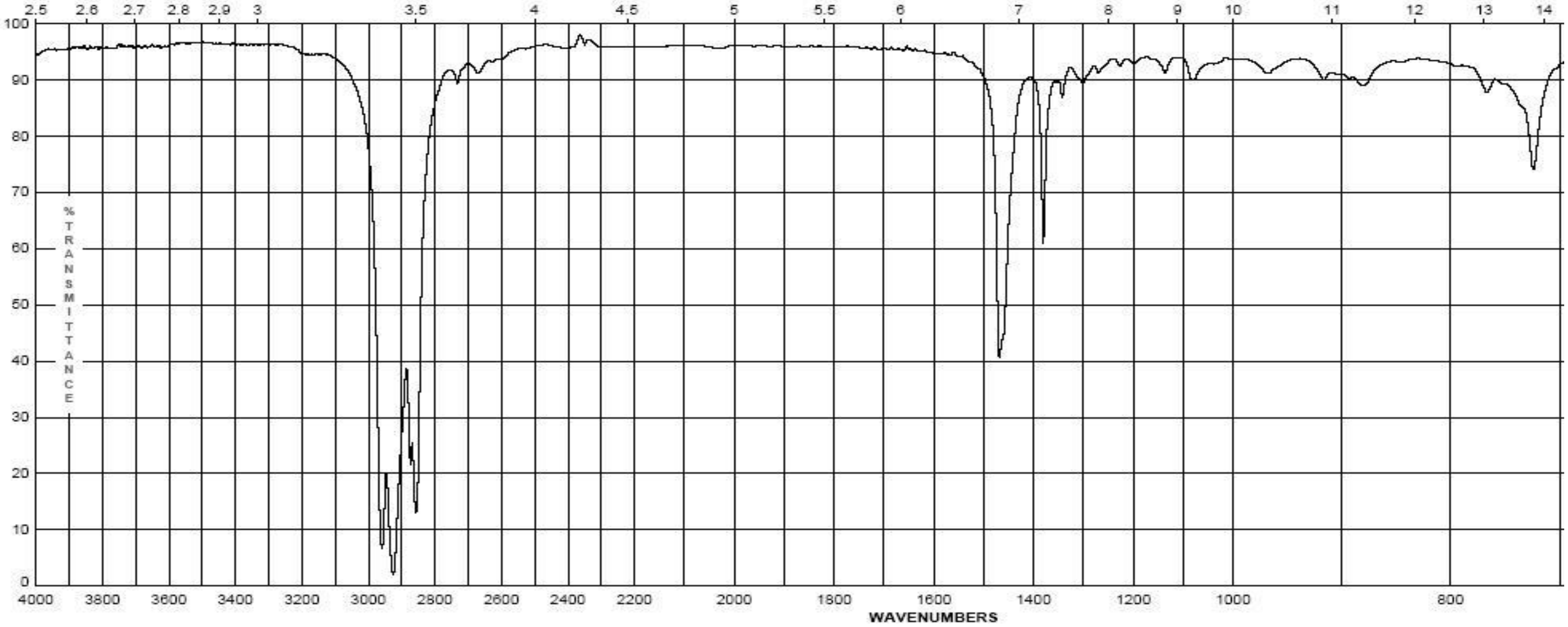
In general:

Lighter atoms will allow the oscillation to be faster – *higher energy*

This is especially true of bonds to hydrogen – C-H, N-H and O-H

Stronger bonds will have higher energy oscillations

Triple bonds > double bonds > single bonds in energy

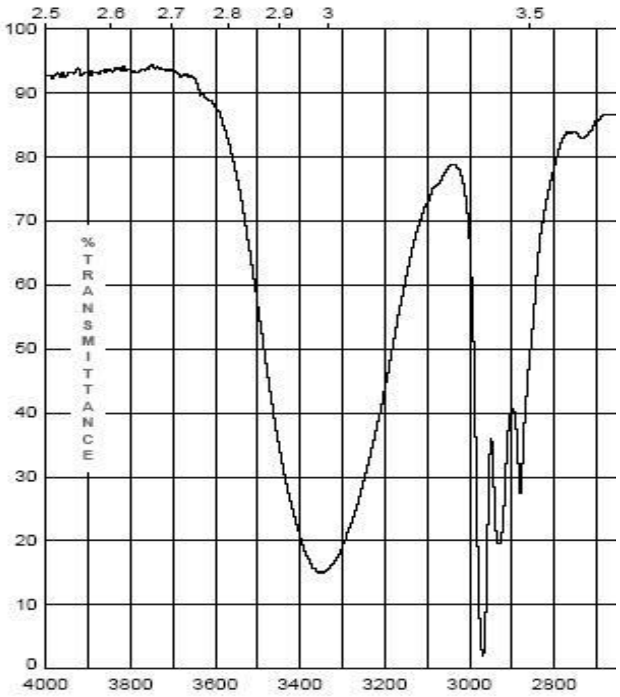


Energy/ν of oscillation

Interpretation of IR spectrum

As opposed to chromatography or other spectroscopic methods, the area of a IR band (or peak) is not ***directly*** proportional to concentration of the functional group producing the peak

The intensity of an IR band is affected by two primary factors:



Whether the vibration is one of stretching or bending

Electronegativity difference of the atoms involved in the bond

For both effects, the greater the change in dipole moment in a given vibration or bend, the larger the peak.

The greater the difference in electro negativity between the atoms involved in bonding, the larger the dipole moment

Typically, stretching will change dipole moment more than bending

Interpretation of Infrared Spectrum

It is important to make note of peak intensities to show the effect of these factors:

- ***Strong (s)*** – peak is tall, transmittance is low (0-35 %)
- ***Medium (m)*** – peak is mid-height (75-35%)
- ***Weak* (w)** – peak is short, transmittance is high (90-75%)
- **** Broad (br)*** – if the Gaussian distribution is abnormally broad

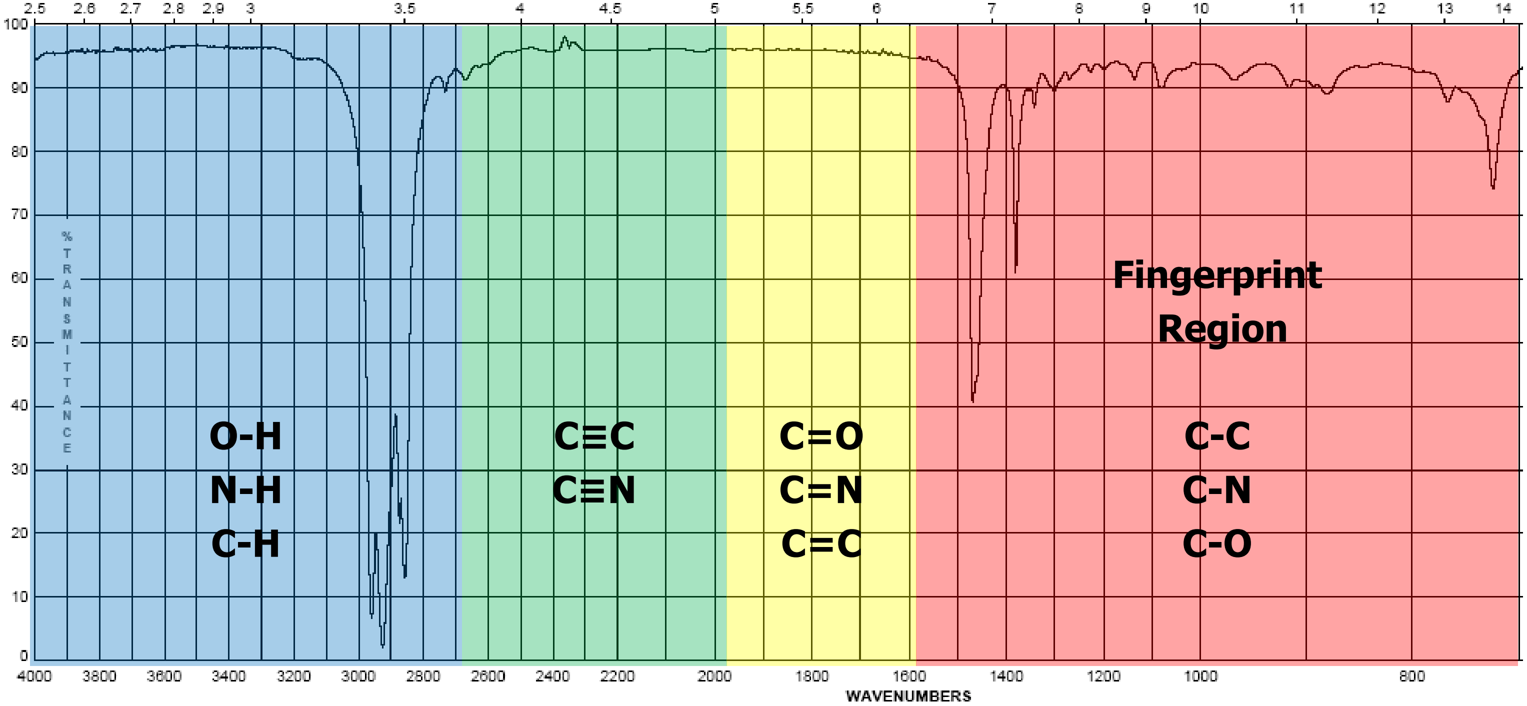
  *(*this is more for describing a bond that spans many energies)*

Exact transmittance values are rarely recorded

Interpretation of Infrared Spectrum

The four primary regions of the IR spectrum

Bonds to H **Triple bonds** **Double bonds** **Single Bonds**



O-H
N-H
C-H

C≡C
C≡N

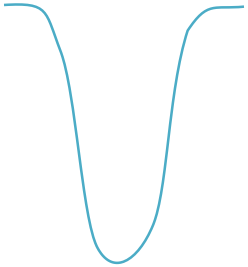
C=O
C=N
C=C

Fingerprint Region

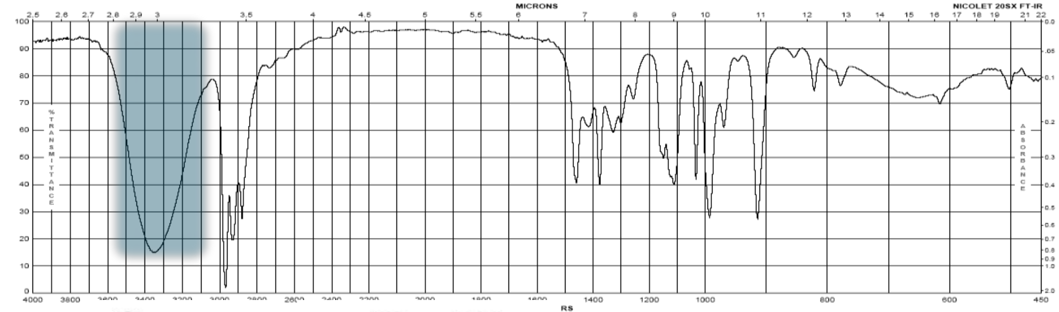
C-C
C-N
C-O

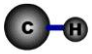
4000 cm^{-1} **2700 cm^{-1}** **2000 cm^{-1}** **1600 cm^{-1}** **600 cm^{-1}**

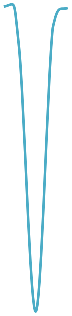
Interpretation of Infrared Spectrum



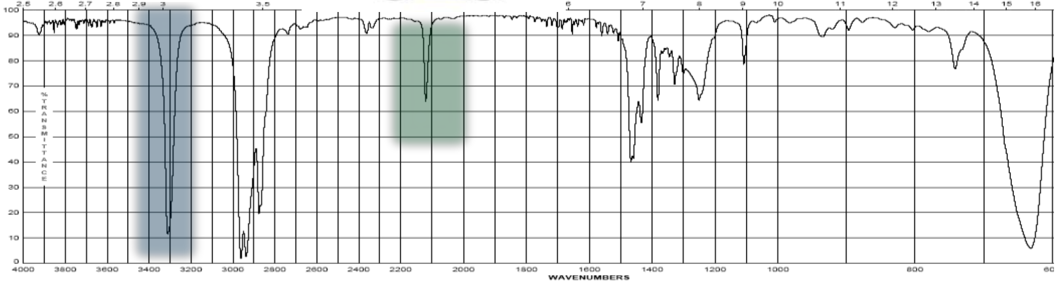
Broad U-shape peak
-**O—H** bond

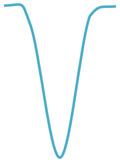




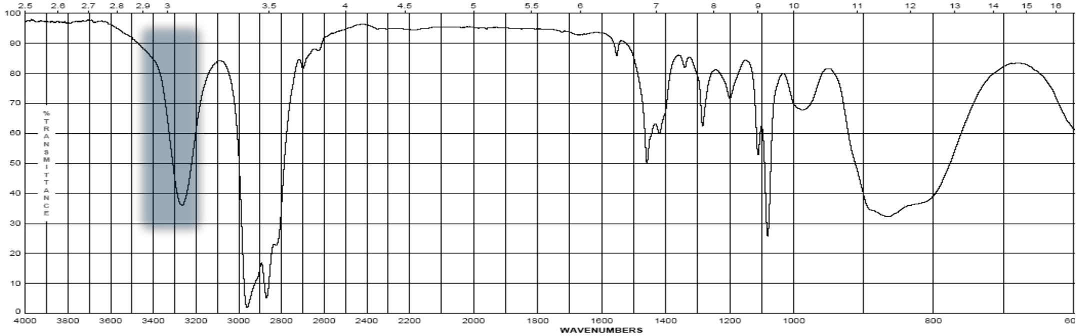


Sharp spike
-C≡**C—H** bond



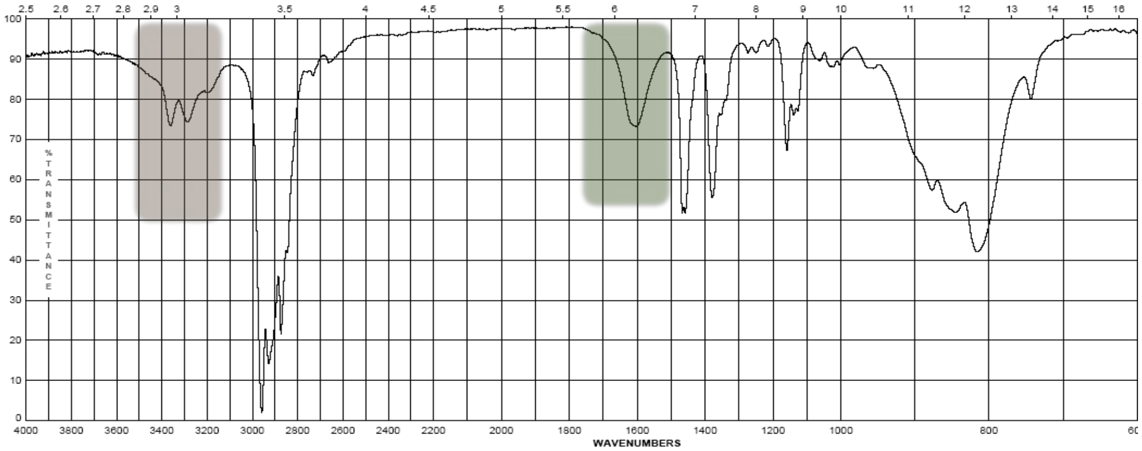


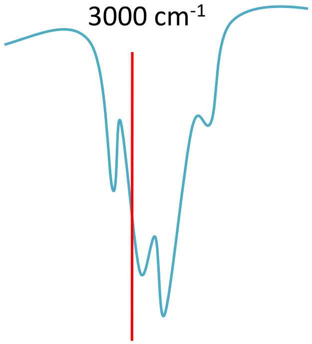
V-shape peak
-N—H bond for 2^o amine (R_2**N—H**)



Interpretation of Infrared Spectrum

W-shape peak
-N—H bond for
1^{o} amine (R**NH$_2$**)





Small peak
shouldered just
above 3000 cm^{-1}
C=**C—H** or
Ph—**H**