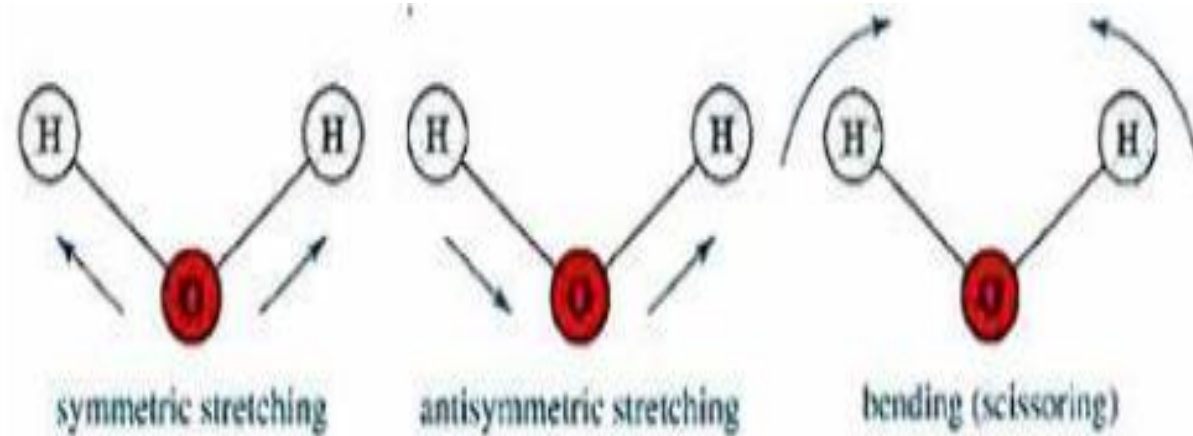
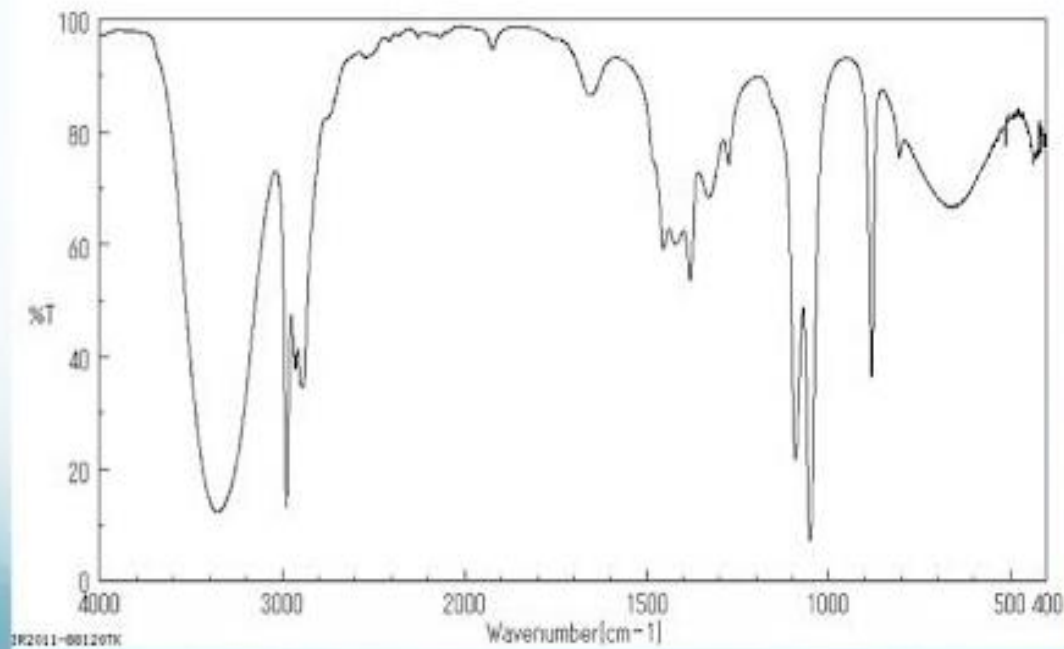


(IR)

Chapter-3

Infrared Spectroscopy

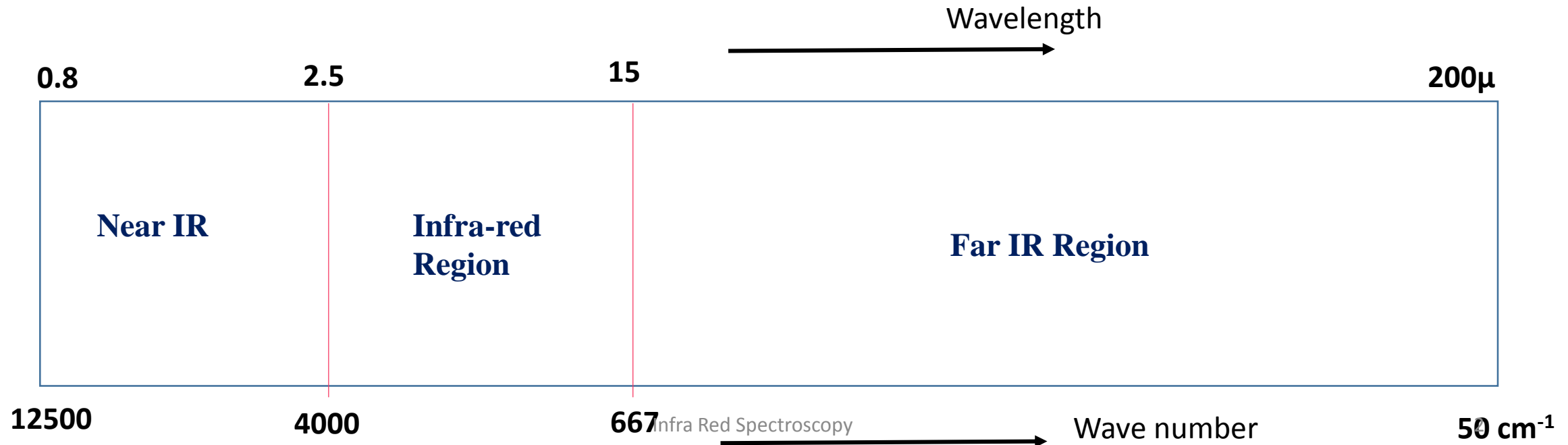


Dr. Amita Chaudhary
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Chemical Analytical Techniques (2CHOE01)

Infrared Spectroscopy/ Vibrational-rotational spectroscopy

Definition:

IR Spectroscopy is a technique that uses infrared electromagnetic radiations to determine the functional groups present in the analysed sample.



Conversion of wavenumber to corresponding wavelength

The relation between wavelength and wave number is as follows:

Wave number = $\frac{1}{\text{wavelength in centimetres}}$

If wavelength (λ) is $2.5\mu = 2.5 \times 10^{-4} \text{ cm}$, then

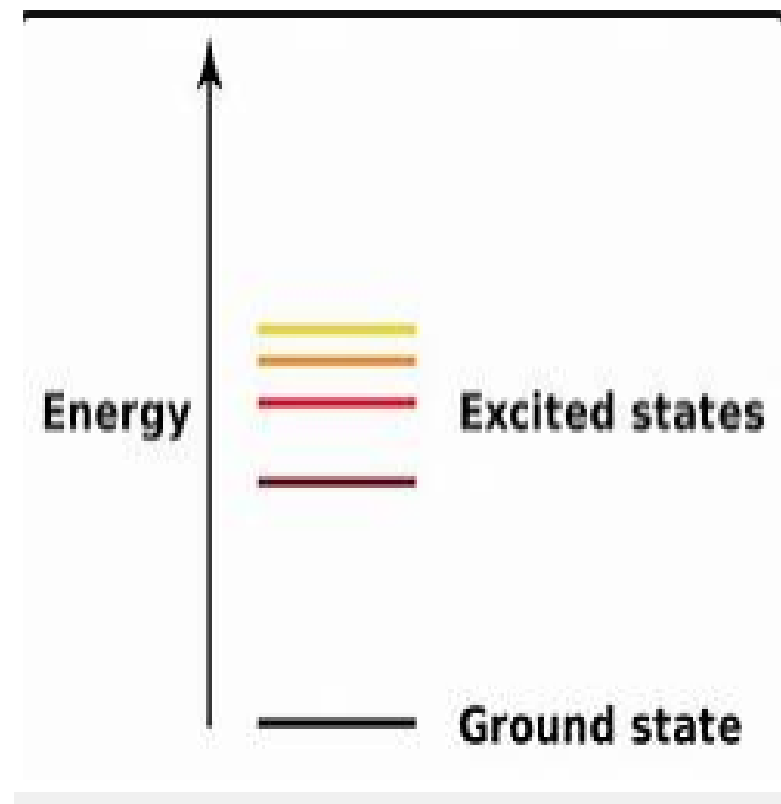
$$\text{Wave number } (\bar{\nu}) = \frac{1}{2.5 \times 10^{-4} \text{ cm}} = 4000 \text{ cm}^{-1}$$

Similarly determine wave number ($\bar{\nu}$) corresponding to 15μ .

The Infra-red region covers 4000 cm^{-1} to 667 cm^{-1} .

Principle of Infra-red Spectroscopy

- The absorption of Infra-red radiations causes an excitation of molecule from a lower to the higher vibrational levels. We know that each vibrational level is associated with a number of closely spaced rotational levels.
- Molecules that shows change in dipole moment will absorb in the infra-red region. The vibrational transitions occurred are infra-red active transitions. These molecules are infra-red active. For example, $\text{C}=\text{O}$, $\text{N}-\text{H}$, $\text{O}-\text{H}$, etc.



Theory-Molecular Vibrations

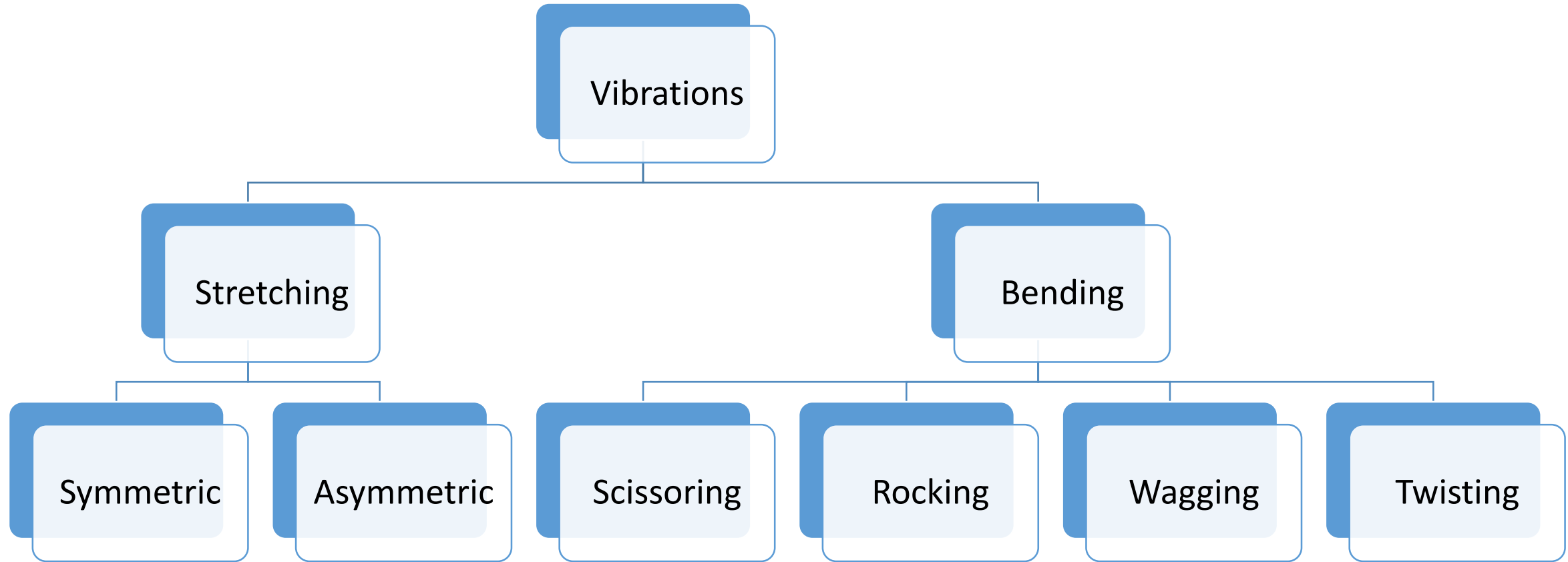
- A single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appears as vibrational-rotational bands. The changes in the molecule depends on:

1. Masses of the atoms present in the molecule
2. Strength of the bonds, and
3. The arrangements of atoms within the molecule.

The fundamental vibrations are of two types:

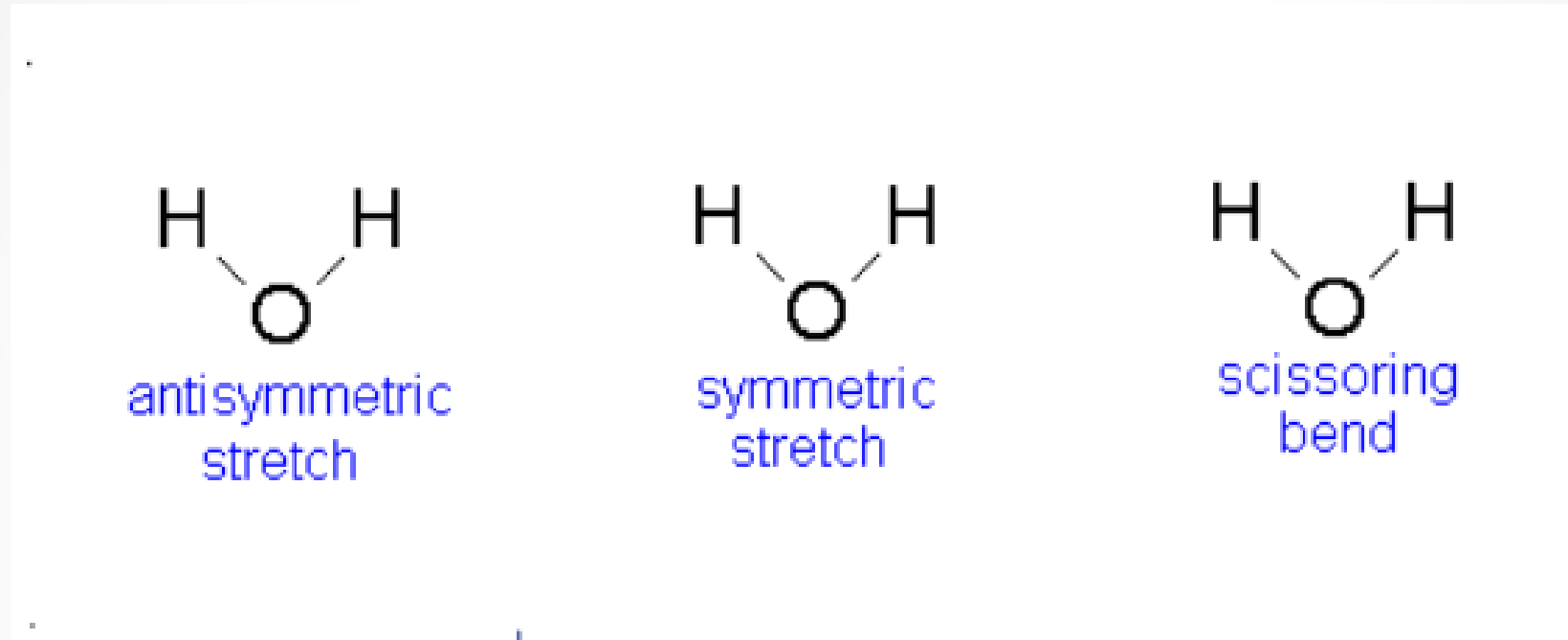
- (a) Stretching
- (b) Bending

Type of Molecular Vibrations



Bending vibrations require lesser energy and hence occur at higher wavelength or lower numbers than stretching vibrations.

Vibrational modes - water



The angle between the bonds does not change

asymmetric stretch
 $\nu_{as} \text{OH}$ 3756 cm^{-1}

symmetric stretch
 $\nu_s \text{OH}$ 3657 cm^{-1}

The angle between bonds change

Scissoring bend
 $\delta_s \text{HOH}$ 1595 cm^{-1}

Calculation of Vibrational Frequency

As per the Hooke's Law

$$\frac{v}{c} = \bar{\nu} = \frac{1}{2\pi c} \sqrt{\left(\frac{k}{\frac{m_1 m_2}{m_1 + m_2}} \right)}$$
$$= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

μ = reduced mass

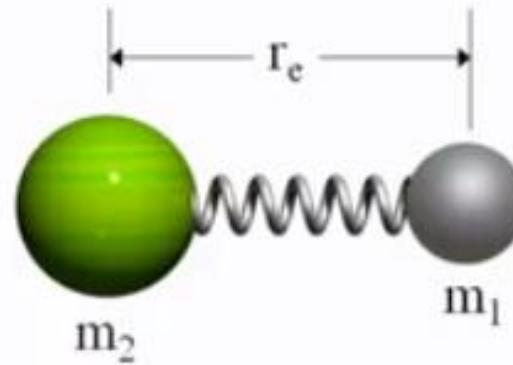
m_1 & m_2 are the masses of the atoms concerned in grams in a particular bond.

k = Force constant of the bond. It relates to the strength of the bond. For a single bond, it is approximately $5 \times 10^5 \text{ gm sec}^{-2}$.

c = Velocity of the radiation = $2.998 \times 10^{10} \text{ cm sec}^{-1}$

Simple Harmonic Oscillator

Treat a diatomic molecule as two masses joined by a spring



Q. Calculate the approximate frequency of C-H stretching vibration from the given data.

$$k = 5 \times 10^5 \text{ gm sec}^{-2}$$

Mass of carbon atom (m_1) = 20×10^{-24} gm, Mass of hydrogen atom (m_1) = 1.6×10^{-24} gm

$$\text{Ans: Frequency} = 9.3 \times 10^{13} \text{ sec}^{-1} \quad \text{wave number} = 3100 \text{ cm}^{-1}$$

Q. Calculate the wave number of stretching vibration of a carbon-carbon double bond.

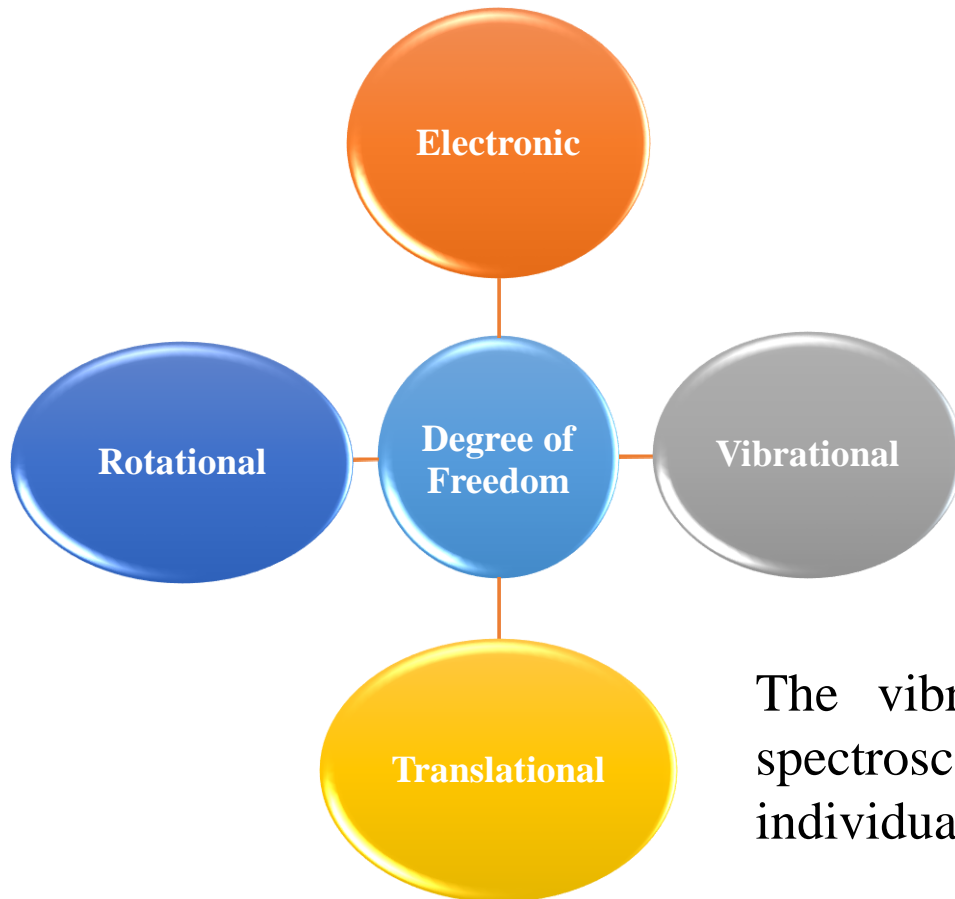
$$\text{Ans: Reduced mass} = 9.97 \times 10^{-24} \text{ gm}$$

$$\text{Wave number} = 1680 \text{ cm}^{-1}$$

Applications of IR Spectroscopy

- I. Identification of an unknown Compound
- II. Structure Determination
- III. Qualitative analysis of functional groups
- IV. Distinction between two types of hydrogen bonding
- V. Quantitative analysis
- VI. Detection of Impurity in a compound

Fundamental Vibrations Modes



1. In electronic motion, the electrons change energy levels or directions of spins.
2. The translational motion is characterized by a shift of an entire molecule to a new position.
3. The rotational motion is described as a rotation of the molecule around its centre of mass.
4. When the individual atoms within a molecule change their relative position then we say that the molecule vibrates.

The vibrational transitions are the most important transitions for IR spectroscopy because IR radiation is too low to affect the electrons within the individual atoms and too powerful for rotational and translational transitions.

Potential energy diagram of a harmonic oscillator

If the absorption of IR radiation is equal to the energy of difference between two vibrational energy levels (ΔE_{vib}), then a vibrational transition occurs.

$$E_{\text{vib}} = \left(V + \frac{1}{2} \right) h\nu \text{ where } V = \text{vibrational Level}$$

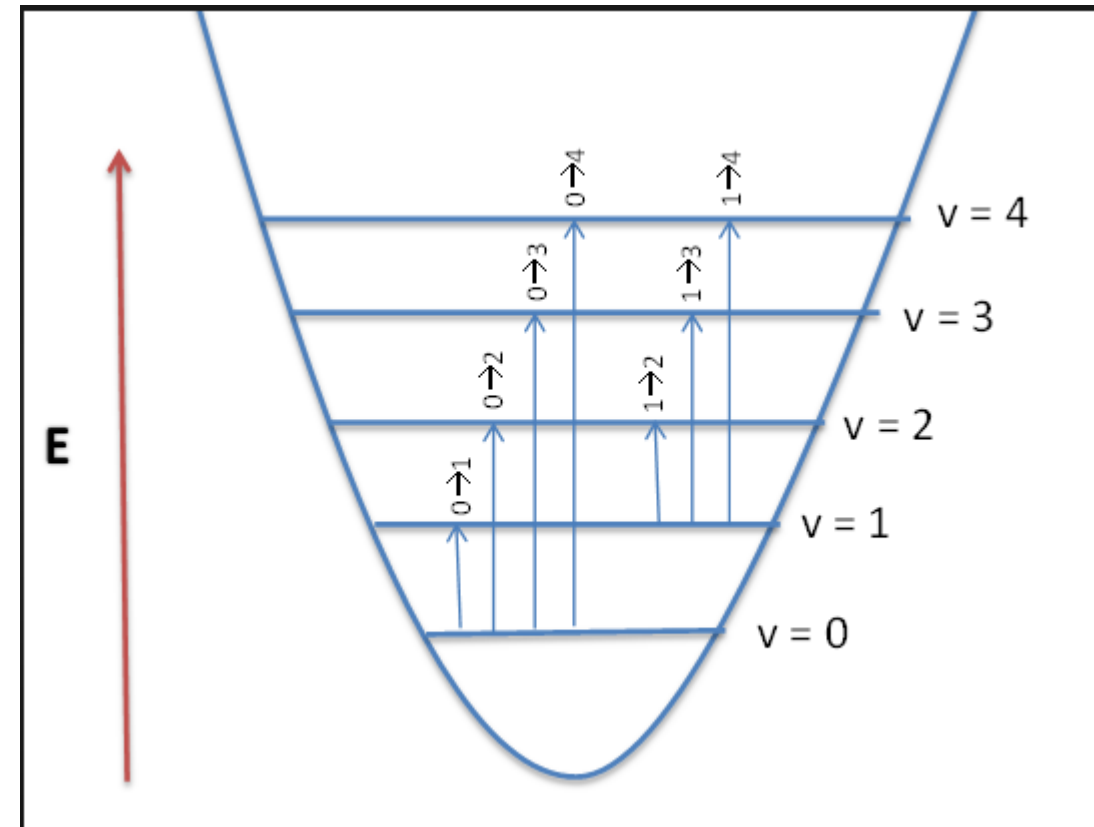
Transition from the ground state ($v=0$) to the first excited state ($v=1$) give rise to intense bands called the Fundamental Bands.

Transitions from the ground state ($v=0$) to the second excited state ($v=2$) with the absorption of IR radiation give rise to weak bands called overtones.

The energy difference (ΔE_{vib}) between the two levels can be calculated using the following formula:

$$\Delta E_{\text{vib}} = E_{v=1} - E_{v=0} \dots \text{First Fundamental Band}$$

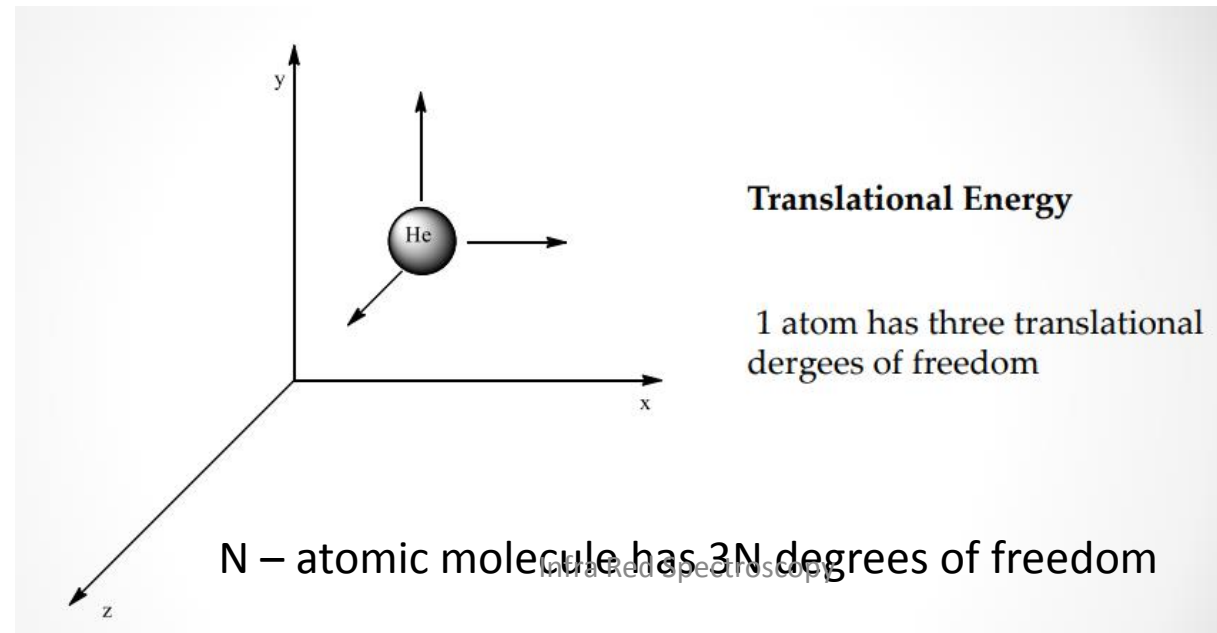
$$\Delta E_{\text{vib}} = E_{v=2} - E_{v=0} \dots \text{First overtone Band}$$



Degree of Freedom

The polyatomic molecules may exhibit more than one fundamental vibrational absorption bands called degree of freedom in a molecule.

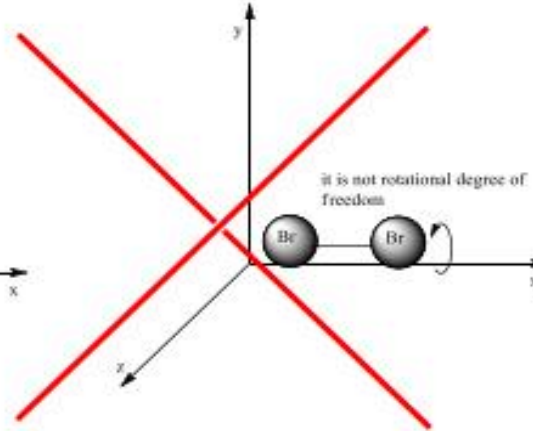
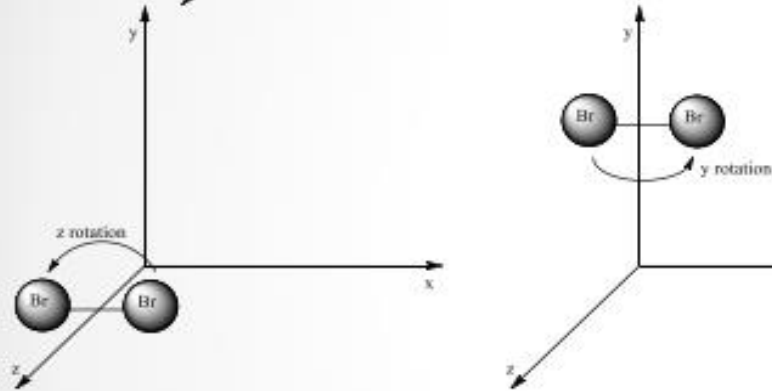
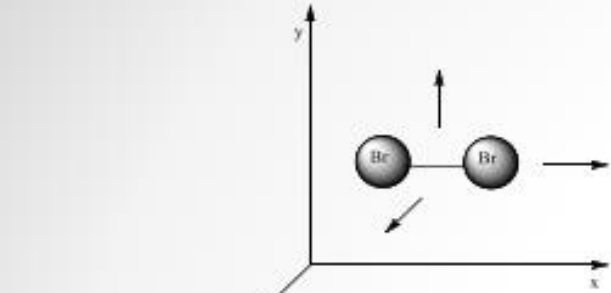
The number of degree of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space.



Degree of freedom.....

Translational Energy

Molecule also has three translational degrees of freedom



Rotational Energy

Two atomic (linear) molecule has two rotational degrees of freedom



Vibrational Energy

Two atomic (linear) molecule has one vibrational degree of freedom

Number of vibrational degree of freedom is $(3N - 5)$ for linear molecule

Degree of freedom..

Translational Energy
3N atomic nonlinear molecule also has **three** translational degrees of freedom

Rotational Energy
3N atomic non-linear molecule has **three** rotational degrees of freedom

Vibrational Energy
3N atomic non-linear molecule molecule has $(3N-6)$ vibrational degree of freedom

● Number of vibrational degree of freedom is $(3N - 6)$ for non-linear molecule ●

The diagrams illustrate the degrees of freedom for a water molecule (H₂O), which is a non-linear triatomic molecule (3N = 6).
1. **Translational Energy:** A 3D coordinate system (x, y, z) shows the molecule moving along each axis, represented by three arrows originating from the molecule's center.
2. **Rotational Energy:** Three separate 3D coordinate systems show the molecule rotating about the x, y, and z axes, indicated by curved arrows.
3. **Vibrational Energy:** Three diagrams of the water molecule show different vibrational modes. In each, arrows on the atoms indicate their displacement from equilibrium positions, representing the stretching and bending of bonds.

For Linear Molecule of n atoms:

Total degrees of freedom = $3n$

Translational degrees of freedom = 3

Rotational degree of freedom = 2

Vibrational degree of freedom = $3n - 3 - 2 = 3n - 5$

For Non-Linear Molecule of n atoms:

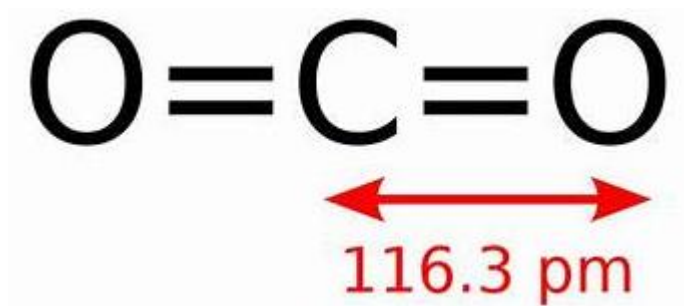
Total degrees of freedom = $3n$

Translational degrees of freedom = 3

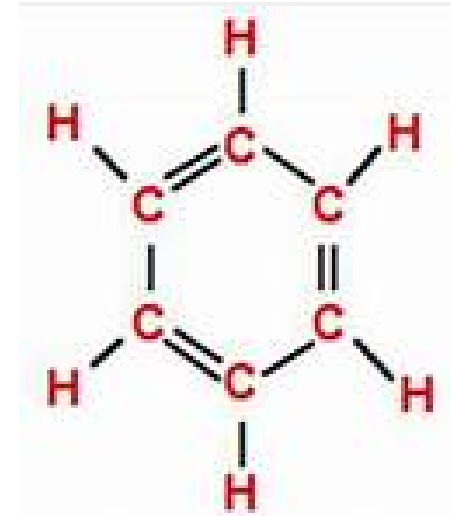
Rotational degree of freedom = 3

Vibrational degree of freedom = $3n - 3 - 3 = 3n - 6$

Calculation of vibrational mode in the following molecules ?



vibrational mode of carbon dioxide is 4



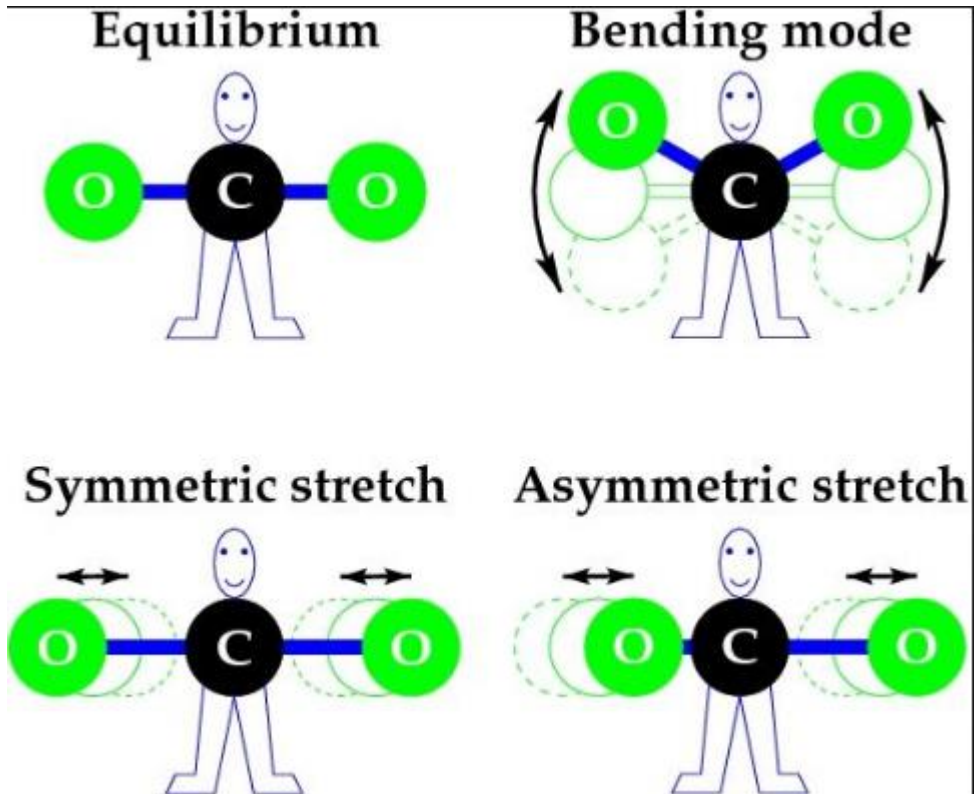
Vibrational mode of Benzene is 30

The theoretical number of fundamental bands in the IR spectrum are not actually appears. The reason for this is:

1. Fundamental vibrations that fall outside the region under investigation, i.e., 2.5 to 15 μ .
2. Fundamental vibrations that are too weak to be observed as bands.
3. Fundamental vibrations that are so close, they overlap, i.e., degenerate vibrations.
4. Certain vibrational bands do not appear for due to the less change in dipole moment in a molecule.

Selection Rules (Active and Forbidden Vibrations)

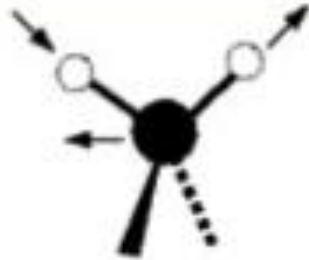
1. If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are inactive in the Infra-red.
2. The vibrations which are not centrosymmetric are active in Infra-red.



- I. First and second mode are said to be degenerate.
- II. Does not give rise to any change in dipole-moment, it is infra-red inactive.
- III. Asymmetric stretching causes, a net change in dipole-moment and thus is infra-red active and absorbs at 2350 cm^{-1}

Vibrational Modes for a CH₂ Group

stretching vibrations



asymmetrical stretching
(ν_{as} CH₂)
2928 cm⁻¹



symmetrical stretching
(ν_s CH₂)
2853 cm⁻¹

bending vibrations



in-plane bending or
scissoring
(δ_s CH₂)
1465 cm⁻¹



out-of-plane bending or
wagging
(ω CH₂)
1465 cm⁻¹



out-of-plane bending or
twisting
(τ CH₂)
1350-1150 cm⁻¹



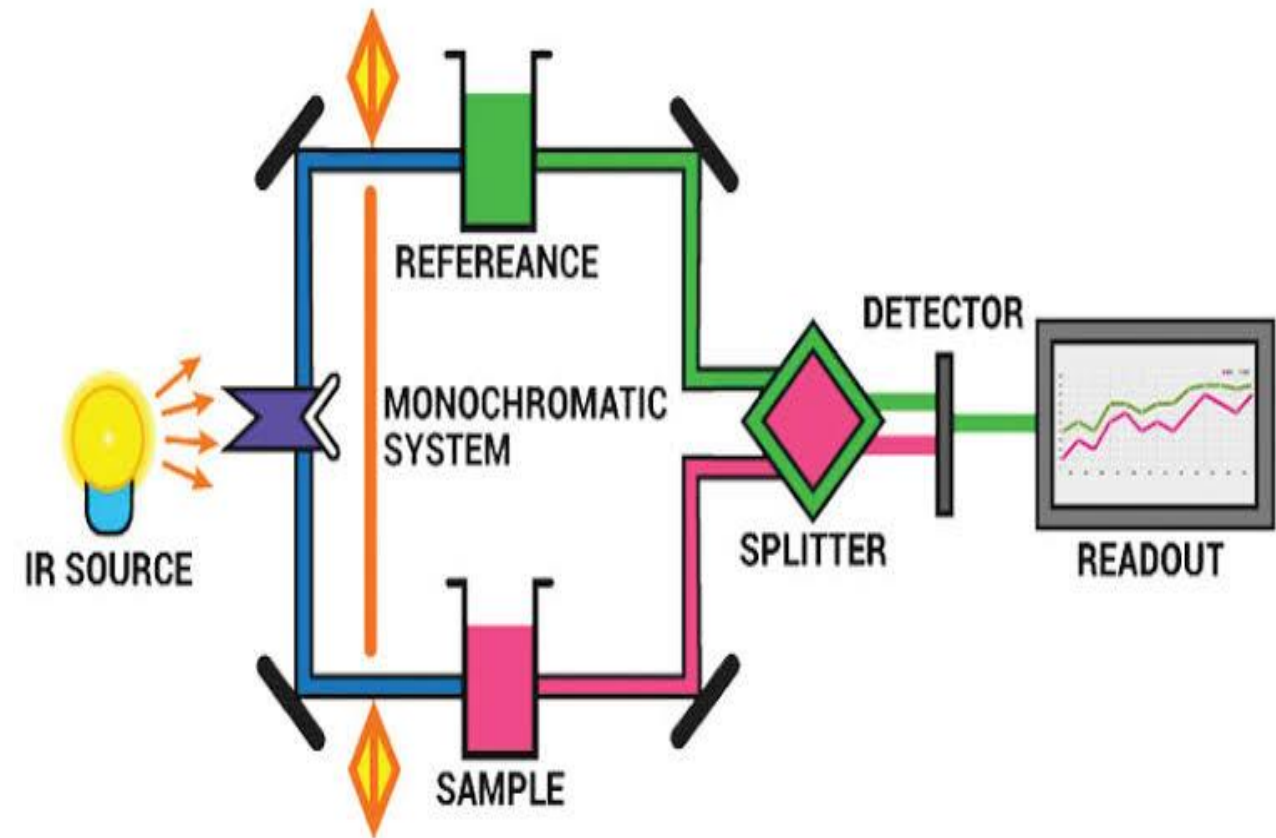
in-plane bending or
rocking
(ρ CH₂)
720 cm⁻¹

Instrumentation of IR Spectroscopy

Instrumentation

The main parts of an IR spectrometer are as follows:

- IR radiation sources
- Monochromators
- Sample cells and sampling of substances
- Detectors



The IR Radiation Sources

Infrared instruments need a source of radiant energy which provides a means for isolating narrow frequency band. The radiation source must emit IR radiation which should be :

- a. Intense enough for detection
- b. Steady.
- c. Extend over the desired wavelengths.

The various popular source of IR radiation are as follows:

A. **Globar source** : It is consists of silicon carbide rod. When heating at 1300°C - 1700°C . It is produced IR radiation.

B. **Nernst glower** :- It consists of zirconium oxide, chromium oxide and yttrium oxide. It is produced IR radiation when heating at 1000°C - 1800°C .

C. **Incandescent lamp** :- It consists of Nichrome coil in a glass tube. When it is heating at 1100°C .

Monochromators

The radiation source emit radiation of various frequency as the sample in IR spectroscopy absorb only at certain frequency, it thus becomes essential to select desired frequencies from the radiation source and reject the radiation of other frequencies. Thus selection has been achieved by means of Monochromators which are mainly of two types :

a. Prism Monochromators

b. Grating Monochromators.

Monochromator filters made up of lithium fluoride or prisms made of potassium bromide, like alkali metal halide.

Sample cells and sampling of substance

The sample should be transparent to IR radiation.

There are mainly two types of sampling technique in IR

1. solid sampling technique
2. Liquid sampling technique

1.solid sampling technique

A. Palletisation : In this technique we are using diluent like NaCl or KCl which are IR inactive compound. We mixed with the sample with NaCl using motra and piston. After it is compressed it and prepare pellets. This pellets we put in sample holder.

B. Mulling : the sample can be mixed with Nujol (mineral oil) and is applied on a liquid sample cell.

2. Liquid sampling technique: Sample can be held using a liquid sample cell made of alkali halide.

Aqueous solvent can not be used as they will dissolve alkali halide. Only organic solvent like chloroform is used.

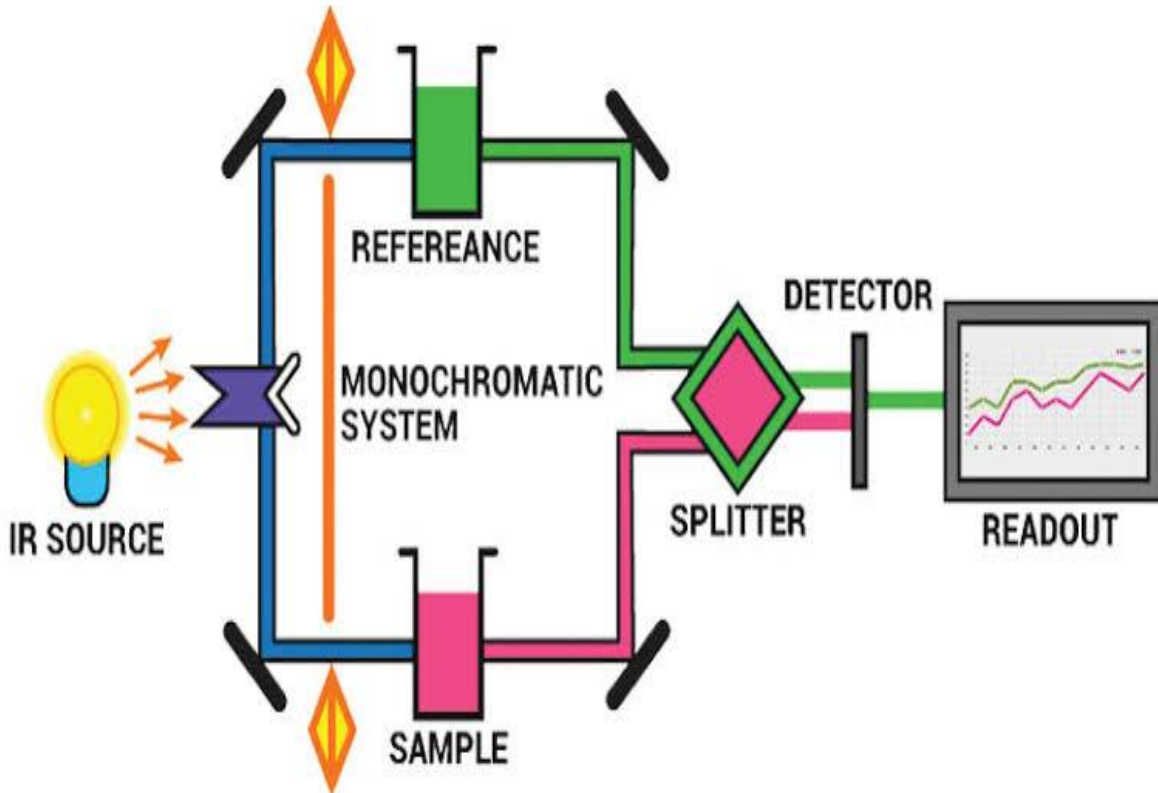
Detector

Detector is to measure the intensity of unabsorbed IR, we used different type of detector like,

- 1. Thermocouple :** In this detector we are detected potential difference between two junction.
- 2. Bolometers :** Thin metal conductor. This detector work on sample principal that increase in temperature when IR radiation comes. So, ultimately increase resistance and current flow is change.
- 3. Thermistor :** Fused metal oxide mixture is used. In this increasing temperature decrease resistance by 5% at 1°C.

Process

1. In the single beam system, the radiation is emitted by the source through the sample and then through a fixed prism and rotating Littrow mirror.
 2. Both prism and Littrow mirror select the desired wave length and then permit it to pass on to the detector..
 3. The detector measures the intensity of radiation after passes through the sample.
 4. Intensities of the bands can be recorded as a linear function T against the corresponding wave-number.
- Intensities of the two beams are converted into and measured as electrical signals, the absorption spectrum of the sample can be obtained.



Let I_0 be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively.

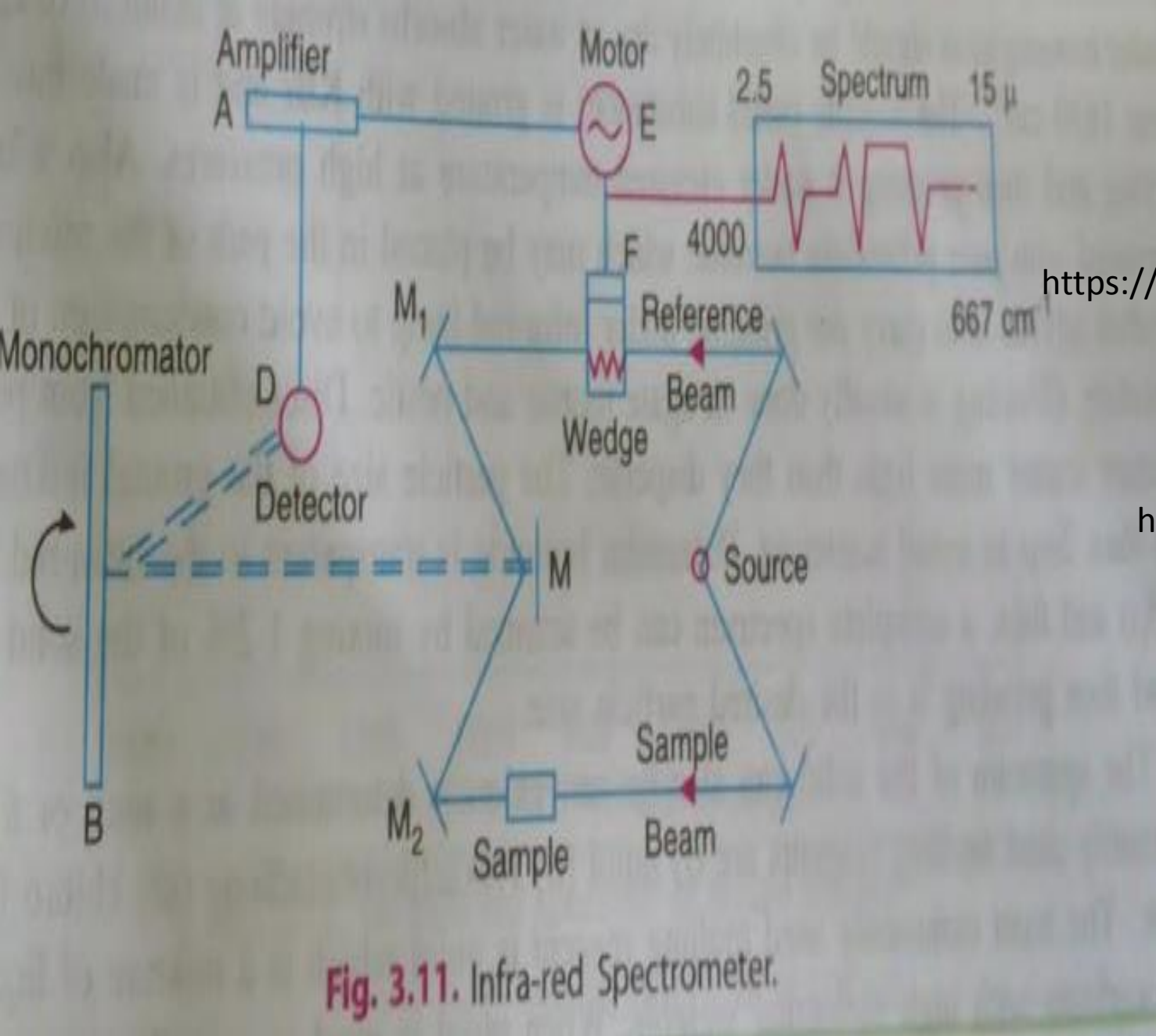
The absorbance of the sample at a particular frequency can be calculated as:

$$A = \log \left(\frac{I_0}{I} \right)$$

Also transmittance, $T = \frac{I_0}{I}$

Or

$$A = \log \left(\frac{1}{T} \right)$$

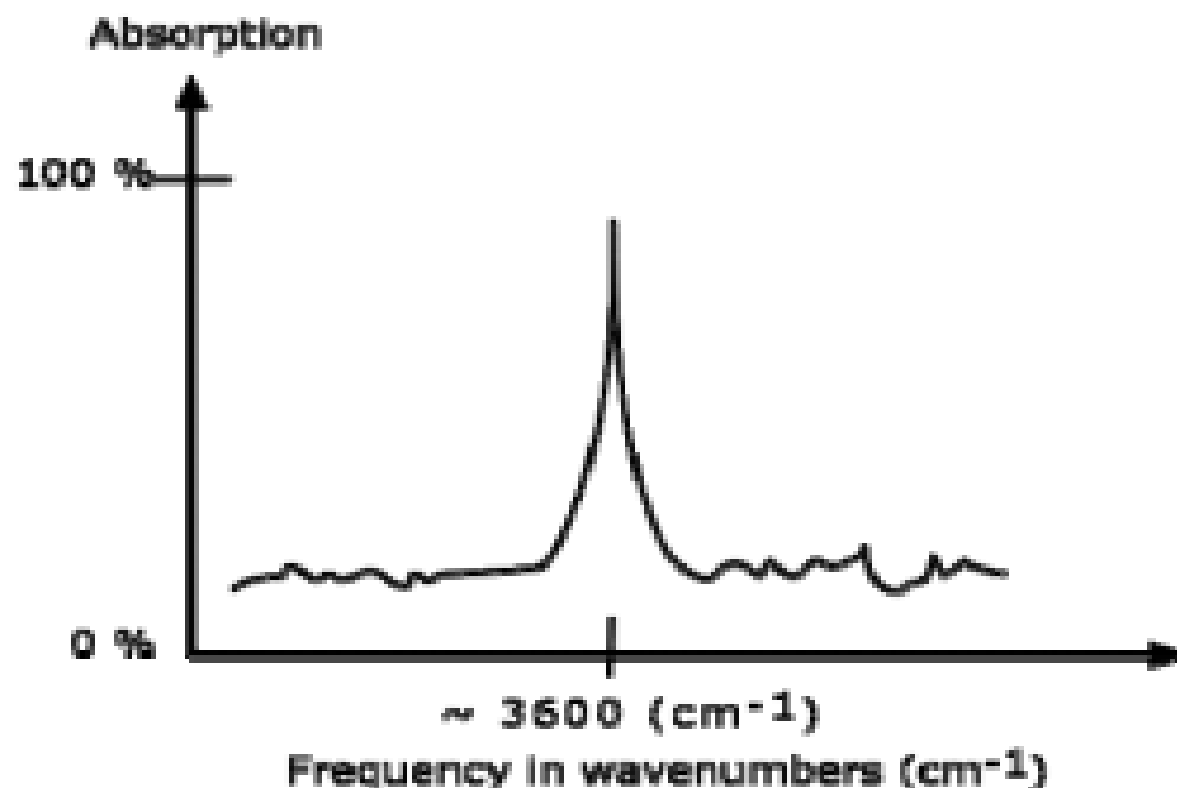


<https://www.youtube.com/watch?v=OiukFtC8E04&t=112s>

<https://www.youtube.com/watch?v=ntjHg6BT1E0>

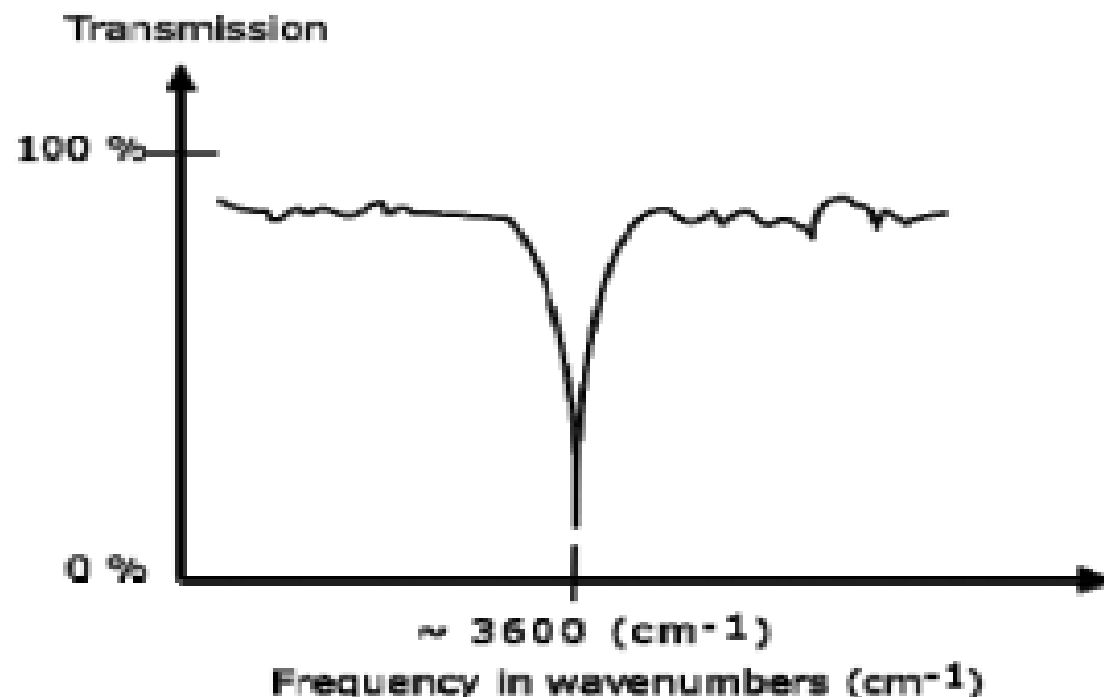
AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the x-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the y-axis in percentage units.



The graph above shows a spectrum in absorption mode.

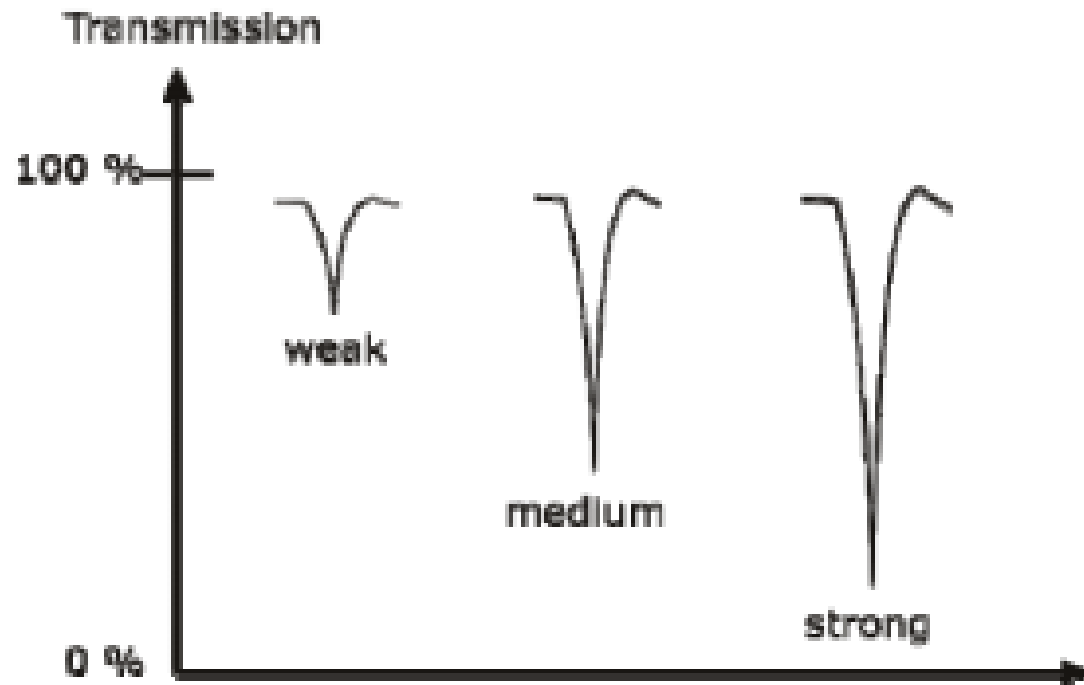
AN IR SPECTRUM IN TRANSMISSION MODE



The graph above shows a spectrum in **transmission** mode. **This is the most commonly used representation** and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.

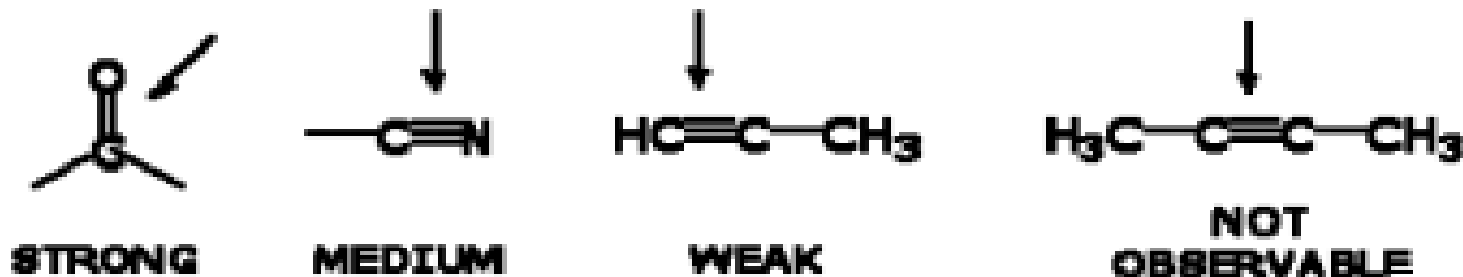


INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active.**

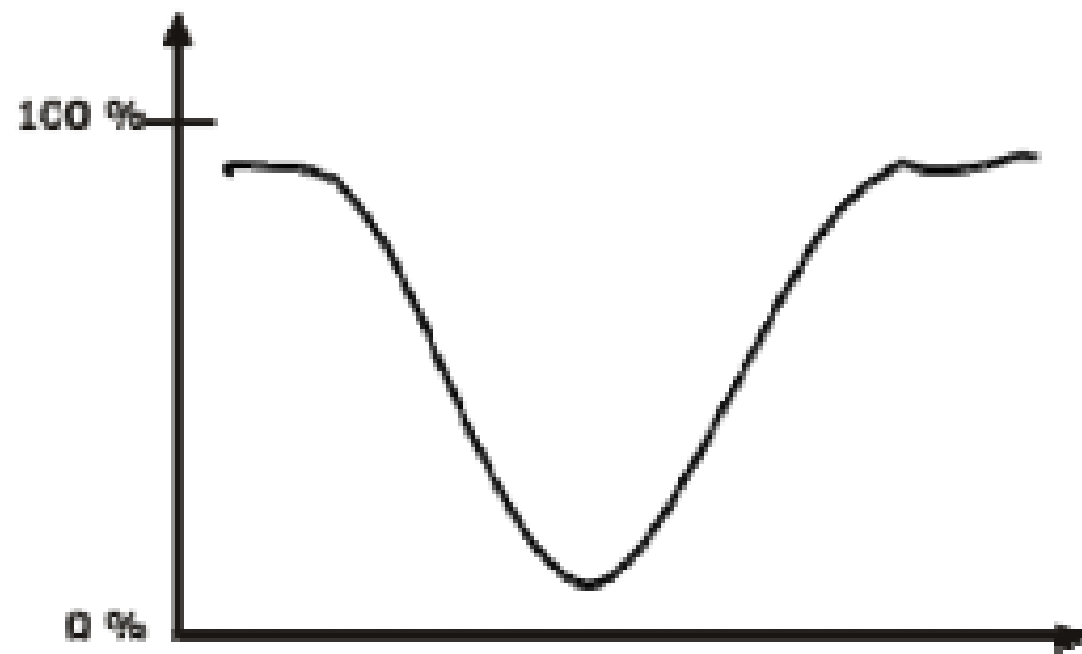
The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



INFRARED BAND SHAPES

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.

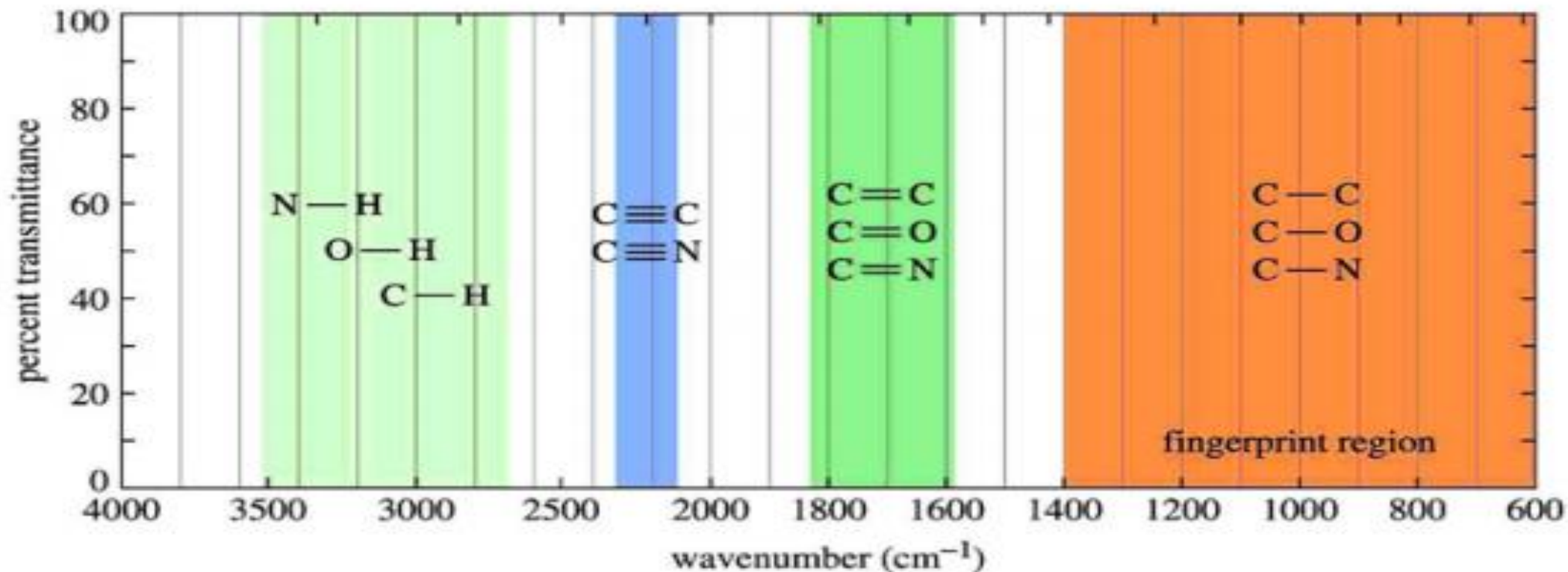


INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups**.
- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

IR ABSORPTION RANGE

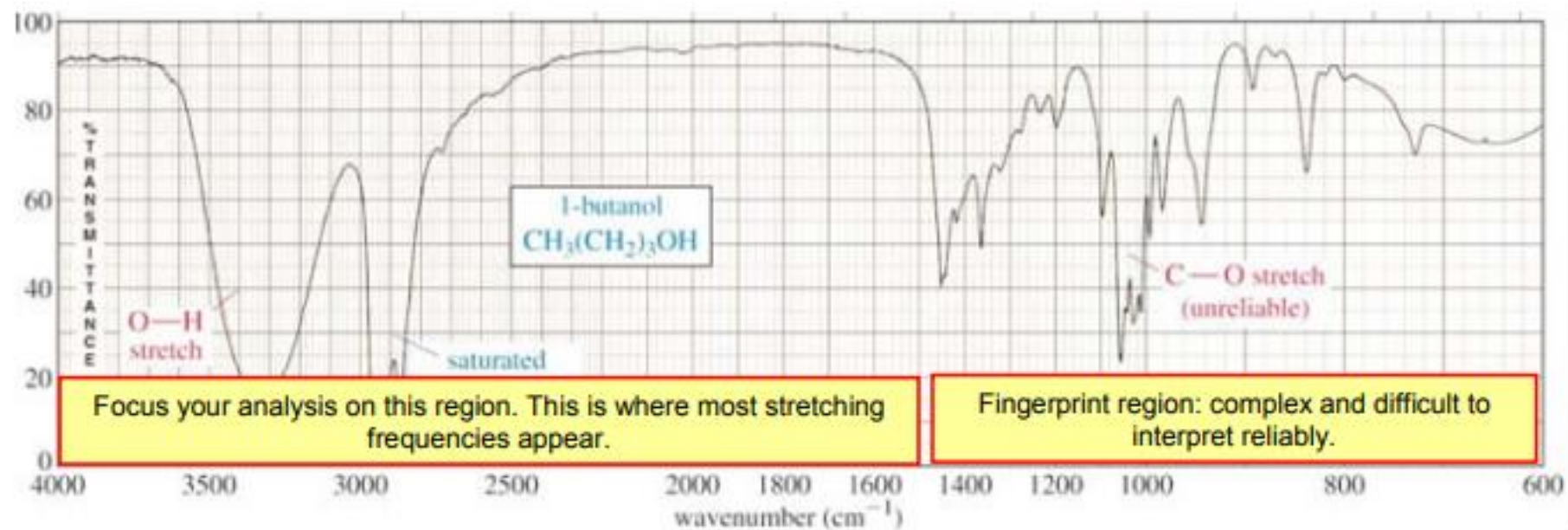
The typical IR absorption range for covalent bonds is **600 - 4000 cm⁻¹**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm⁻¹ would indicate the possible presence of a C-N or a C-C triple bond.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

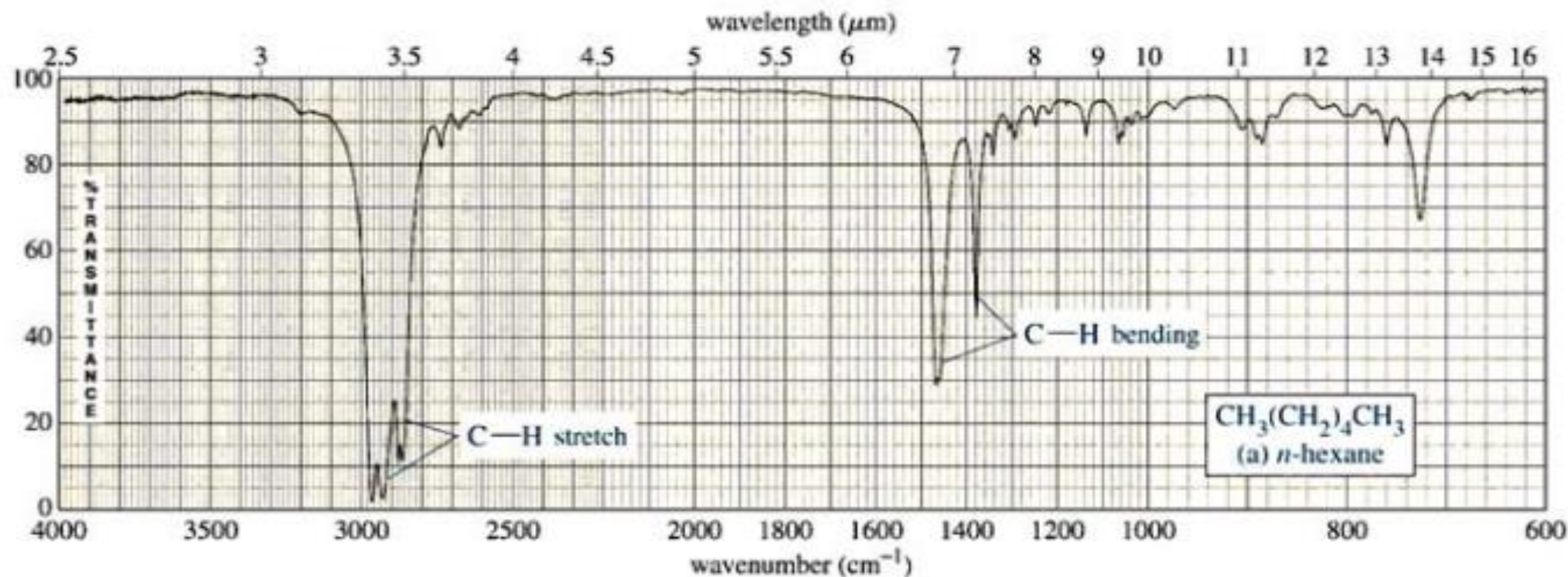
THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1} .



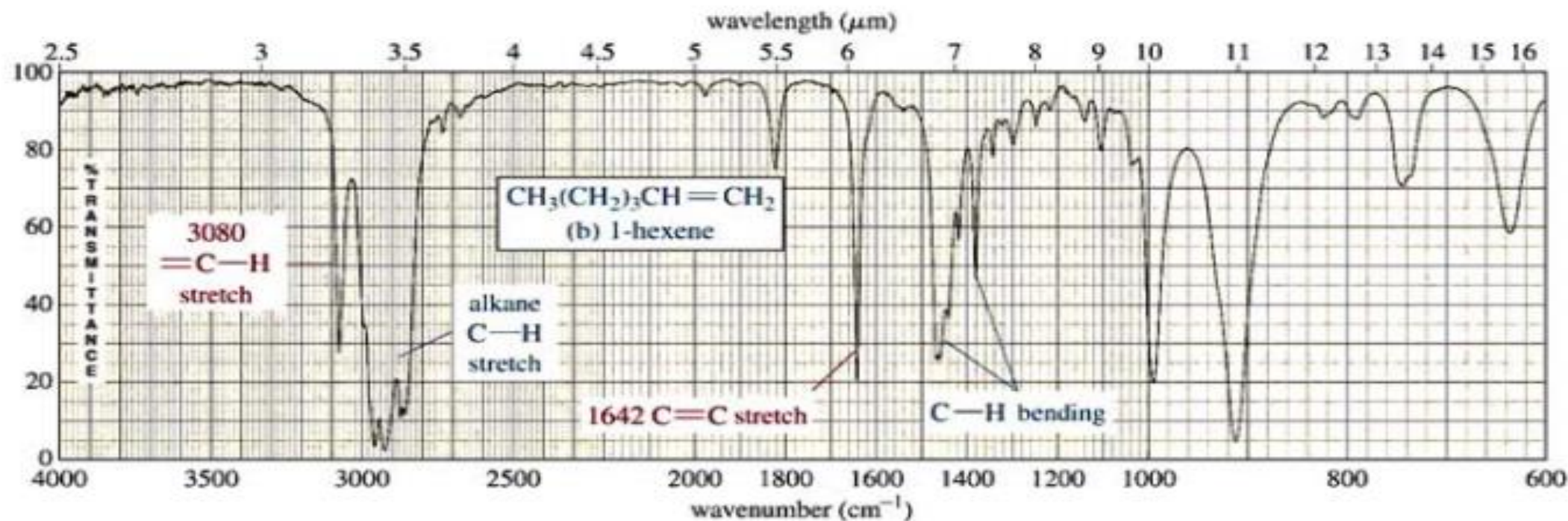
IR SPECTRUM OF ALKANES

Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm⁻¹**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



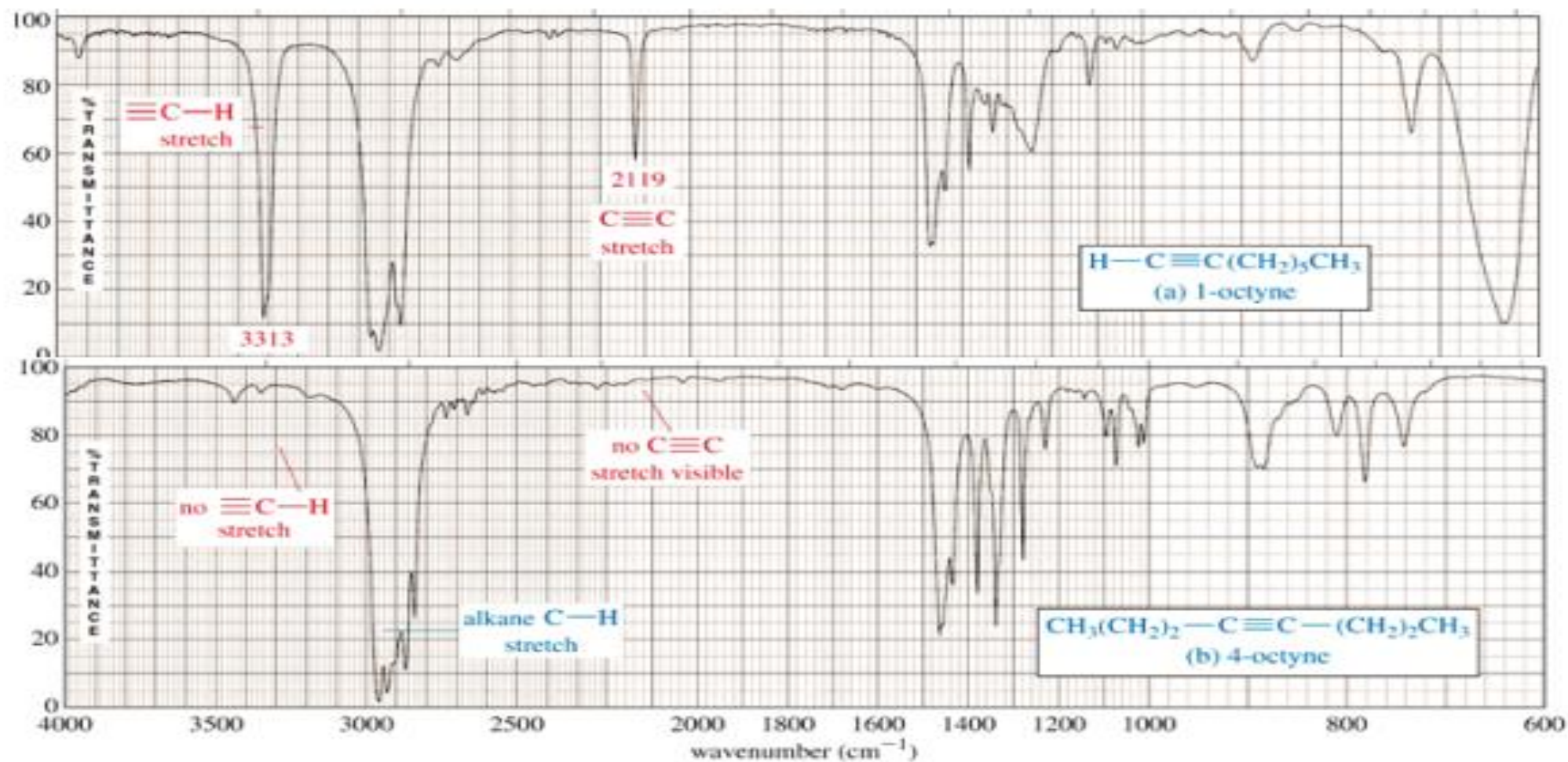
IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm⁻¹**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm⁻¹** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm⁻¹ (see next slide)



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

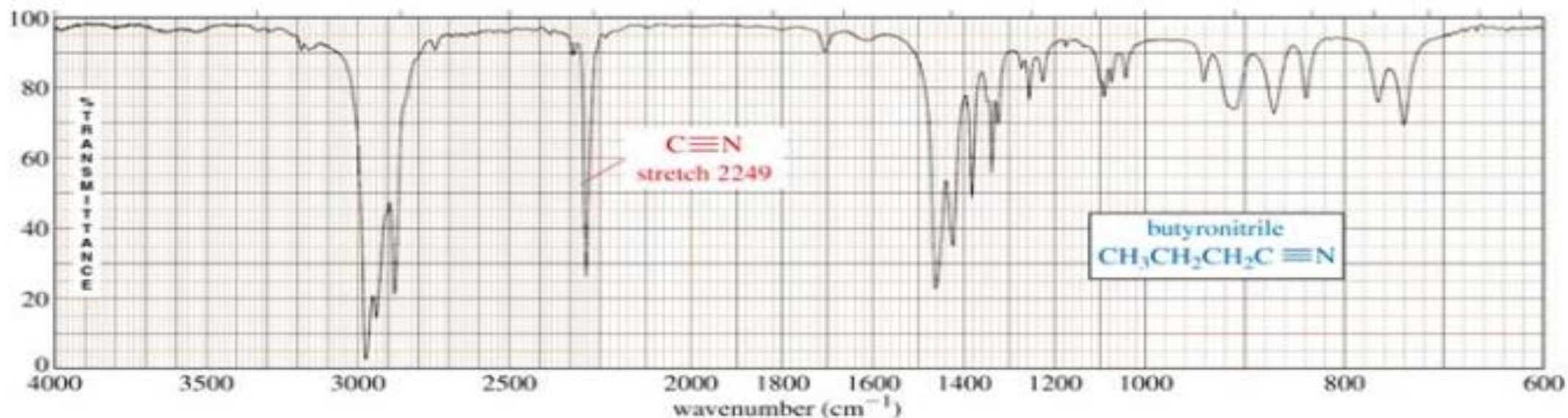
IR SPECTRUM OF ALKYNES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRUM OF A NITRILE

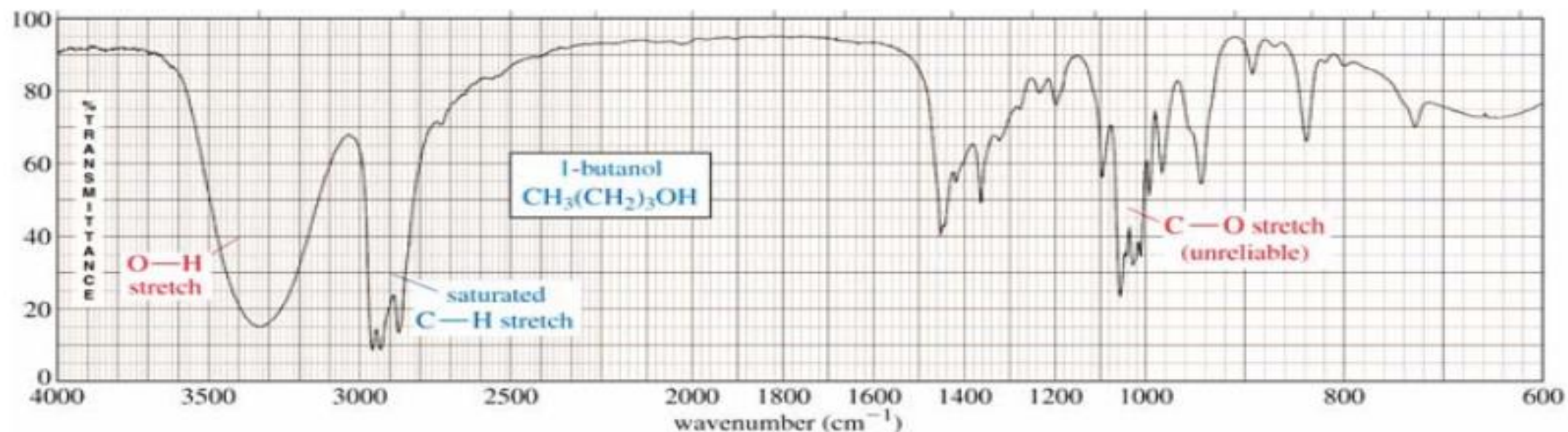
In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm⁻¹**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



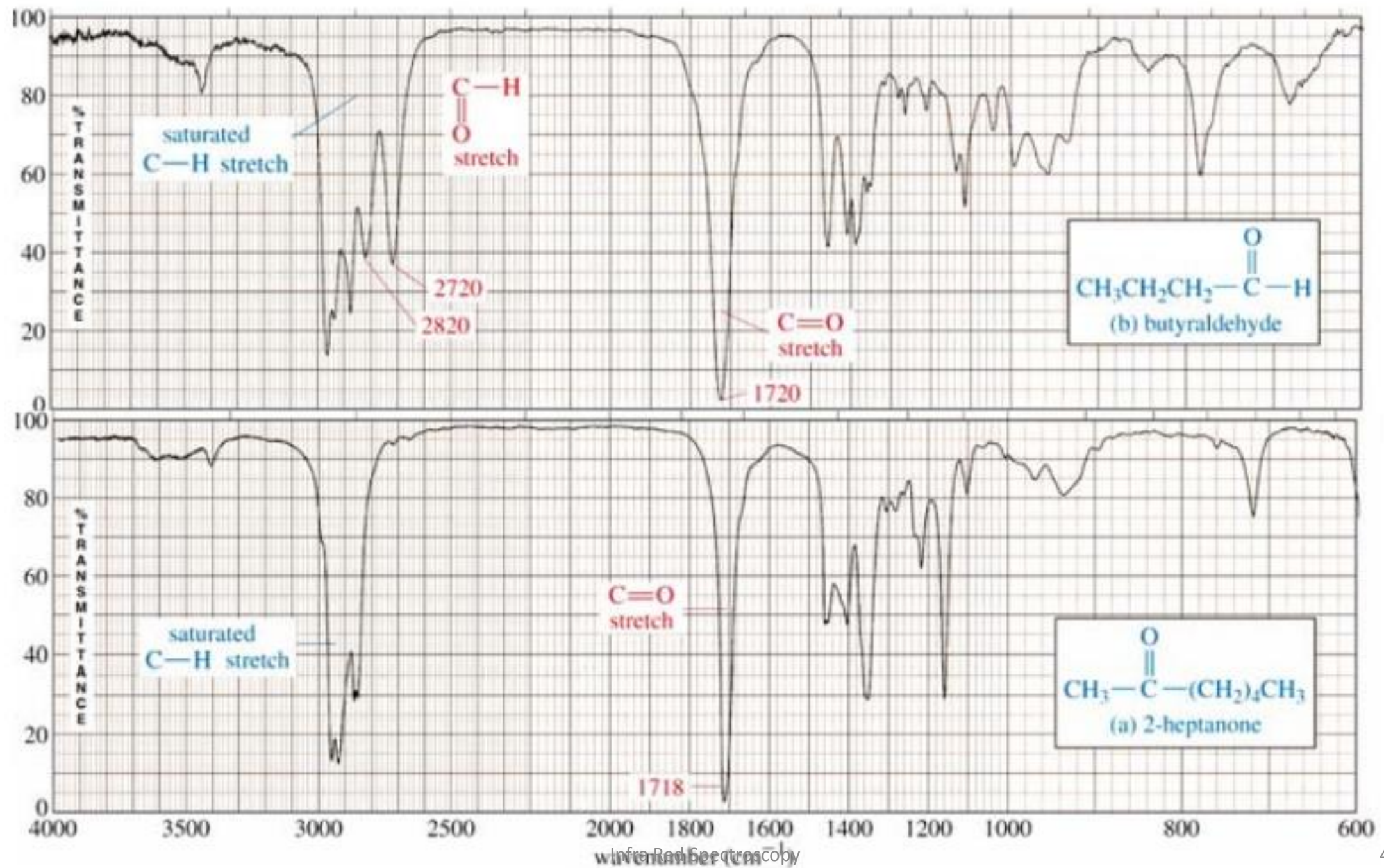
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRUM OF ALDEHYDES AND KETONES

Carbonyl compounds are those that **contain the C=O functional group**. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.

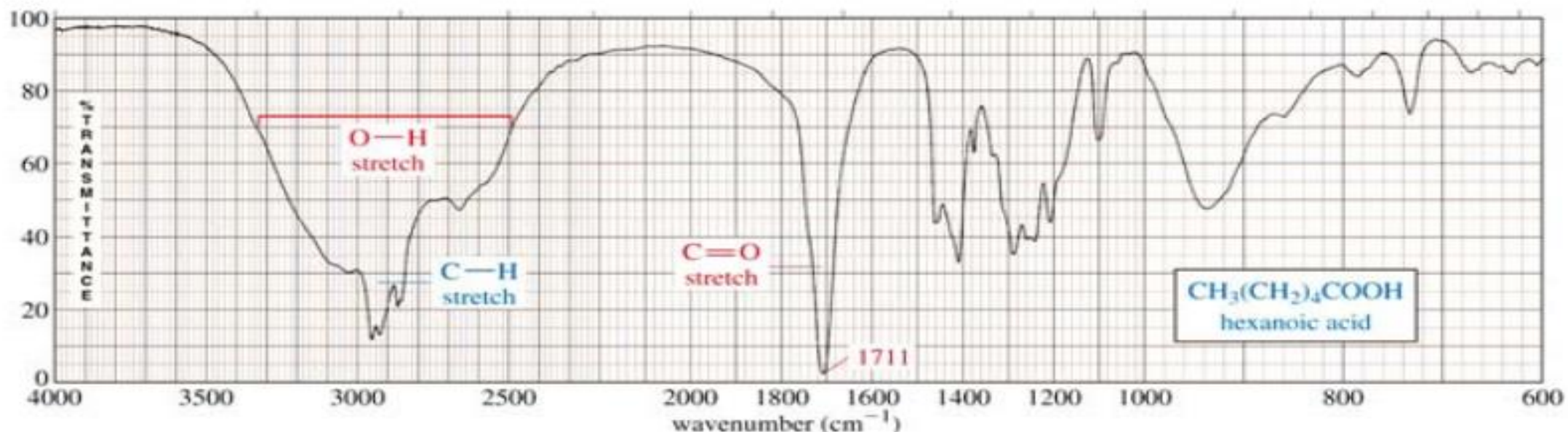
Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm⁻¹** (right in the middle of the spectrum). This band is due to the **highly polar C=O bond**. Because of its position, shape, and size, it is hard to miss.

Because aldehydes also contain a C-H bond to the sp^2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700 and 2800 cm⁻¹**. These bands are missing in the spectrum of a ketone because the sp^2 carbon of the ketone lacks the C-H bond.



IR SPECTRUM OF A CARBOXYLIC ACID

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.

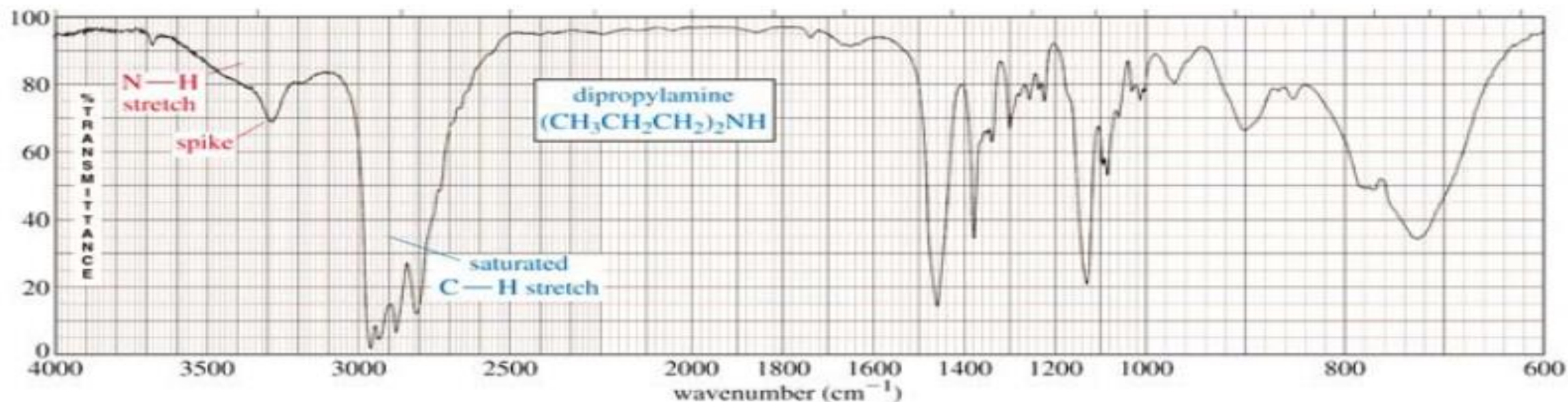


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRA OF AMINES

The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the left end of the spectrum, in the range of about **3200 - 3600 cm⁻¹**.

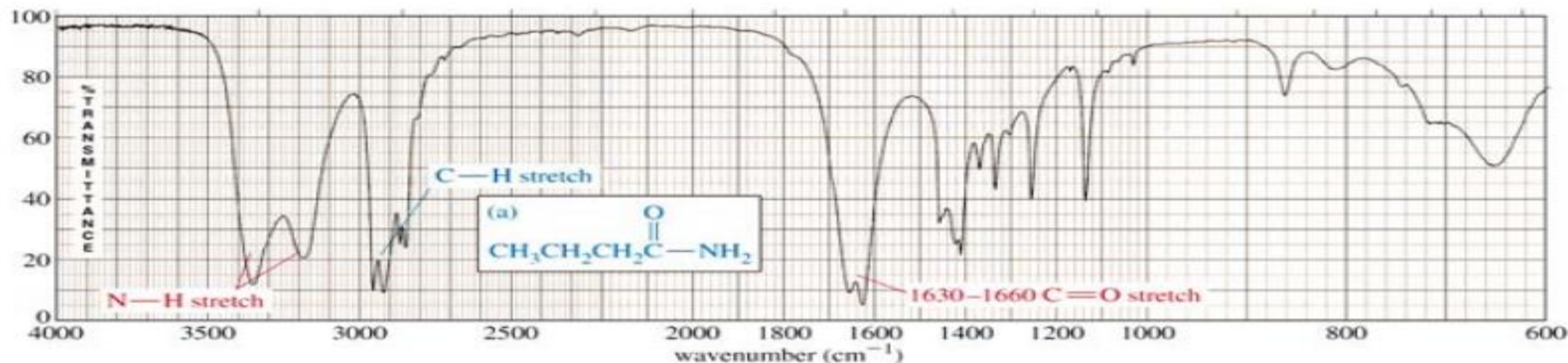
Primary amines have two N-H bonds, therefore they typically show two spikes that make this band resemble a molar tooth. Secondary amines have only one N-H bond, which makes them show only one spike, resembling a canine tooth. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

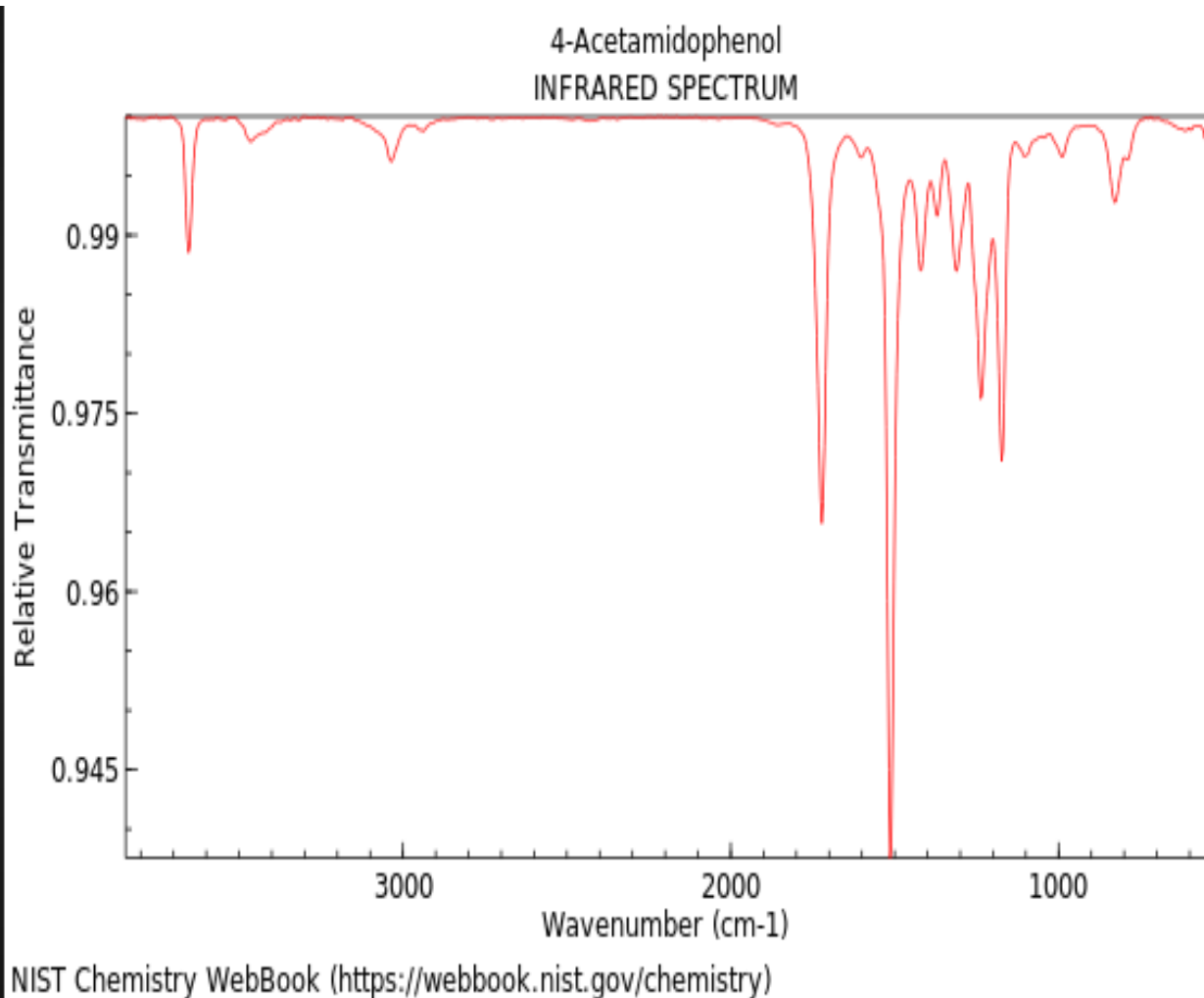
IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR Spectrum



Regions

A spectrograph is often interpreted as having two regions.

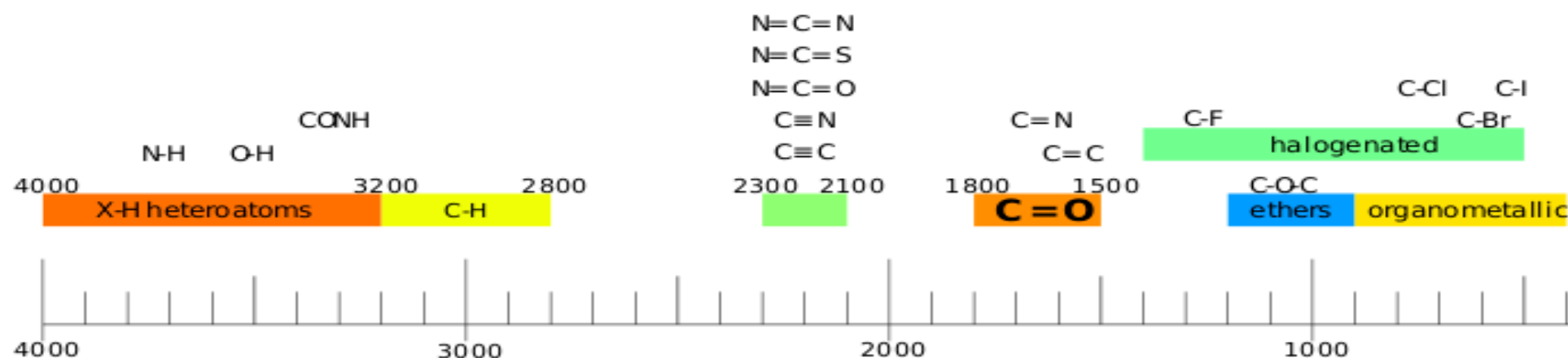
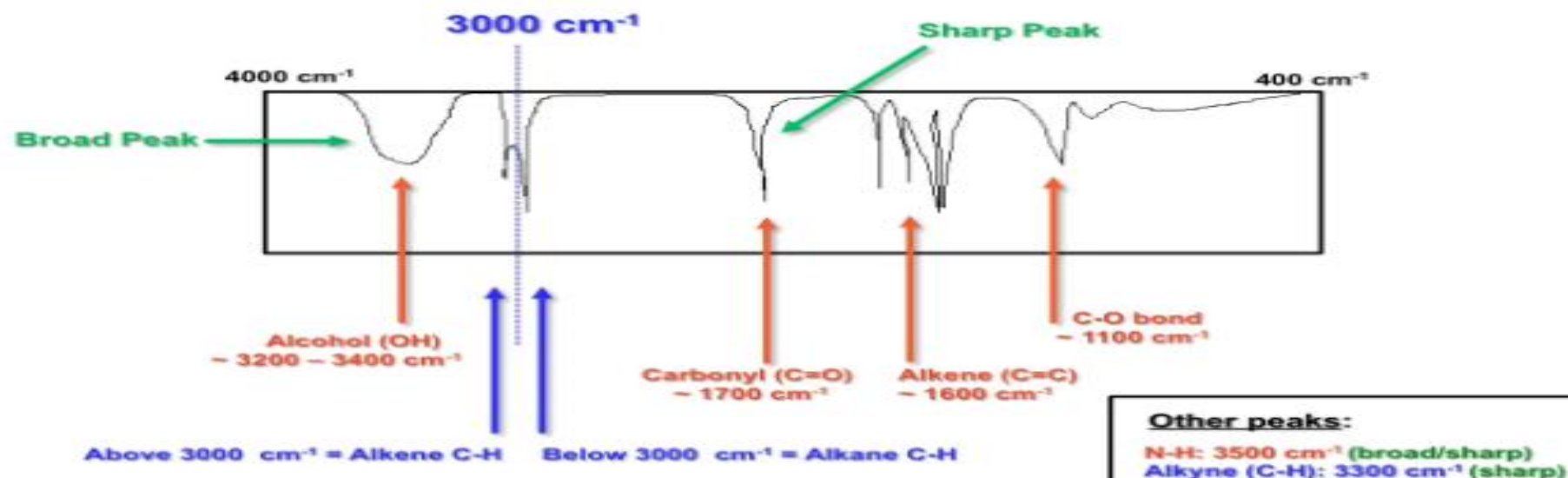
- functional group region**

In the functional region there are one to a few troughs per functional group.

- fingerprint region**

In the fingerprint region there are many troughs which form an intricate pattern which can be used like a fingerprint to determine the compound.

Most Commonly Used IR Values In Organic Chemistry



List of main IR spectroscopy bands. For example, the carboxyl group will contain a C=O band at 1700 cm^{-1} and an OH band at 3500 cm^{-1} (total group -COOH). Wavenumbers listed in cm^{-1} .

Applications of Infrared Spectroscopy

1. Identification of substance

Infrared spectroscopy is used to establish whether a given sample or an organic substance is identical with another or not like : Alkanes, Alkenes, Alkynes, Aromatic ring etc.

2. Determination of Molecular structure

Infrared spectroscopy is helpful in determining molecular structure of unknown substance.

From an examination of the position of absorption band in the spectrum.it is possible to establish the nature of the gas groups present in the molecule.

3. Detection of impurities.

4. Isomerism in organic chemistry

5. Identification of functional groups

6. Miscellaneous Examples

The following are some important application ;

- a. Determination of purity
- b. Shape of symmetry of a molecule.
- c. Presence of water in a sample.
- d. Measurement of paints And varnishes