

Spectroscopy

- **ULTRAVIOLET-VISIBLE Spectroscopy**
- **Conducto-metry**
- **P^H – Metry**
- **IR**
- **NMR**

Definitions

- **Electro-analytical** methods are a class of techniques in analytical chemistry, which deals with study of an analyte (test solution) by using suitable instrumental techniques. Eg. pH-Metry, Conductometry etc.
- **Spectrophotometry** is a method to measure intensity of light absorbed by a chemical substance when a beam of light passes through a sample solution.
It is the combination of spectrometry (interaction of electromagnetic radiation of particular wavelength) and photometry (measurement of intensity of transmitted radiation in terms of absorbance). The basic principle is that each compound absorbs or transmits light over a certain range of wavelength.
- **Spectroscopy** is the branch of science that deal with the study of interaction of matter with electromagnetic radiation of particular wavelength and vice-versa

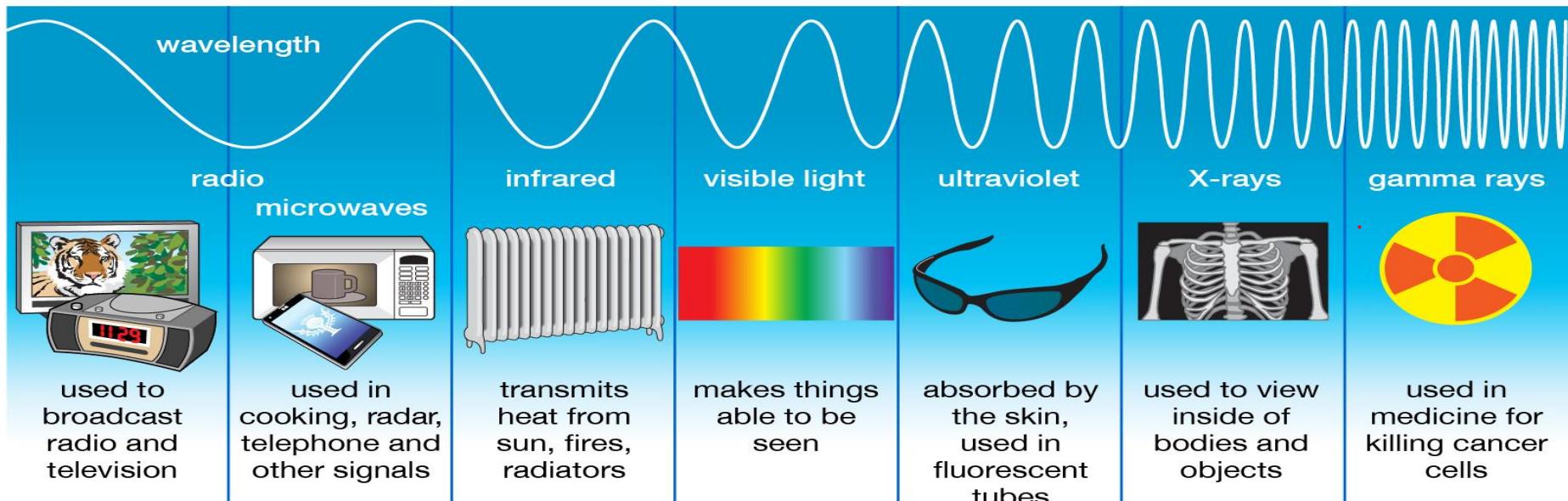
Spectroscopy

Every chemical compound absorbs, transmits, or reflects light (electromagnetic radiation).

Spectroscopy is a measurement of how much a chemical substance absorbs or transmits.

Spectrophotometry is widely used for quantitative analysis in various areas.

Types of Electromagnetic Radiation



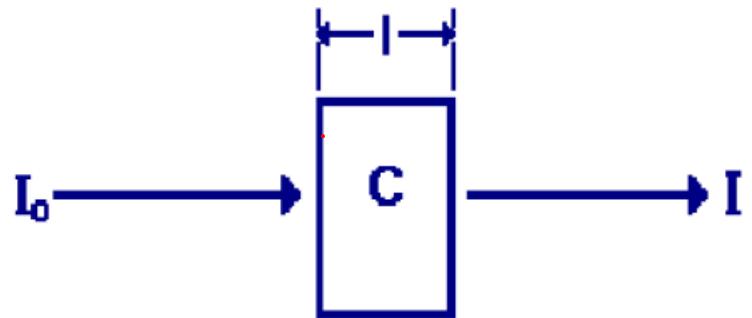
LIGHT AND THE PERCEPTION OF COLOR

- Light is a form of electromagnetic radiation. When it falls on a substance, certain wavelengths can be absorbed and the remainder transmitted or reflected.
- Suppose we shine a beam of white light at a substance that absorbs blue light. Since the blue component of the white light gets absorbed by the substance, the light that is transmitted is mostly yellow, the complementary color of blue.
- This yellow light reaches our eyes, and we “see” the substance as a yellow colored substance.

Wavelength (nm)	Color Absorbed	Color Observed
435	Blue	Yellow
495	Green	Purple
560	Yellow	Blue
650	Orange	Greenish blue

Ultraviolet-Visible Spectroscopy

- Introduction to UV-Visible
 - Absorption spectroscopy from 160 nm to 780 nm
 - Measurement of transmittance
- Measurement of transmittance and absorbance
- Conversion to absorbance
$$A = - \log T = \epsilon c l$$
- Beer-Lambert's law
- Noise
- Instrumentation



Lambert's Law

Successive layers of equal thickness of a light absorbing species (solution) absorb equal fractions of the incident radiation

OR

When a monochromatic radiation is passed through a light absorbing species (solution), the decrease in the intensity of radiation with thickness of the light absorbing species (solution) is directly proportional to the intensity of incident light

OR

Equal fractions of the incident radiation are absorbed by successive layers of equal thickness containing the same number of absorbing species

Derivation of Lambert's law

The radiation absorbed is directly proportional to the distance covered by the beam.

Mathematically, the law can be expressed as,

$$-\frac{dI}{I} = k_l dl$$

Here, dI is the decrease in the intensity of the beam of initial intensity I_0 after passing through the solution of thickness dl .

Negative sign indicates the decrease in the intensity with increase in path length.

After Integration,

$$-\int \frac{dI}{I} = \int k_l dl$$

$$-\ln I = k l + C_1$$

where, C_1 , is the constant of integration.

When $l = 0$ $I = I_0$ the intensity of the incident beam

$$-\ln I_0 = 0 + c$$

$$-\ln I = k_1 l - \ln I_0$$

$$\ln \frac{I_0}{I} = k_1 l$$

$$2.303 \log \frac{I_0}{I} = k_1 l$$

$$\log \frac{I_0}{I} = \frac{k_1}{2.303} l \quad \text{— Lambert's Law Expression}$$

Beer's Law

Equal changes in concentration of absorbing species in paths of constant length absorb equal fractions of the incident radiation.

OR

Equal fractions of the incident radiation are absorbed by successive layers of the medium containing equal concentration of absorbing species provided the layers have same thickness.

The decrease in the intensity of incident radiation due to absorption is directly proportional to the concentration of absorbing species.

Mathematically,

$$-\frac{dI}{I} = k_2 dc$$

After integration,

$$-\int \frac{dI}{I} = \int k_2 dc$$

$$-\ln I = k_2 c + C_2$$

at $c = 0 \quad I = I_0$

$$\ln I_0 = 0 + C_2$$

$$-\ln I = k_2 c - \ln I_0$$

$$\ln \frac{I_0}{I} = k_2 c$$

$$\log \frac{I_0}{I} = \frac{k_2}{2.303} c$$

Beer's Law Expression

Combining Both Laws we will obtain expression for Beer-Lambert's Law

$$\log \frac{I_0}{I} = \frac{k_1}{2.303} l \quad \text{Lambert's Law Expression}$$

$$\log \frac{I_0}{I} = \frac{k_2}{2.303} c \quad \text{Beer's Law Expression}$$

$$2.303 \log \frac{I_0}{I} = K \cdot C \cdot l$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} C \cdot l$$

Where, $\log \frac{I_0}{I} = A$ — Absorbance

$$\frac{K}{2.303} = \epsilon \quad \text{Molar extinction coefficient}$$

$$A = \epsilon \cdot C \cdot l$$

Definitions

Absorbance (A)

- It is the logarithm of the ratio of the incident light (I_0) to the transmitted light (I)
- It is a unit-less quantity

Molar extinction coefficient or Molar Absorptivity (ϵ)

It is defined as the absorbance of that solution which has concentration of the absorbing species $1 \text{ mol} \cdot \text{dm}^{-3}$ and the path length is 1 cm

Formulae for numerical

$$A = \epsilon \cdot C \cdot l$$

Where, ϵ = molar absorptivity, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$

C = concentration, $\text{mol} \cdot \text{dm}^{-3}$

l = path length, cm

$$A = -\log_{10} \% T$$

$$A = -\log T = \log_{10} (1/T)$$

Numerical-1

7.5×10^{-4} M solution of an absorbing species is placed in a cell of path length 2 cm. Transmittance measured is 60 % at 470 nm. Calculate the molar absorptivity?

Solution:

$$\% T = 60 \%$$

$$A = 2 - \log_{10} \% T = 2 - \log_{10} 60 = 2 - 1.7782 = 0.2216$$

$$A = \epsilon \cdot C \cdot l$$

Therefore,

$$\begin{aligned}\text{Molar absorptivity } (\epsilon) &= A / C \cdot l \\ &= 0.2216 / 7.5 \times 10^{-4} \times 2\end{aligned}$$

$$\text{Molar absorptivity } (\epsilon) = 1.477 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

Numerical-2

If the transmittance of the solution is 19.4 %, what will be its absorbance ?

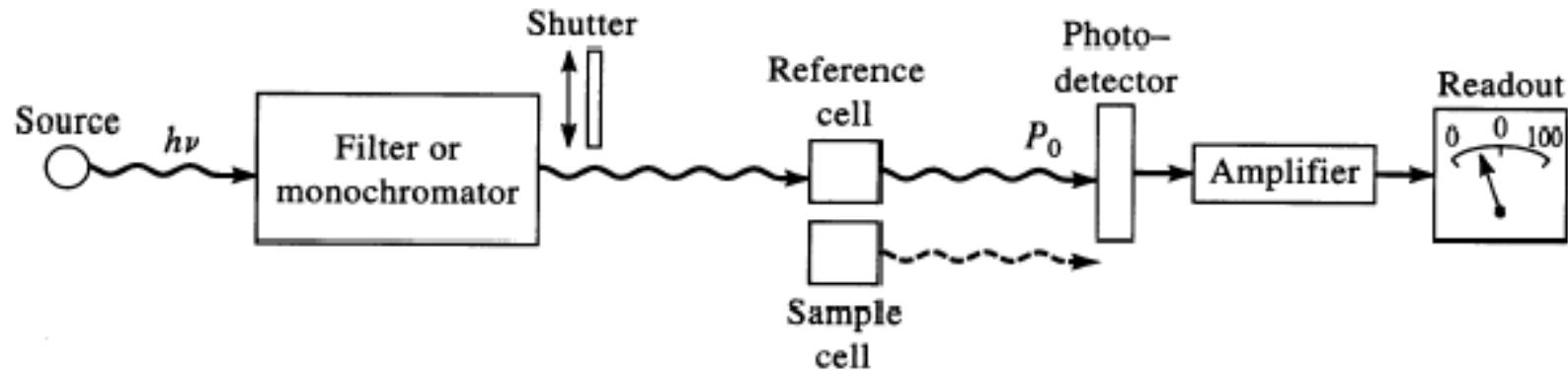
Numerical-3

The transmittance of 2×10^{-4} M solution was found to be 76.2 % in path length of 1 cm. calculate the i) absorbance ii) Molar absorptivity iii) % T for the path length of 2 cm.

Limitations of Beer-Lambert's Law

- The linearity of the Beer-Lambert Law is limited by chemical and instrumental factors
- The law does not valid for solutions having concentration greater than 10^{-2} M.
- Molar extinction coefficient depends on the refractive index of the solution and changes with changes in it.
- Interaction with solvent: hydrogen bonding affects ϵ .
- Scattering of light due to particulates in the sample.
- Fluorescence or Phosphorescence
 - positive deviation in % T and negative deviation for A
- Shifts in chemical equilibrium as a function of concentration
- Temperature fluctuation and Stray light may affect absorbance measurement

Single beam spectrophotometer



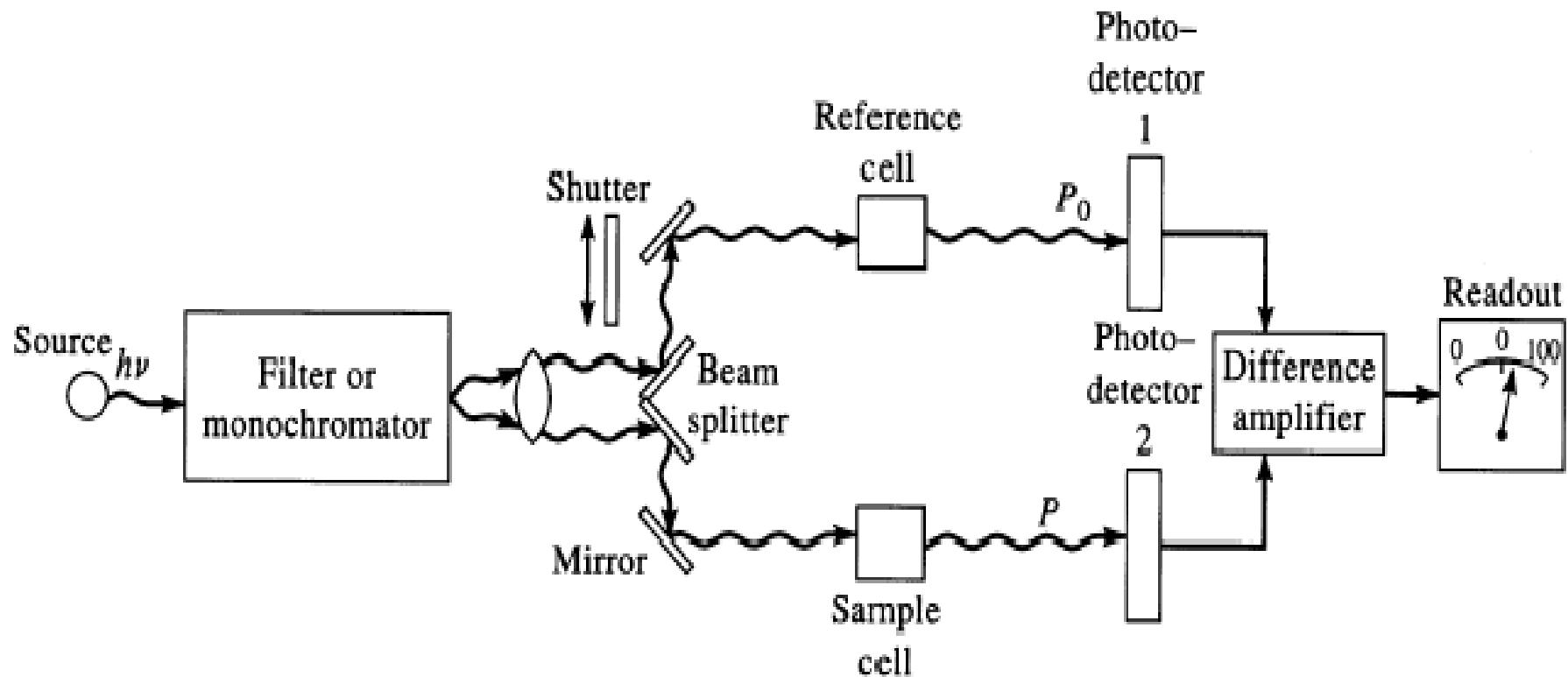
Instrumentation

- **Light source**
 - Deuterium and hydrogen lamps (190-400 nm)
 - Tungsten filament lamp (300-750 nm)
- **Sample containers**
 - Cuvettes (Quartz)
- **Mono-chromators**
 - Prisms can be used as mono-chromator
 - Diffraction gratings
- **Detectors**
 - Photomultiplier tube
 - Photodiode
 - Photodiode array

Working of Single beam spectrophotometer

- The instrument is useful for both Ultraviolet and Visible regions.
 - For UV light Deuterium lamps (190-400 nm)
 - For Visible light Tungsten filament lamp (380-750 nm) are used depending on the requirement.
- Light beam is focused on the mono-chromator, where after reflection and dispersion nearly monochromatic beam emerges out.
- This emergent monochromatic beam passed through a quartz cuvette containing a sample solution
- Transmitted radiation from the cuvette is allowed to fall on a photoelectric cell, which converts radiant energy into electrical signal as absorbance.
- Water is generally used as blank solution.

Double beam Spectrophotometer



Instrumentation

- **Light source**
 - Deuterium and hydrogen lamps (190-400 nm)
 - Tungsten filament lamp (300-750 nm)
- **Sample containers**
 - Cuvettes (Quartz)
- **Beam splitters**
 - Mirrors
- **Mono-chromators**
 - Prisms can be used as mono-chromator
 - Diffraction gratings
- **Detectors**
 - Photomultiplier tube
 - Photodiode
 - Photodiode array

Working of Double beam spectrophotometer

- The instrument is useful for both Ultraviolet and Visible regions.
 - For UV light Deuterium lamps (190-400 nm)
 - For Visible light Tungsten filament lamp (380-750 nm) are used depending on the requirement.
- The variation in the intensity of the source light is compensated by splitting the incident beam into **two light beams** by passing through beam splitter.
- One of the beam passes through the blank solution while other through the sample solution.
- Transmitted radiations from the cuvette is allowed to fall on a photoelectric cell, which converts radiant energy into electrical signal as absorbance.
- Simultaneously, absorbance of blank and sample solution can be measured.
- Water is generally used as blank solution.

Application of UV-Visible Spectroscopy

- Quantitative determination of analyte concentration
- Identification of inorganic and organic species
- Magnitude of molar absorptivity
- Used as a detector in HPLC
- Used in semiconductor industry to measure thickness and optical properties of thin films.
- To study absorbance of organic compounds

CONDUCTOMETRY

- CONDUCTOMETRY is based on the principle of determination of change in conductivity of different ions in the solution.
- Conductivity of the solution could be changed with the replacement of ions.
- Conductance is the flow of electricity through an electrolyte due to migration of ions by applying potential difference between two electrodes.
- When the solution contains one single electrolyte, the measured conductance of the solution can be related to concentration of that electrolyte.
- It is reciprocal of resistance, $[G = 1/R]$ expressed as Ohm⁻¹ or Siemens

CONDUCTOMETRY

Property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it

Conductance

Conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimeter apart

Specific Conductance

Conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Equivalent conductance

Conductance of all the ions produced by ionization of 1 g mole of an electrolyte when present in V mL of solution

Molar conductance

Conductometric Titration

- Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added to the other.
- The equivalence point is the point at which the conductivity undergoes a sudden change.
- Marked increase or decrease in conductance is associated with the changing concentrations of the two most highly conducting ions, viz. the hydrogen and hydroxyl ions.
- The method can be used for titrating colored solutions or homogeneous suspension

Principle

- When solution of one electrolyte is added to another electrolyte, the conductance of the solution will alter, if an ionic reaction occurs.
- If no ionic reaction takes place then the conductance of the solution will simply increase.
- If an ionic reaction occurs, the ion added may replace another ion and hence bring about change in the conductance.
- Let A^+B^- be the ions of titrand and C^+D^- be ions of the titrant, the ionic reaction in the titration is combination of A^+ and D^- , AD formed may be insoluble or weakly ionized.



Principle

- Thus as the titration proceeds, A^+ are replaced by C^+ . The conductance of the solution increases or decreases depending on whether conductance of C^+ is greater than or less than that of A^+ . After equivalence point the ionic reaction does not occur and hence, the conductance of the solution will raise due to the excess addition of titrant C^+D^- .
- The principle of conductometric titration is changes in the conductance of the solution due to difference in the ionic conductance or due to production of more number of ions in the solution.

Procedure

- A definite volume of the solution to be estimated is pipetted out in a beaker.
- A dip type conductivity cell is placed in a beaker. Addition of distilled water may be necessary if the cell does not dip completely in the solution.
- The cell is connected to a conductometer and the conductance of the solution is measured. The titrant is filled in the burette.
- The titrant is added in the small portions, generally 0.5 mL at a time. The solution is stirred after each addition.
- The solution is allowed to stand for a minute or two after stirring before conductance is measured.
- Addition of titrant is continued till about seven to eight readings beyond the equivalence point are obtained.
- The plot of conductance against volume of the titrant added is used to locate the equivalence point.

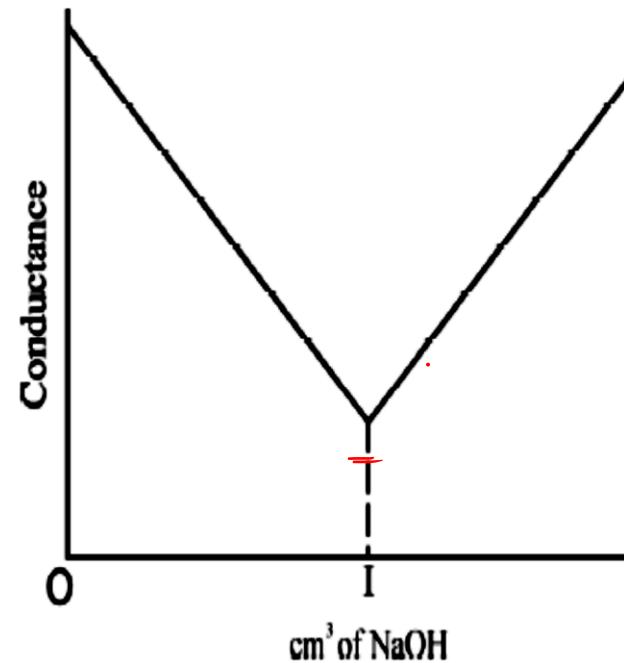
Some Conductometric Titrations

- Strong Acid with a Strong Base, [HCl Vs NaOH]
- Weak Acid with a Strong Base, [CH₃COOH Vs NaOH]
- Strong Acid with a Weak Base, [H₂SO₄ Vs dil. NH₄OH]
- Weak Acid with a Weak Base, [CH₃COOH Vs dil. NH₄OH]
- Mixture of a Strong Acid (H₂SO₄) and a Weak Acid (CH₃COOH) vs. a Strong Base (NaOH) or a Weak Base (dil. NH₄OH)

Strong Acid with a Strong Base

[HCl with NaOH]

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H⁺ ions react with OH⁻ ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH⁻ ions

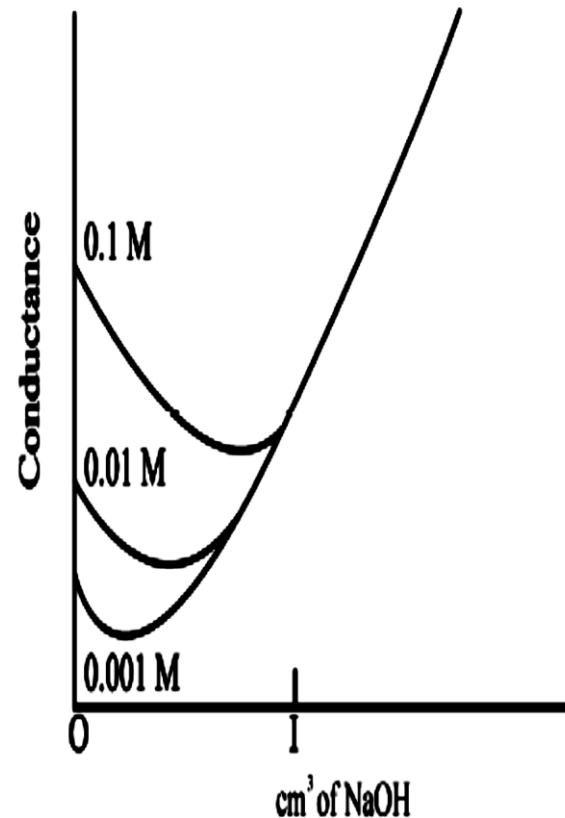


Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

Weak Acid with a Strong Base

[CH_3COOH with NaOH]

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the undissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions.

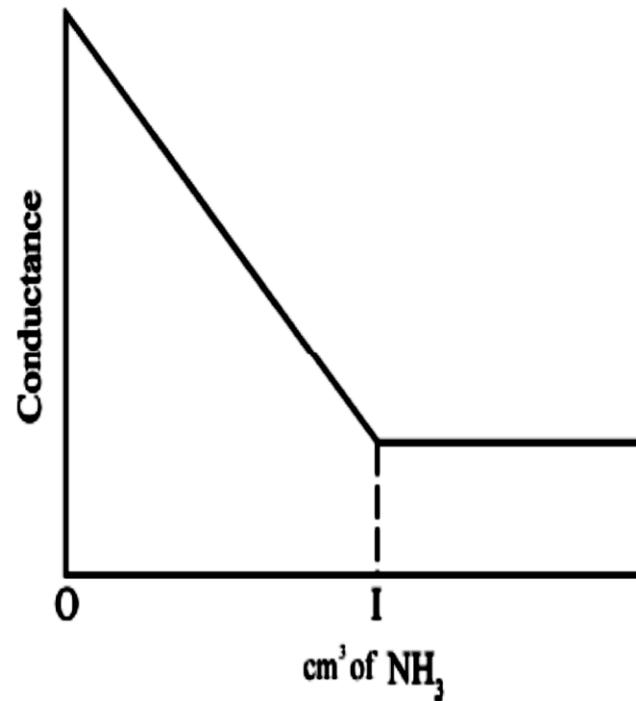


**Conductometric titration of a weak acid (acetic acid) vs. a strong base
(NaOH)**

Strong Acid with a Weak Base

[H_2SO_4 with NH_4OH]

Initially the conductance is high and then it decreases due to the replacement of H^+ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.

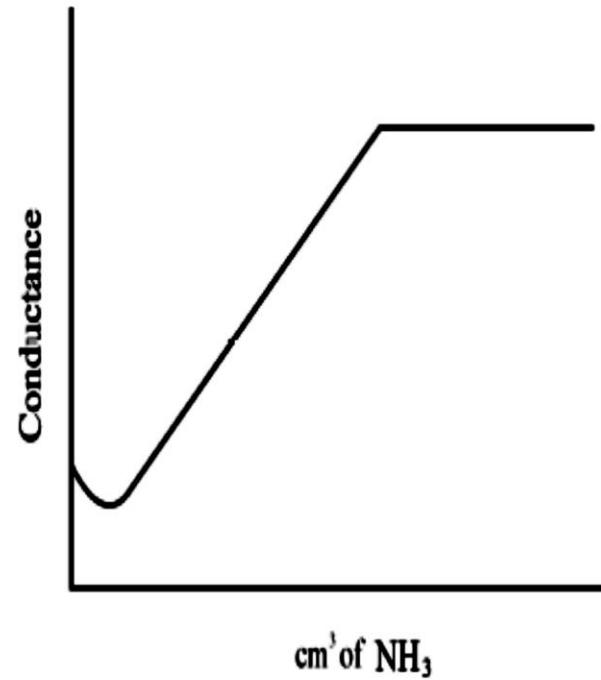


Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

Weak Acid with a Weak Base

[CH₃COOH with NH₄OH]

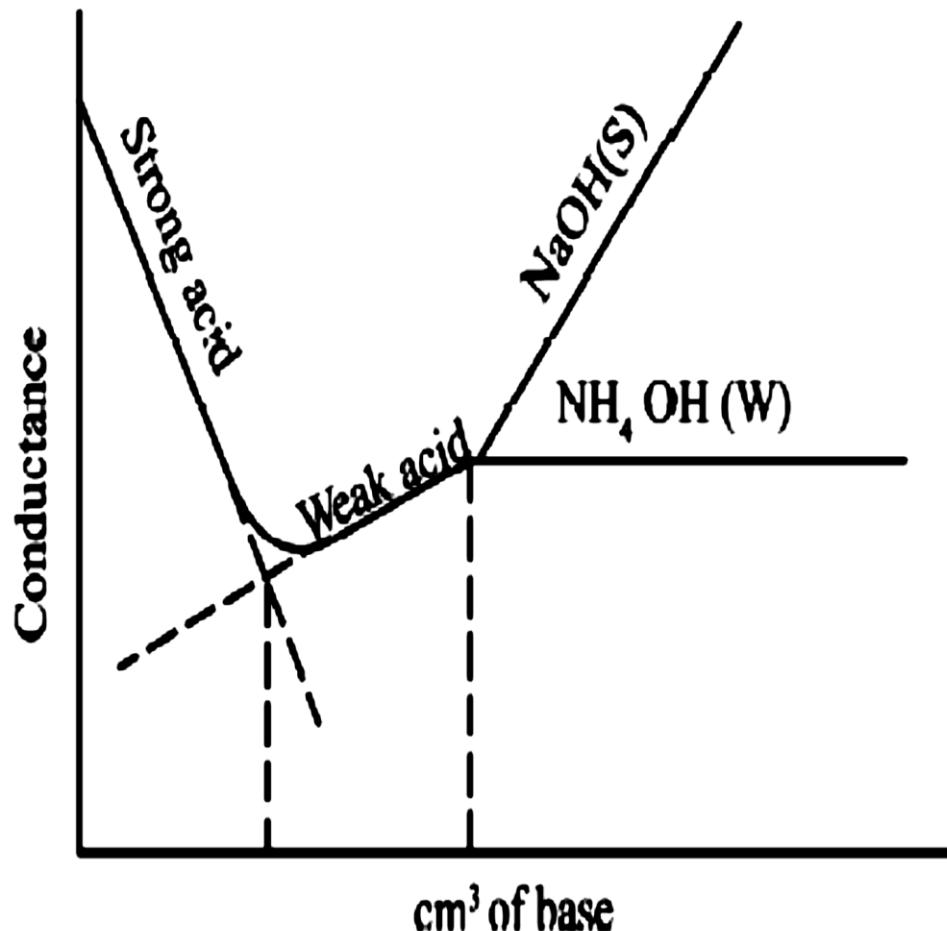
The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting.



**Conductometric titration of a weak acid (acetic acid) vs. a weak base
(NH₄OH)**

Mixture of Strong Acid and Weak Acid vs. Strong Base or Weak Base

In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH⁻ ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to Fig



Advantages of Conductometric titrations

Conductometric titration are found to possess several advantages over normal titrimetry namely,

- Coloured solutions can be titrated.
- The method works equally well for dilute solutions also, as it is based on the changes in the conductance, rather than the absolute value of the conductance.
- In conductometric titrations, it is not necessary to make observations around the equivalence point, with small increments of the titrant added.
- The observations, far away from the equivalence point, on either side are of importance.
- An extremely weak acid or a weak base can be titrated conductometrically, which may not be possible in normal titrimetry.
- A mixture of weak and strong acids, can also be titrated with relative ease. Thus, making the simultaneous determination possible.

Limitations

- In dilute solutions, obtuse curves are obtained. With obtuse curves it is difficult to locate the equivalence point accurately.
- The overall accuracy of the conductometric titrations is limited as the technique does not permit addition of small increments of the titrant.

P^H Metry

Definition of pH is an abbreviation of “pondus hydrogenii” and was proposed by the Danish scientist S.P.L. Sørensen in 1909 in order to express the very small concentrations of hydrogen ions.

pH is defined as the negative base 10 logarithm of the hydrogen ion concentration.

$$\text{pH} = - \log_{10}[\text{H}^+]$$

This definition is closely related to the operational pH definition which is currently defined using a standardised hydrogen electrode setup and buffers standardised in accordance with IUPAC recommendations.

pH is measured using a setup with two electrodes: the indicator electrode and the reference electrode.

These two electrodes are often combined into one - a combined electrode.

When the two electrodes are immersed in a solution, a small galvanic cell is established. The potential developed is dependent on both electrodes. Ideal measuring conditions exist when only the potential of the indicator electrode changes in response to varying pH, while the potential of the reference electrode remains constant.

$$E = E_{\text{ind}} - E_{\text{ref}}$$

$$E = E^{\circ} - \left(\frac{RT}{nF} \right) \ln[\text{conc.}]$$

A reference electrode is an electrode which has a stable and well-known electrode potential

Saturated calomel electrode Construction:

It consists of a tube at the bottom of which a small mercury drop is placed. It is covered with a paste of solid Hg_2Cl_2 . The aqueous phase in contact with the mercury and the mercury (I) chloride (Hg_2Cl_2 , "calomel") is a saturated solution of potassium chloride in water. The electrode is normally linked *via* a porous frit to the solution in which the other electrode is immersed. This porous frit is a salt bridge.

In cell notation the electrode is written as:



Working:

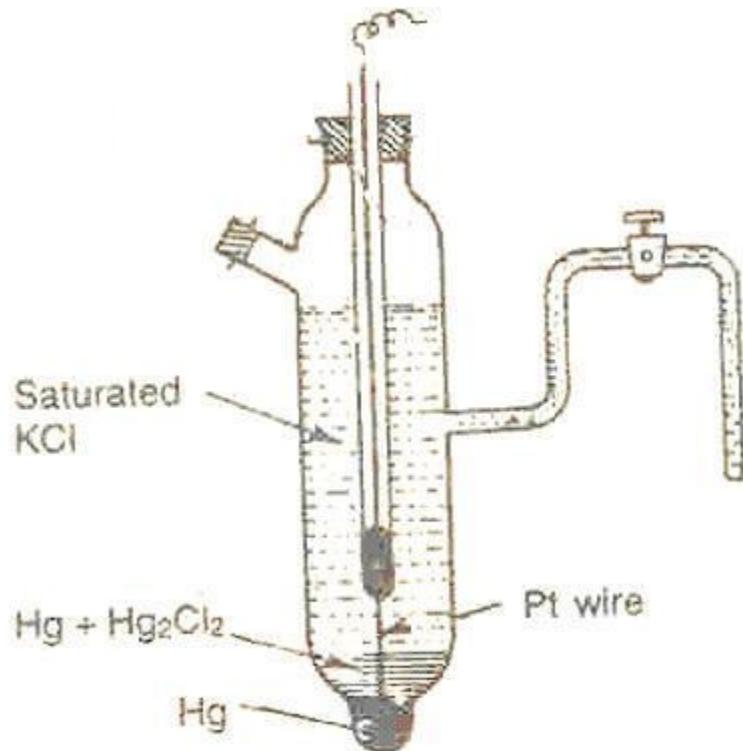
The electrode reaction when the cell acts as cathode is



$$E = E^{\circ}_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Pt}} - \frac{RT}{F} \ln a_{\text{Cl}^-}$$

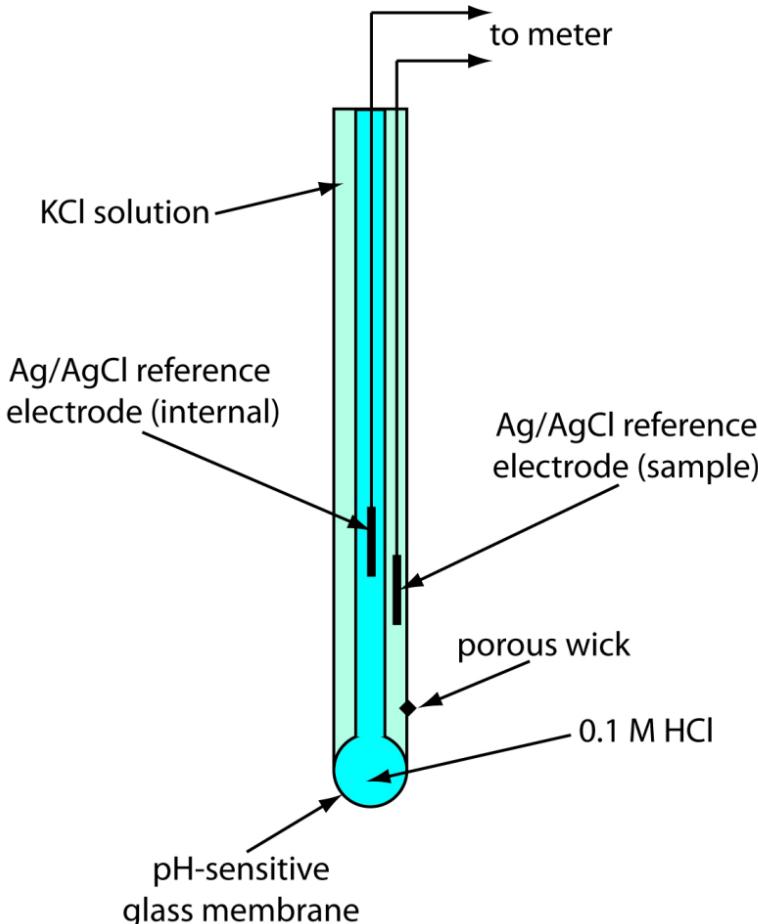
Advantages:

- i) It is simple to construct
- ii) Results of cell potential measurements are reproducible
- iii) Stable over a long period



Ion Selective electrode

A **glass electrode** is a type of [ion-selective electrode](#) made of a doped glass membrane that is sensitive to a specific ion.



Construction:

It consists of glass membrane, it separates an internal solution and silver / silver chloride electrode from the studied solution

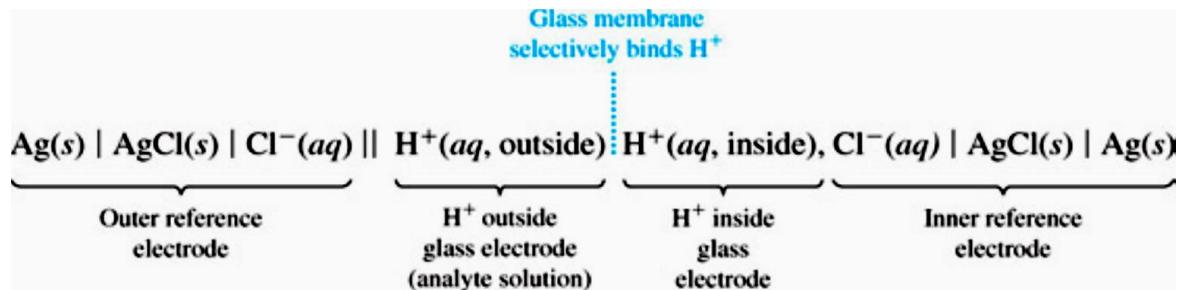
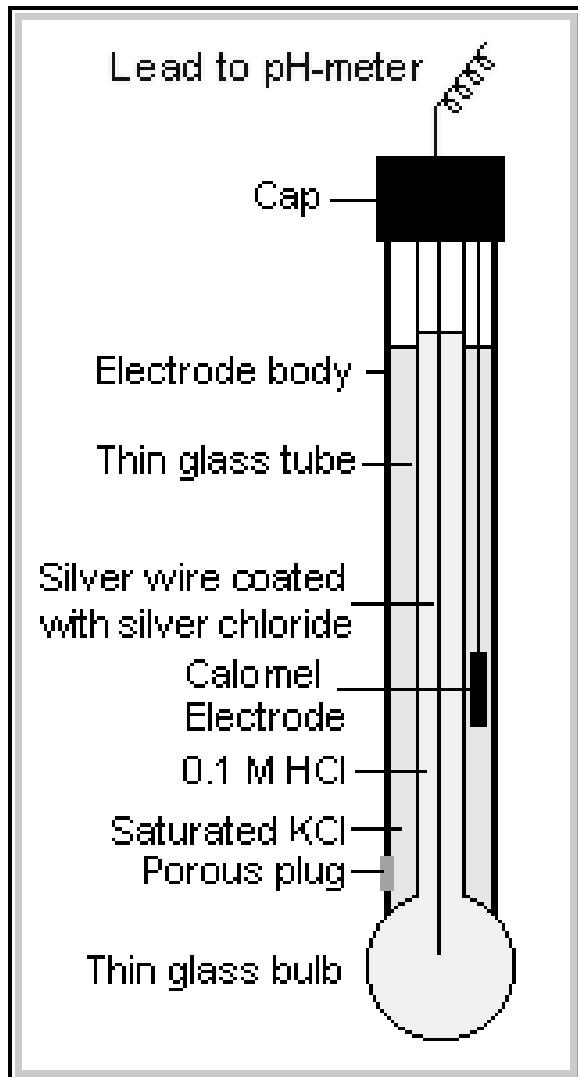


$$E = E^0 - \frac{2.303RT}{F} \text{pH}$$

Applications:

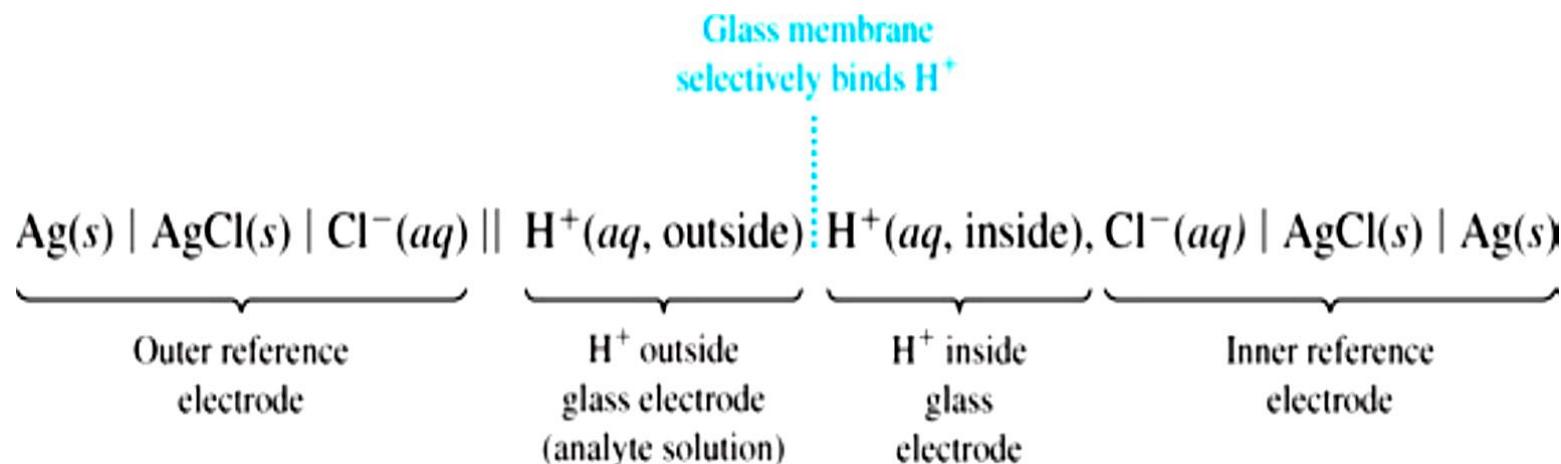
Glass electrodes are commonly used for pH measurements. There are also specialized ion sensitive glass electrodes used for determination of concentration of lithium, sodium, ammonium, and other ions. Glass electrodes have been utilized in a wide range of applications — from pure research, control of industrial processes, to analyze foods, cosmetics and comparison of indicators of the environment and environmental regulations: a microelectrode measurements of membrane electrical potential of a biological cell, analysis of soil acidity, etc.

Combination electrode



Construction: The fig. shows the internal components of the pH electrode. The heart of the electrode is a thin bulb of pH-sensitive glass, which is blown onto the end of a length of glass tubing. The pH-sensitive glass (glass membrane) is sealed to the electrode and contains a solution of potassium chloride at pH 7. A silver wire plated with silver chloride contacts the solution. The Ag/AgCl combination in contact with the filling solution sets an internal reference potential. This potential depends on the chloride concentration in the filling solution and as long as this electrolyte concentration is maintained, the electrode potential is constant.

Working: The outside surface of the glass membrane is in contact with sample being measured and the inside surface contacts the filling solution. A complex mechanism at each glass liquid interface defines the potential the pH glass electrode, while the inner pH glass/ filling solution potential is constant, the outside potential varies based on the H^+ ions concentration in sample. This equilibrium depends also on temperature.



How to measure the pH of solution: Measurement of pH:

A pH measurement system consists of a pH probe, reference probe, temperature sensor, pH meter and the sample to be measured. In most cases the three probes are combined in one electrode. When the pH probe is in contact with a solution a potential forms between the pH probe and the reference probe. The meter measures the potential and converts it, using the calibration curve parameters, into a pH value.

A typical combination glass electrode is represented as

In order to measure the pH of a sample first the standardization of pH meter is required to be done before analyzing the sample.

a) Standardization of pH meter:

A two point standardization method is used to standardize the pH meter, it involves immersing the pH assembly i.e. glass electrode into a standard reference pH buffer ($\text{pH} = 4.0$) and recording the reading, if the meter reading is more or less than the expected value (4.0) then it is adjusted to pH 4.0 using a crew nob.

Standardization at only one pH value does not assure the validity of reading at other pH values considerably. Hence a second standard reference buffer pH = 9.2 is used. The pH meter reading is recorded using this second buffer solution and the reading is adjusted to pH 9.2 using a crew nob.

During both the steps, the glass electrode is rinsed with distilled water. Immerse the glass electrode previously in water for several hours. Start the measurement more than 5 minutes after switching on. Rinse well the detecting unit with water, and blot the water gently with a piece of filter paper very time.

b) To measure pH of solution:

Wash well the detecting unit with water, and blot the water gently with a piece of filter paper. Place glass electrode in solution you wish to measure pH. Be sure that it is stirring slowly during measure and pH adjustment and take readings.

c) Precautions:

When analysis is complete, put pH meter in stand-by mode. Remove electrode from solution and rinse thoroughly with water. Blot dry and put back in yellow pH storage buffer. Place parafilm over the hole and around the bottle to minimize evaporation.

IR spectroscopy

- Near IR 15000 cm^{-1} to 3000 cm^{-1}
- Mid IR 4000 cm^{-1} to 400 cm^{-1}
- Far IR 200 cm^{-1} to 10 cm^{-1}
- Most used 4000 cm^{-1} to 670 cm^{-1}

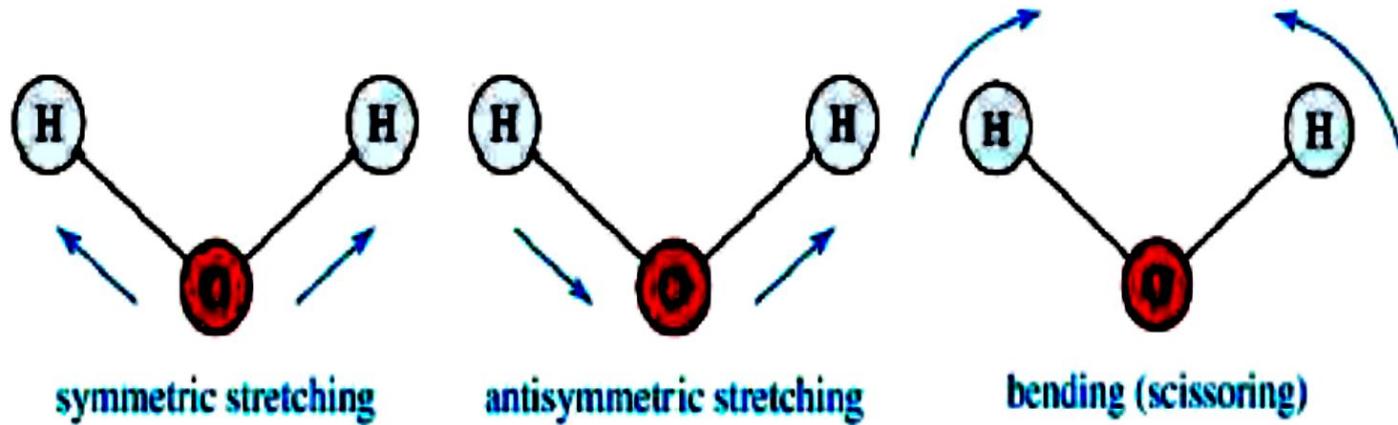
Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

Specific bonds respond to (absorb) specific frequencies.

Fundamental Modes of Vibration

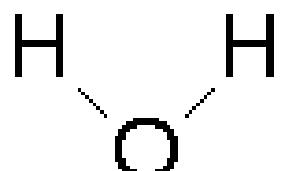
- A **molecular vibration** is a periodic motion of the atoms of a molecule relative to each other, such that the center of mass of the molecule remains unchanged.
- The typical **vibrational frequencies**, range from less than 10^{13} Hz to approximately 10^{14} Hz, corresponding to wavenumbers of approximately 300 to 3000 cm^{-1} .
- In general, a non-linear molecule with N atoms has **($3N - 6$)** normal modes of vibration, but a linear molecule has **($3N - 5$)** modes, because rotation about the molecular axis cannot be observed.
- A diatomic molecule has one normal mode of vibration, since it can only stretch or compress the single bond.
- Vibrations of polyatomic molecules are described in terms of normal modes, which are independent of each other, but each normal mode involves simultaneous vibrations of different parts of the molecule.

VIBRATIONAL MODES

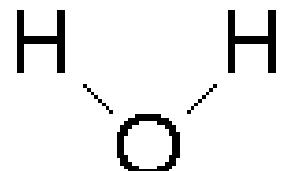


Stretching : in which the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

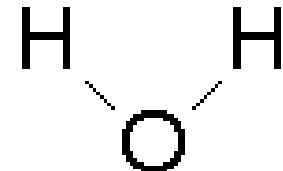
Bending: in which the position of the atom changes relative to the bond axis. Covalent bonds can vibrate in several modes, including stretching, rocking, and scissoring.



antisymmetric
stretch



symmetric
stretch



scissoring
bend

Which substances give a signal in IR spectrum?

Ans:

- The molecules that contain polar bonds i.e. molecules composed of atoms of different elements, organic compounds and inorganic compounds (H_2O , CO_2 , NO_2 , HCl , salts...) can give a signal in IR spectrum.
- Whereas pure chemical elements in molecular or crystal state e.g. Ar, O_2 , O_3 , N_2 , Cl_2 , S_8 , silicon, graphite, Diamond etc. cannot give a signal in IR spectrum.

Basic Principle

- When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies.
- The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called infrared spectrum of the material.
- Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra.
- From the frequencies of the absorption, it is possible to determine whether various chemical groups are present or absent in a chemical structure.

~~Instrumentation of FTIR~~



- 1. The Source:-** Infrared energy is emitted from a glowing black body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
- 2. The Interferometer:-** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample:- The gaseous sample can be directly analysed. Liquid can also be used directly but in diluted form in NaCl plates. Solid compound can be mixed with KBr and formed a pallet and used.

The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

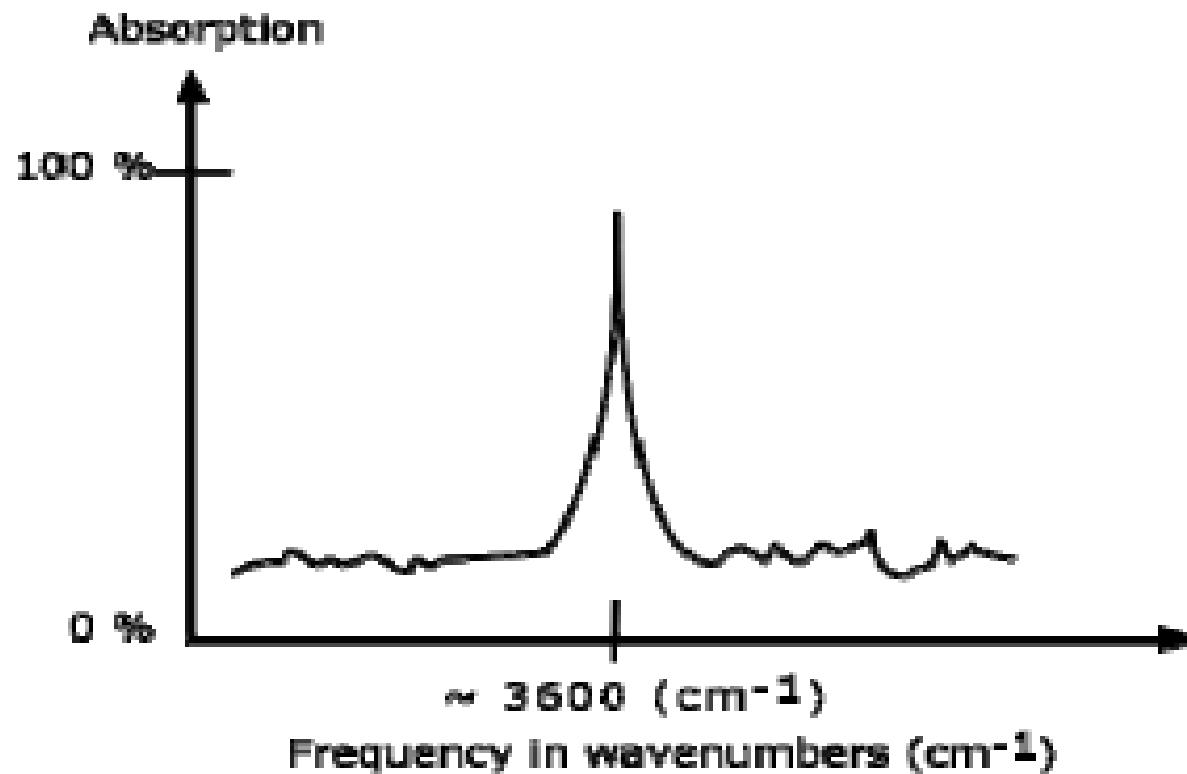
4. The Detector:- The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. The Computer:- The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation

Working:

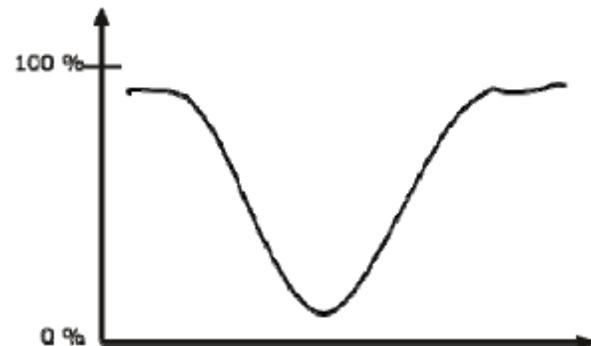
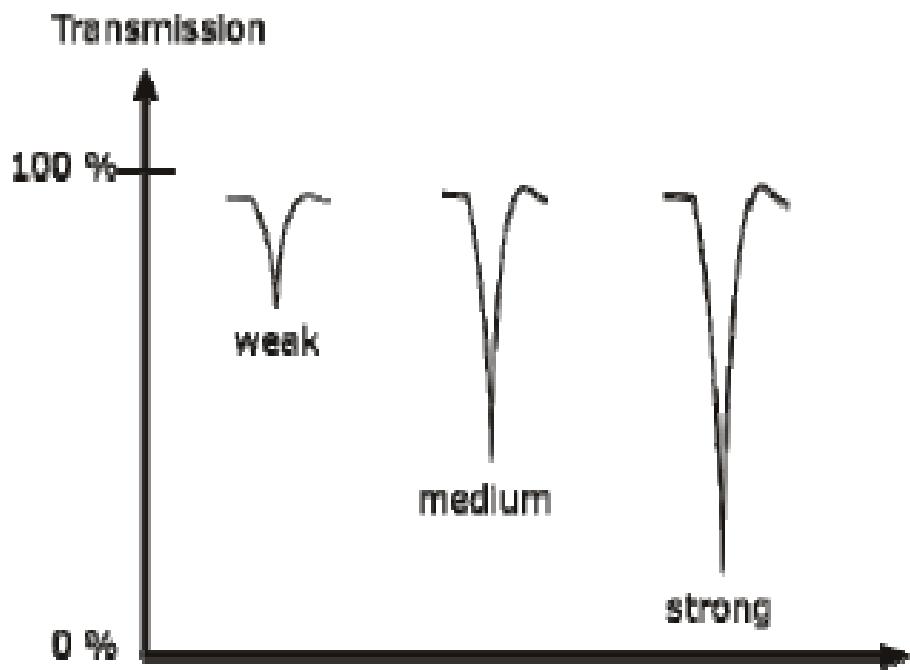
The infrared source emits a broad band of different wavelength of infrared radiation. The IR source used is a SiC ceramic at a temperature of 1550 K. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse Fourier transform on entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally, the intensity of the IR beam is detected by a detector, which is a liquid nitrogen cooled MCT (Mercury–Cadmium–Telluride) detector. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

AN IR SPECTRUM IN ABSORPTION MODE



The graph above shows a spectrum in absorption mode.

CLASSIFICATION OF IR BANDS

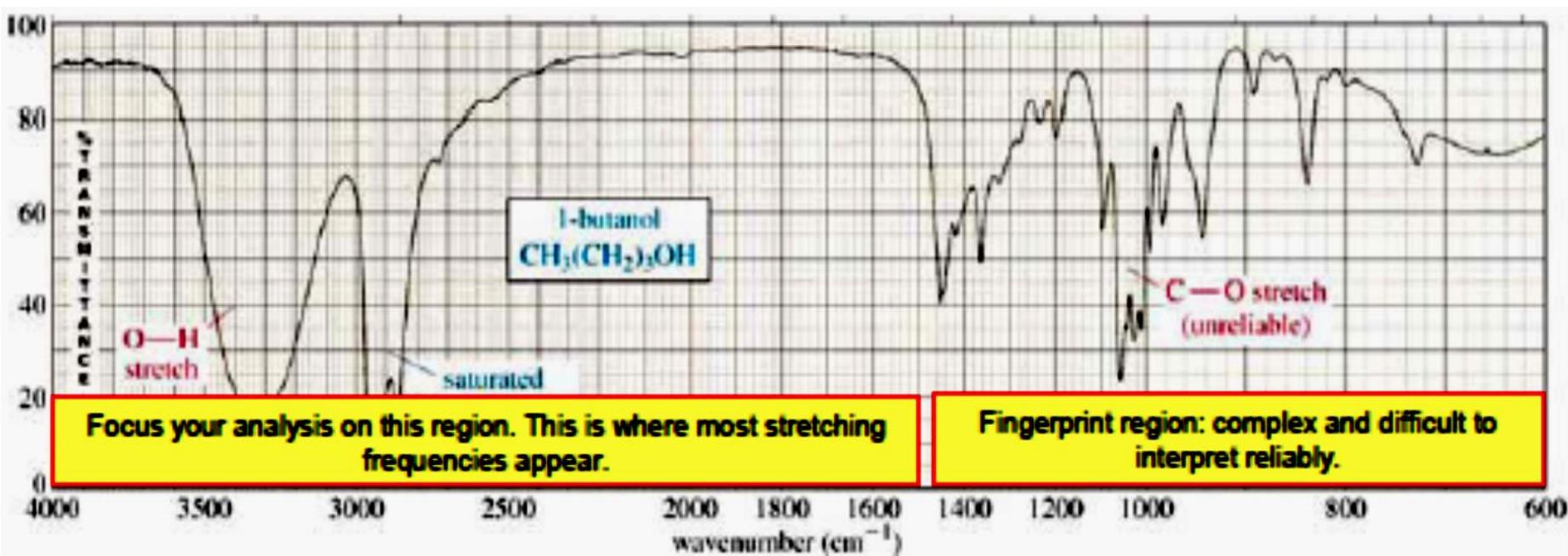


INFORMATION OBTAINED FROM IR SPECTRA

- 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.

FINGERPRINT REGION

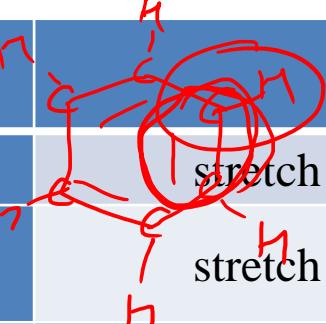
- Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the $600 - 1400 \text{ cm}^{-1}$ range is called the fingerprint region.
- This is normally a complex area showing many bands, frequently overlapping each other.



Functional Groups AND IR Frequencies

Characteristic IR Absorption Frequencies of Organic Functional Groups			
Functional Group	Type of Vibration	Characteristic Absorptions (cm ⁻¹)	Intensity
Alcohol			
O-H	(stretch, H-bonded)	3200-3600	strong, broad
O-H	(stretch, free)	3500-3700	strong, sharp
C-O	(stretch)	1050-1150	strong
Alkane			
C-H	stretch	2850-3000	strong
-C-H	bending	1350-1480	variable
Alkene			
=C-H	stretch	3010-3100	medium
=C-H	bending	675-1000	strong
C=C	stretch	1620-1680	variable

Alkyl Halide				
C-F	stretch	1000-1400	strong	
C-Cl	stretch	600-800	strong	
C-Br	stretch	500-600	strong	
C-I	stretch	500	strong	
Alkyne				
C-H	stretch	3300	strong,sharp	
	stretch	2100-2260	variable, not present in symmetrical alkynes	
Amine				
N-H	stretch	3300-3500	medium (primary amines have two bands; secondary have one band, often very weak)	
C-N	stretch	1080-1360	medium-weak	
N-H	bending	1600	medium	

Aromatic		stretch	3000-3100	medium
C=C		stretch	1400-1600	medium-weak, multiple bands

Analysis of C-H out-of-plane bending can often distinguish substitution patterns

Carbonyl	<u>Detailed Information on Carbonyl IR</u>			
C=O	stretch	- 1670-1820	strong	
(conjugation moves absorptions to lower wave numbers)				
Ether				
C-O	stretch	• 1000-1300 (1070-1150)	strong	
Nitrile				
CN	stretch	2210-2260	medium	
Nitro				
N-O	stretch	1515-1560 & 1345-1385	strong, two bands	

How to Analyse the IR spectrum?

- When analysing the IR spectrum of an unknown molecule, first efforts on determining the presence or absence of a few major functional groups.
- The C=O, O-H, N-H, C-O, C=C, -CN, and NO₂ peaks.
- These peaks are most likely to give immediate structural information if they are present.
- Do not try to make a detailed analysis of the C-H absorption near 3000 cm⁻¹, almost all the compounds have these absorptions.

Follow these steps

- 1) If **carbonyl group is present** ? The $-C=O$ group give rise to a strong absorption in the region $1820-1660\text{cm}^{-1}$. The peak is often strongest in the spectrum and of medium width.
- 2) If **C=O is present**, then check the following types

Acids	Is O-H also present? Broad absorption near $3400-2400\text{cm}^{-1}$ usually overlaps with C-H
Amides	Is N-H also present? Medium absorption near 3400cm^{-1} , sometimes double peaks with same size.
Esters	Is C-O present? Strong intensity absorption near $1300-1000\text{cm}^{-1}$
Anhydrides	Two C=O absorption near 1810 and 1760cm^{-1}
Aldehydes	Is aldehyde C-H present? Two weak absorption near 2850 and 2750cm^{-1}
Ketones	The preceding five choices have been eliminated

3) If C=O absent, then check the following options

Alcohols, Phenols	Check for O-H, broad absorption near $3400\text{-}3300\text{cm}^{-1}$, confirm this by finding C-O near $1300\text{-}1000\text{cm}^{-1}$
Amines	Check for N-H, Medium absorptions near 3400cm^{-1}
Ethers	Check for C-O near $1300\text{-}1000\text{cm}^{-1}$ and absence of O-H near 3400cm^{-1}

4) Double bonds and/or aromatic rings

1. C=C is weak absorption near 1650cm^{-1}
2. Medium strong absorption in the region $1600\text{-}1450\text{cm}^{-1}$, these often imply on aromatic ring
3. Confirm the double bond or aromatic ring by consulting the C-H region; aromatic and vinyl C-H occurs to left of 3000cm^{-1} , aliphatic C-H occurs to right of this value.

4) Triple bonds

- 1) C=N is medium sharp absorption near 2250cm^{-1}
- 2) C=C is e weak, sharp absorption near 2150cm^{-1}
- 3) Check also for acetylenic C-H near 3300cm^{-1}

5) Nitro groups

Two strong absorption at 1600 - 1530cm^{-1} and 1390 - 1300cm^{-1}

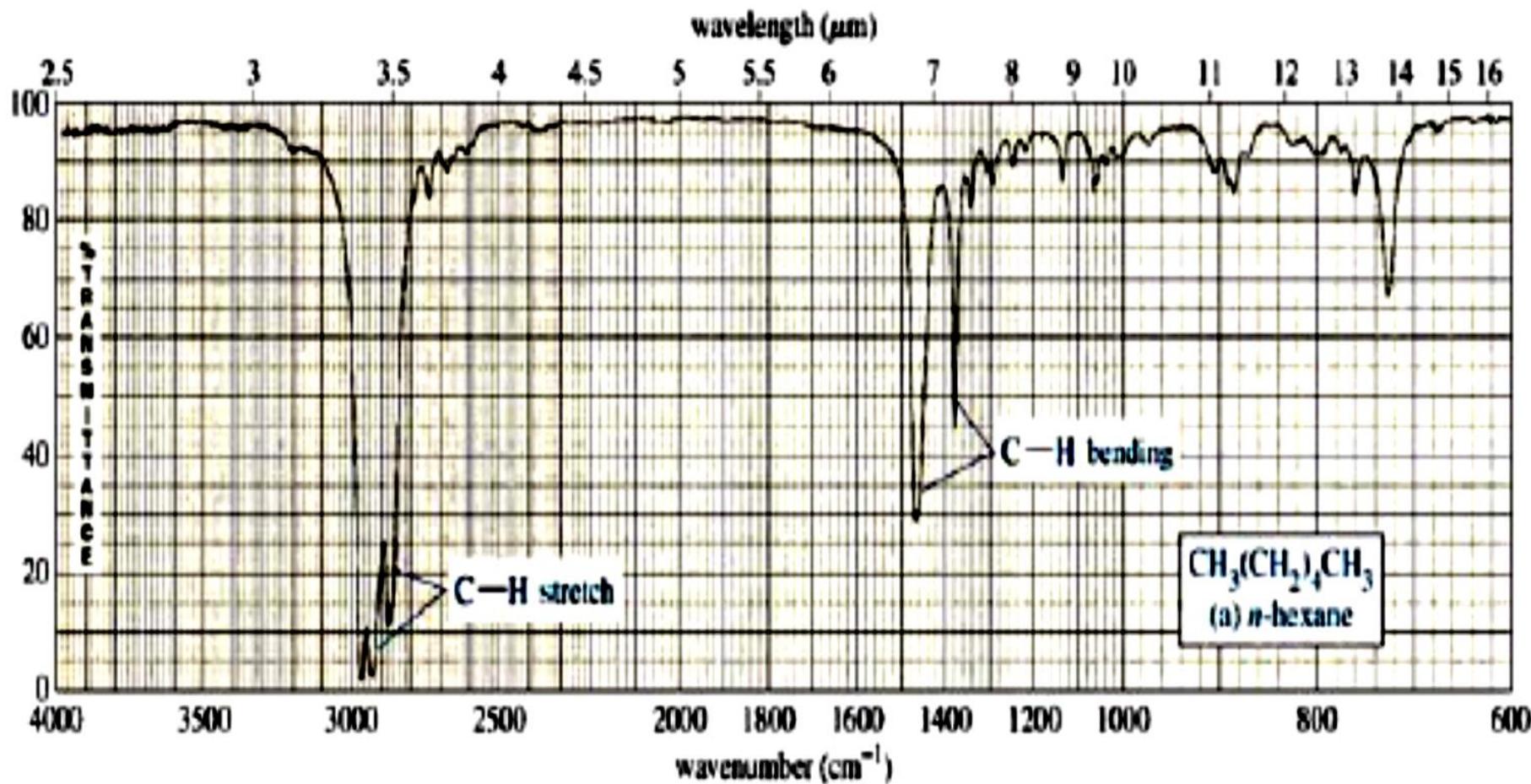
6) Hydrocarbons

None of the preceding found.

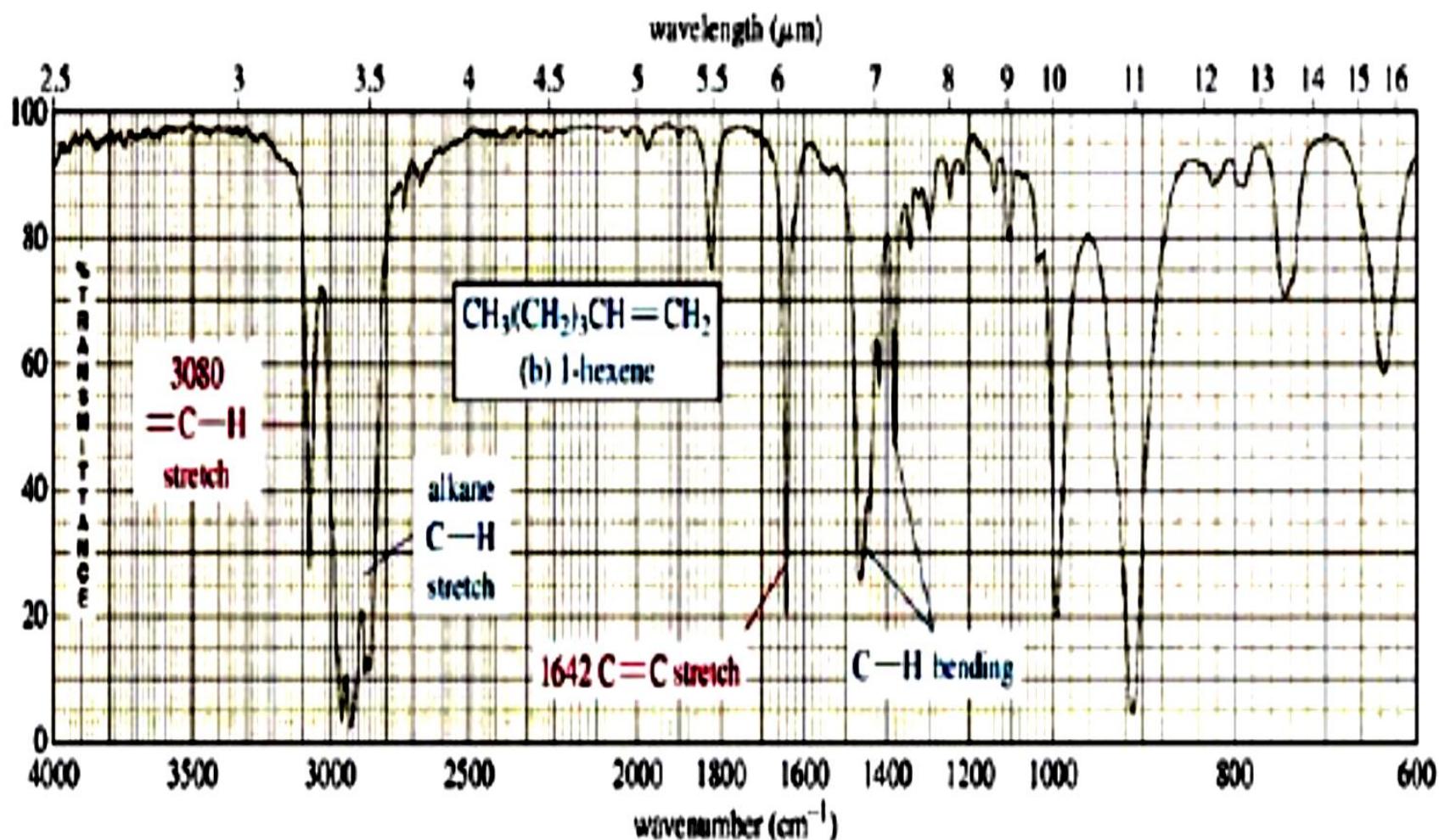
Major absorptions are in C-H region near 3000 cm^{-1}

Very simple structure the only another absorption appear near 1460 and 1375 cm^{-1}

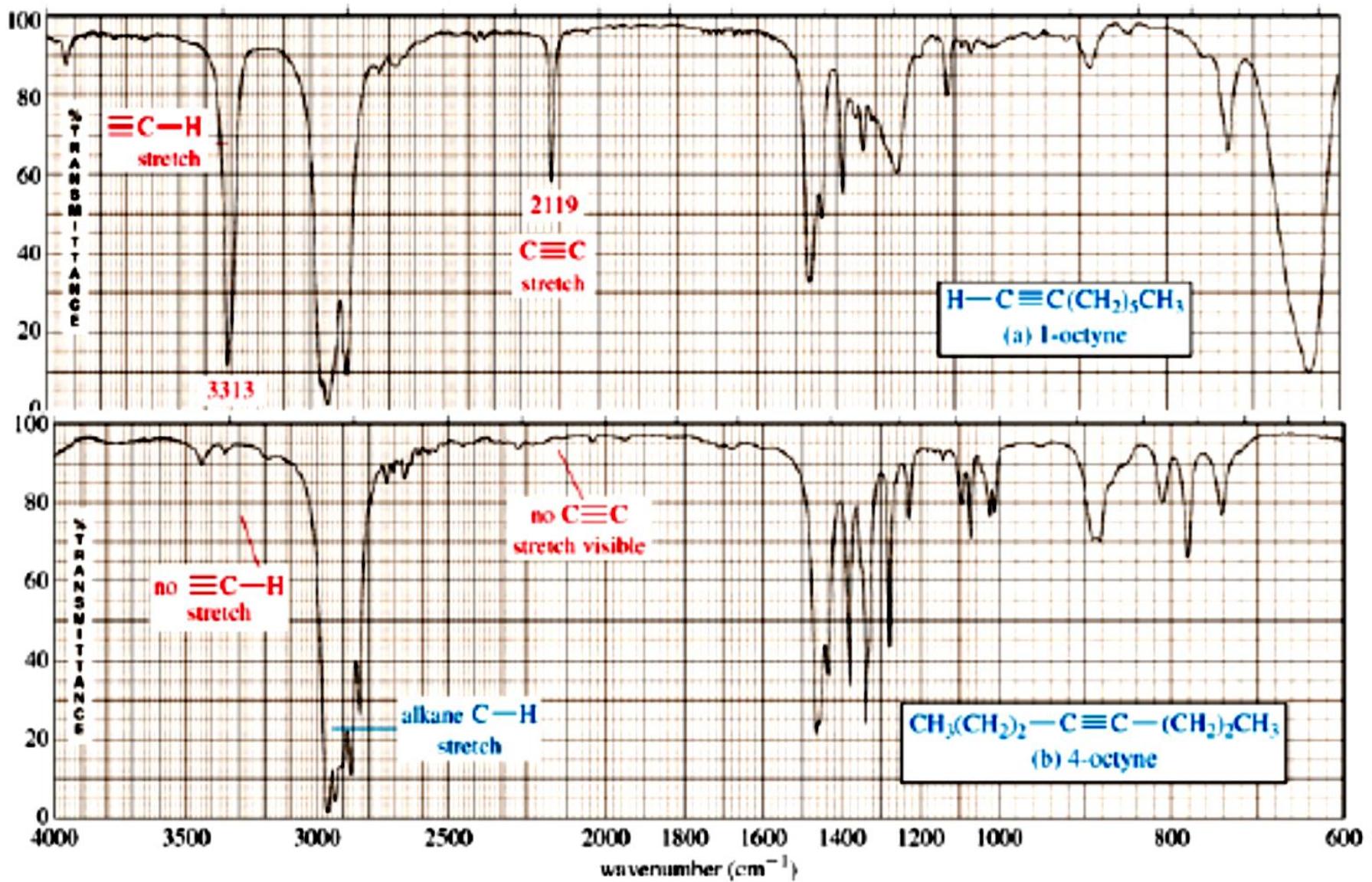
IR spectrum of n-Hexane



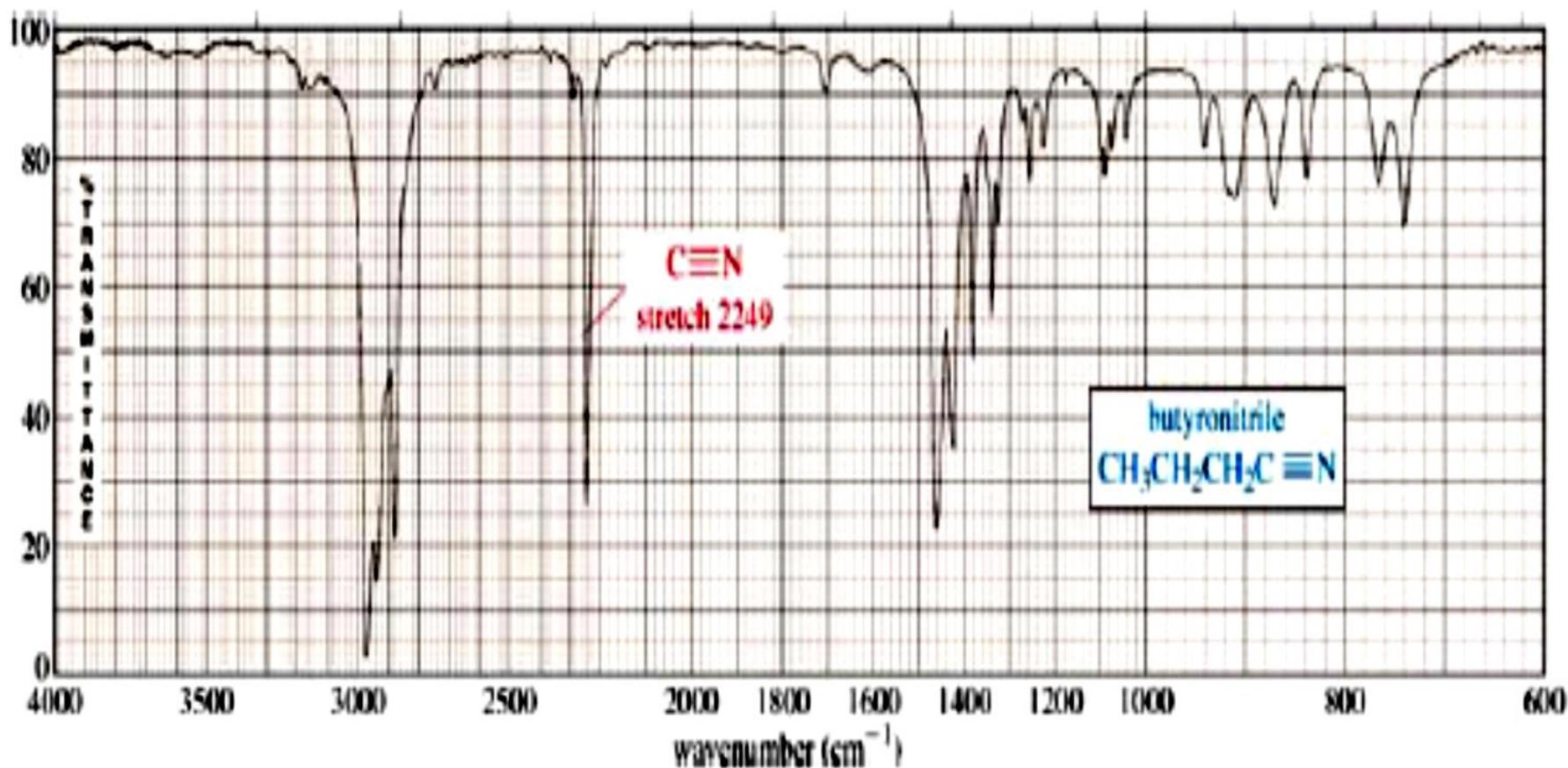
IR spectrum of 1-Hexene



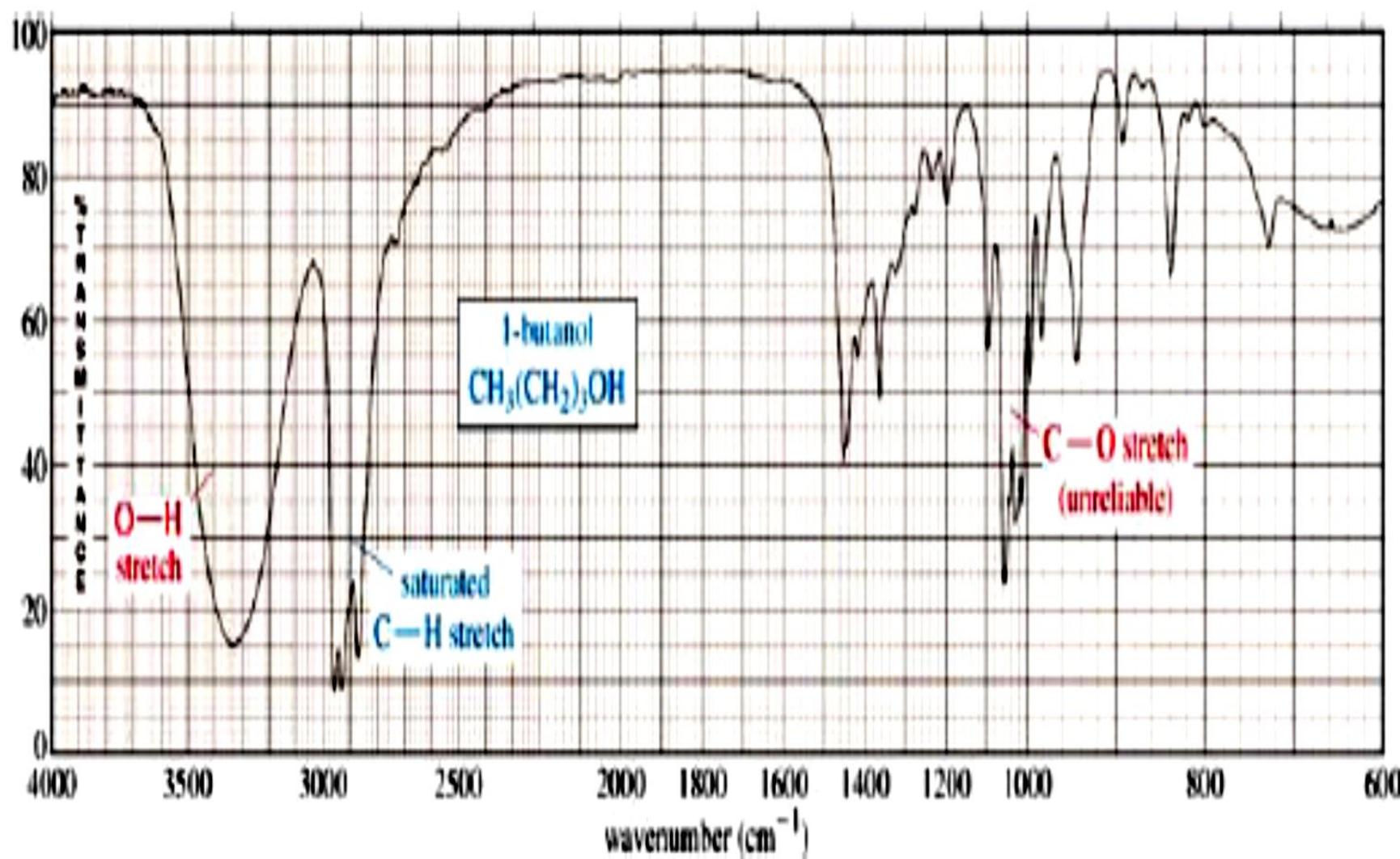
IR spectrum of 1-Octyne and 4-Octyne



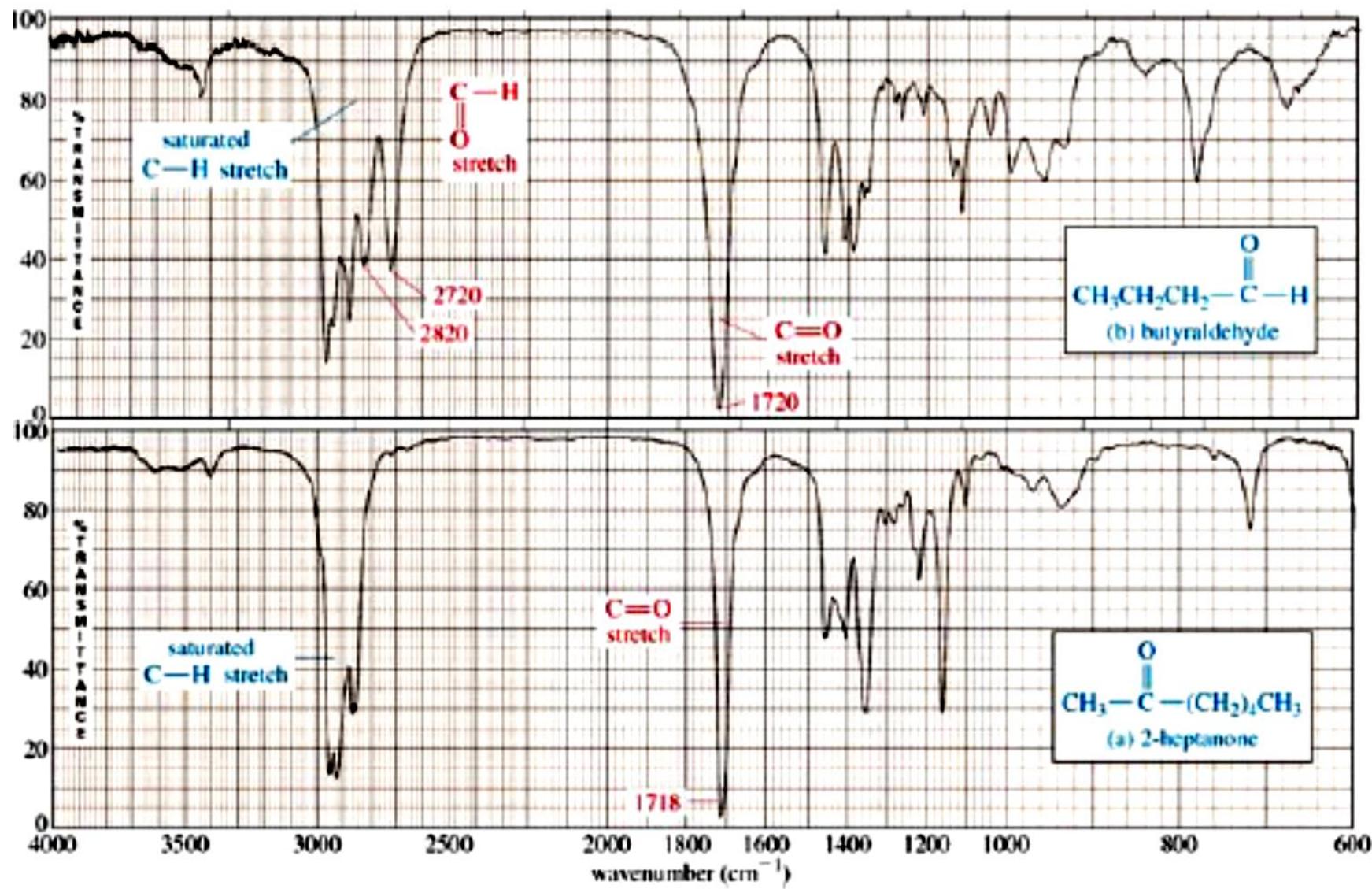
IR spectrum of Butyronitrile



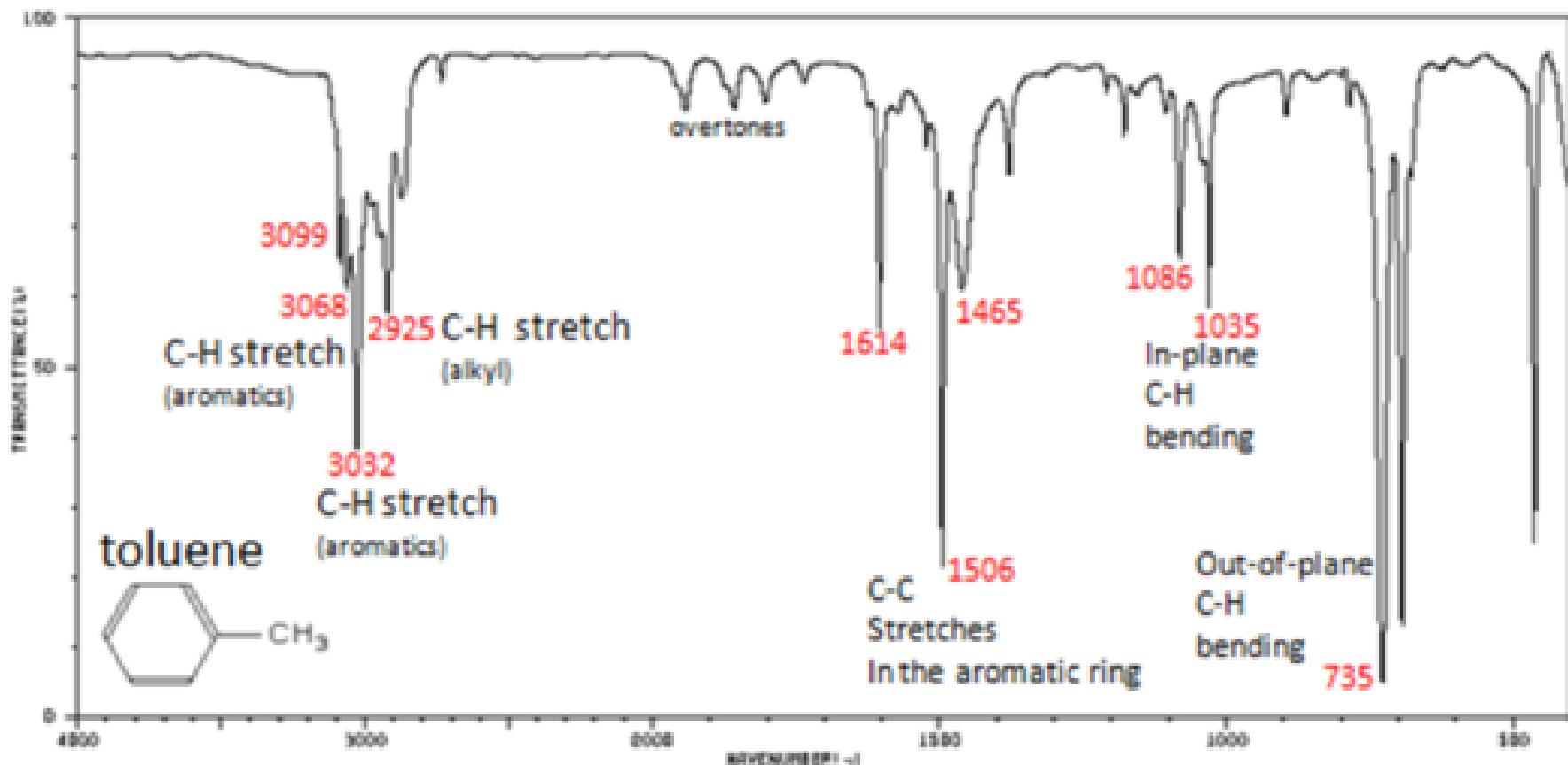
IR spectrum of 1-Butanol



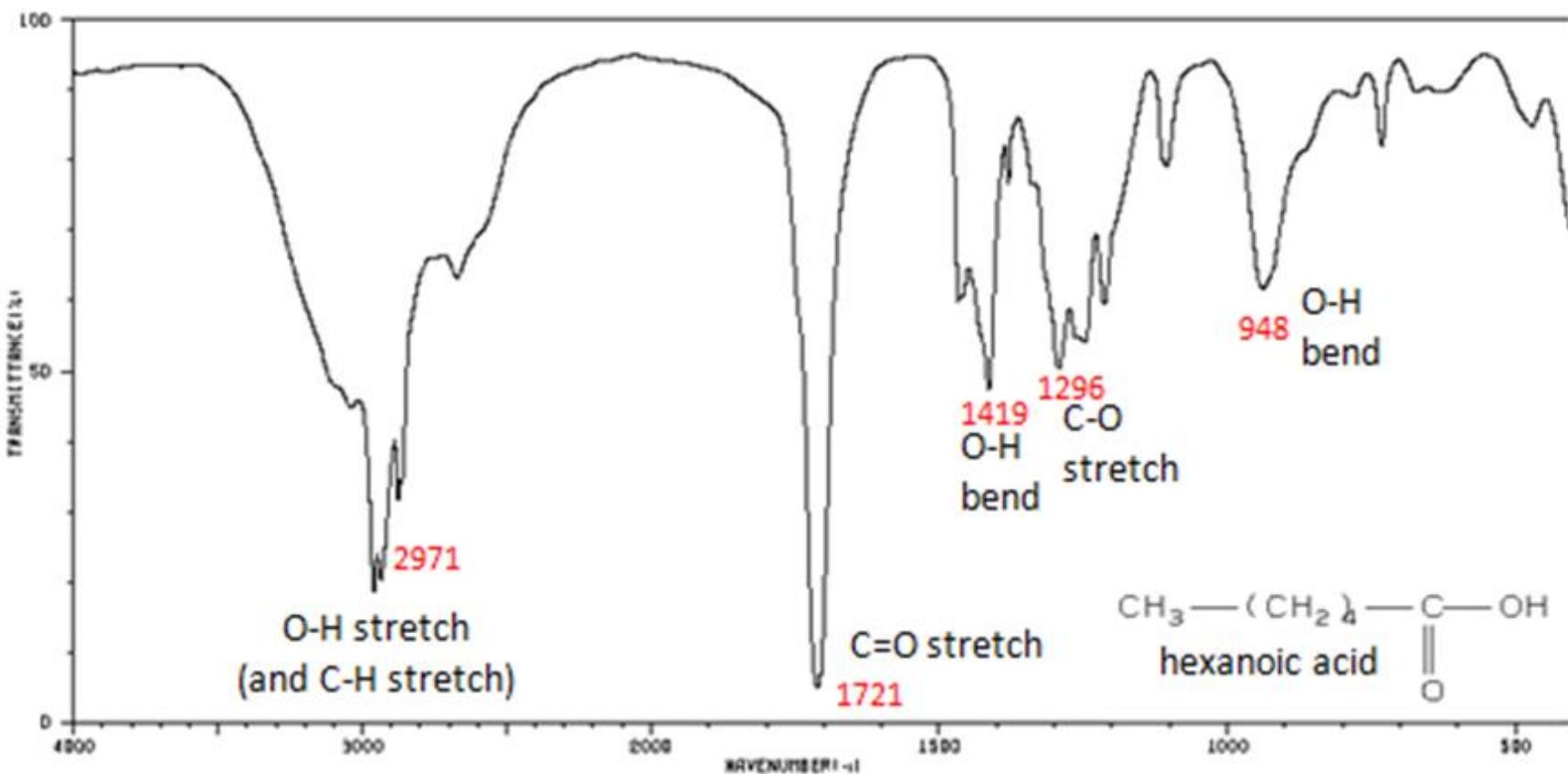
IR spectrum of 1-Butanal and 2-Heptanone



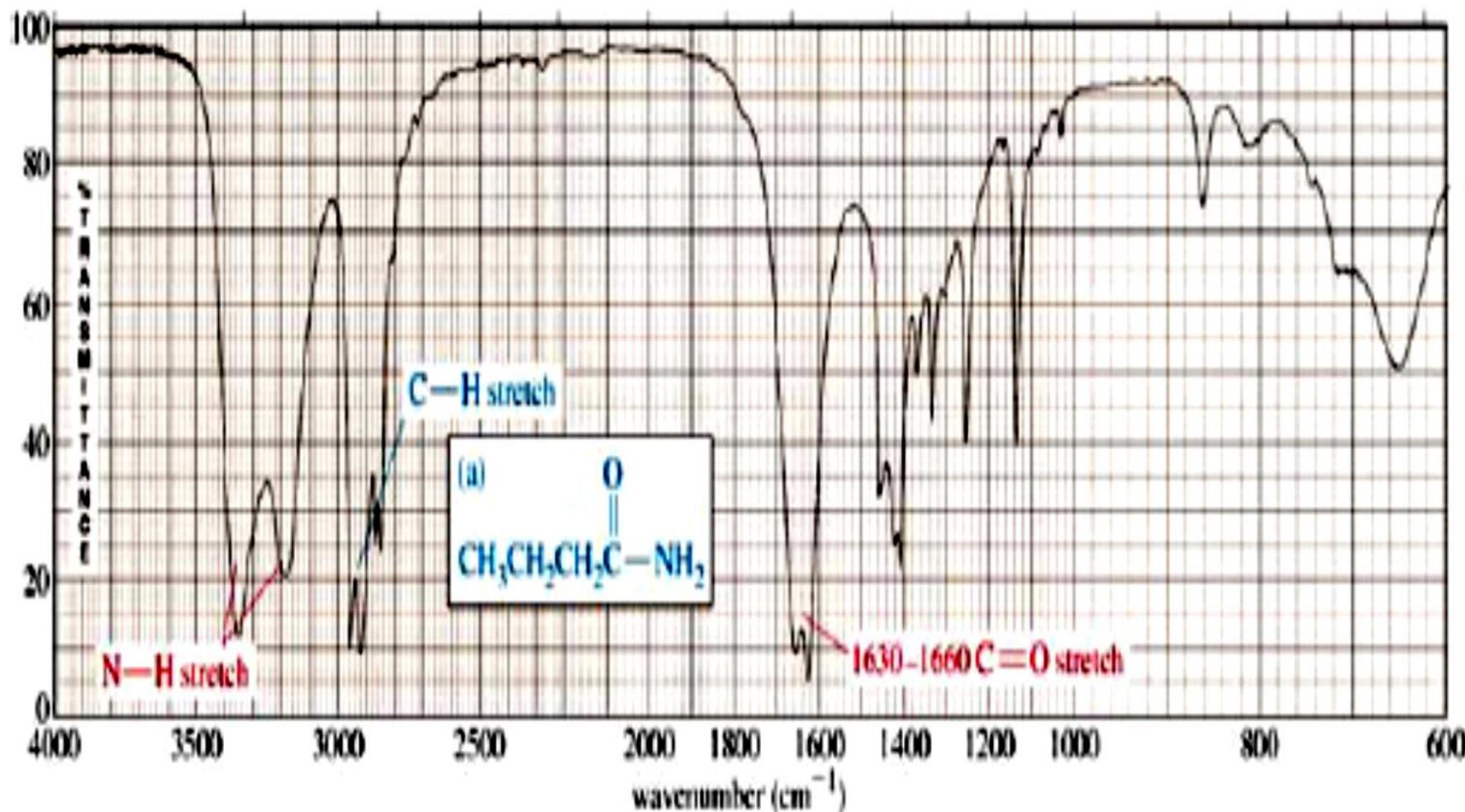
IR spectrum of Toluene



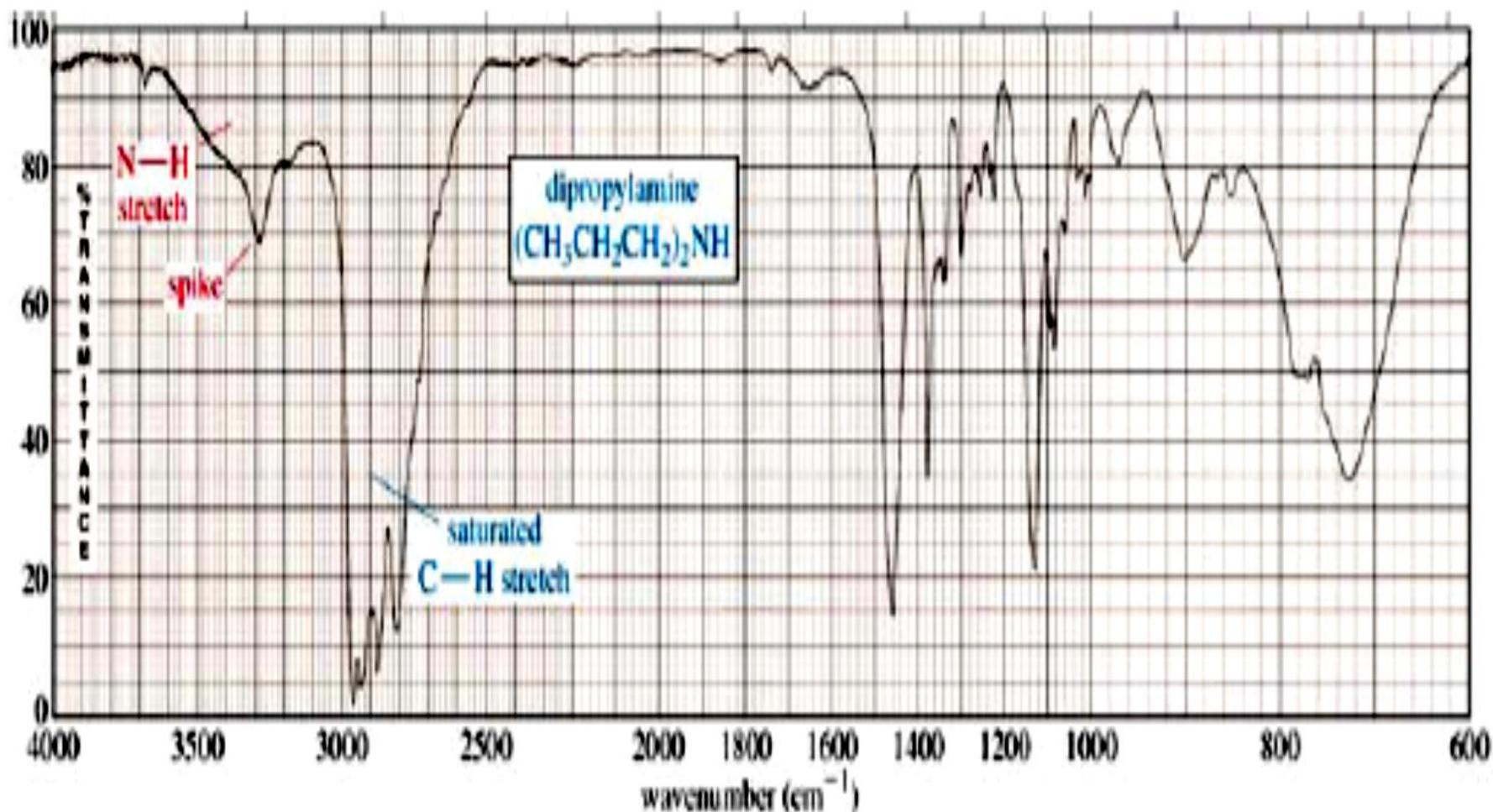
IR spectrum of hexanoic acid



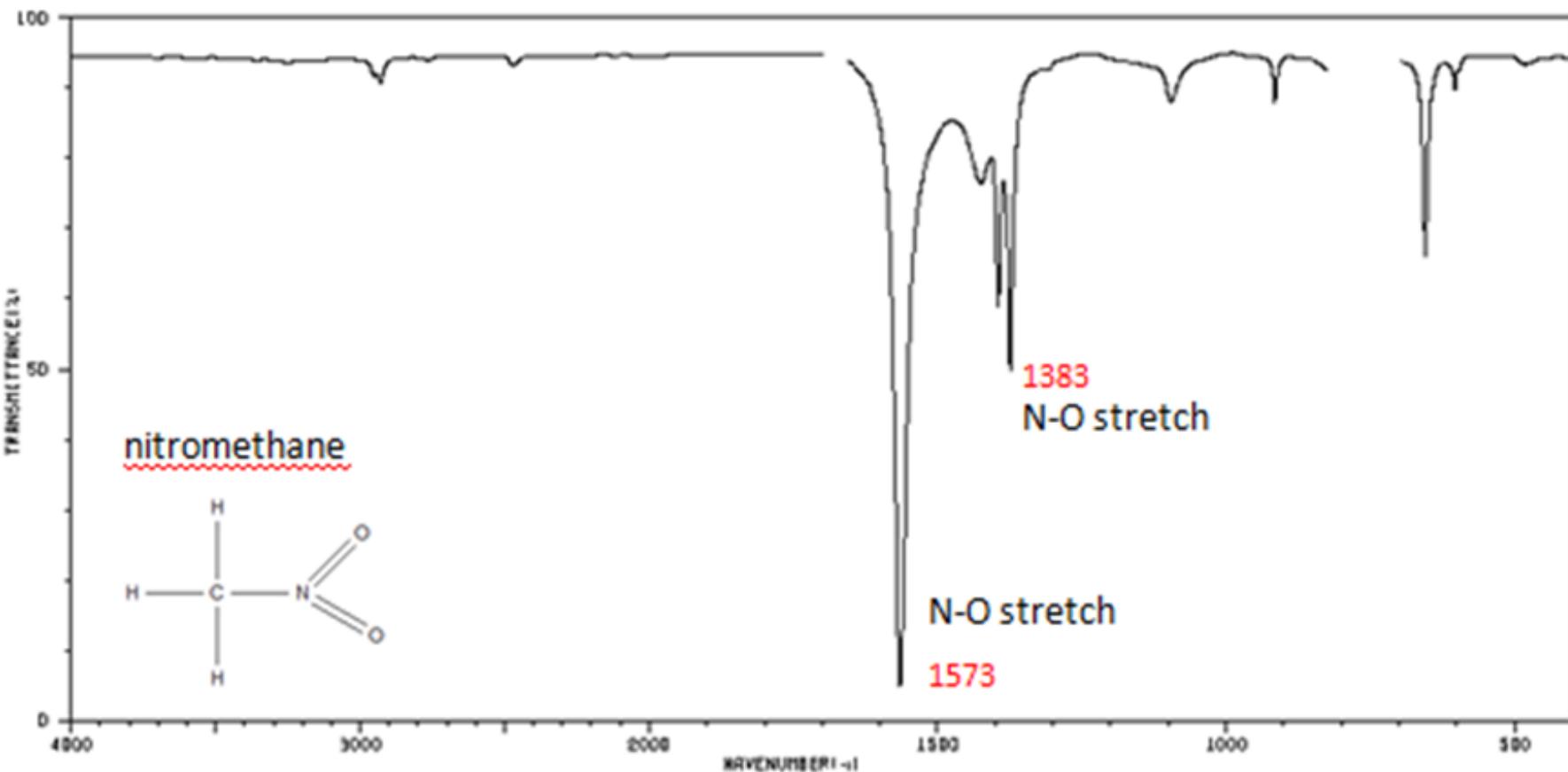
IR spectrum of 1-Butanamide



IR spectrum of dipropylamine



IR spectrum of Nitromethane



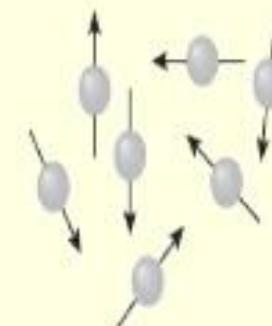
^1H NMR spectroscopy

Effect of Magnetic field...

A spinning proton creates a magnetic field.

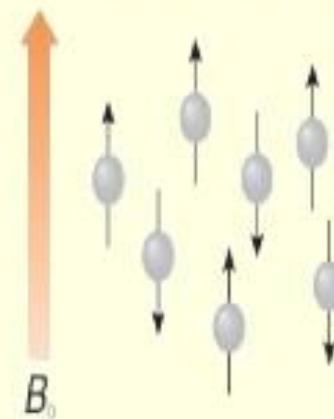


With no external magnetic field...



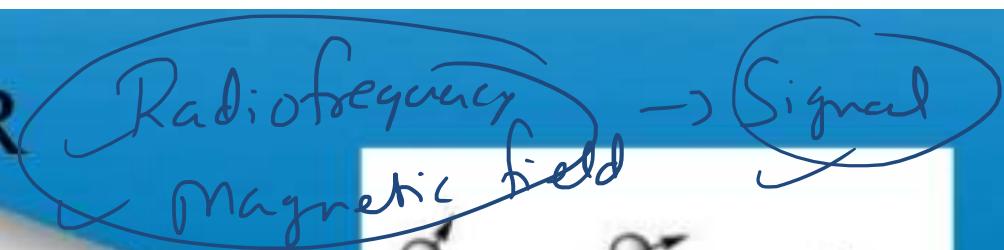
The nuclear magnets are randomly oriented.

In a magnetic field...



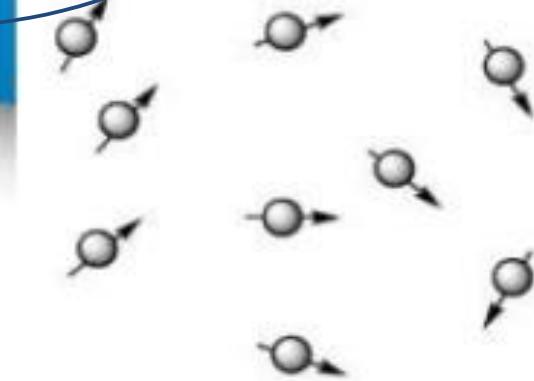
The nuclear magnets are oriented with or against B_0 .

Principles of NMR

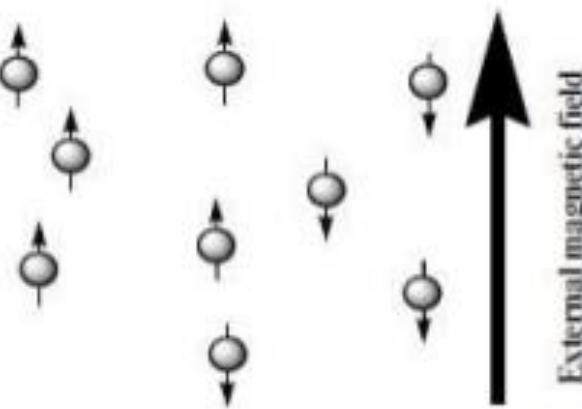


The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in directions.

But when an external magnetic field(B_0), is present the nuclei align themselves either with or against the field of the external magnet.



No external magnetic field



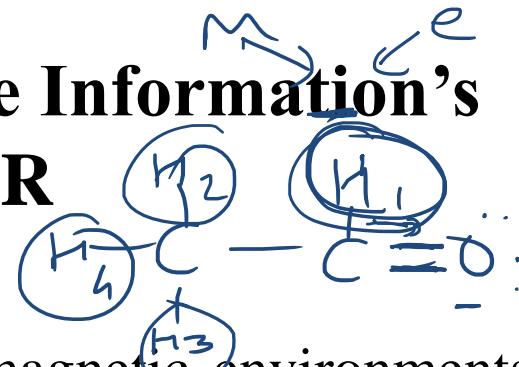
With external magnetic field

Interpreting ^1H NMR Spectra or The Information's obtained from ^1H –NMR

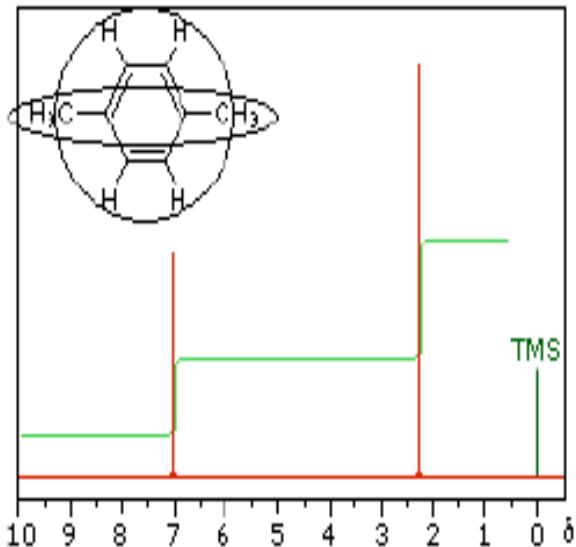
1) Number of signals:

Protons within a compound experience different magnetic environments, which give a separate signal in the NMR spectrum. Hydrogen atom in different environment respond differently in NMR field. The proton can be classified into,

- **Equivalent proton :** Equivalent Protons that reside in the same magnetic environment are termed chemically equivalent protons. For example, in methane CH_4 there are four proton but chemically all four proton will have same chemical environment. Therefore in NMR, CH_4 will give single peak.
- **Non equivalent proton :** They have different chemical environment. For e.g. acetaldehyde, CH_3CHO there are four hydrogen atom but chemically there are two different type of protons. First three shielded proton of CH_3 and second de-shielded proton connected to Carbon atom of Carbonyl group. Hence in NMR, CH_3CHO will give two peaks.

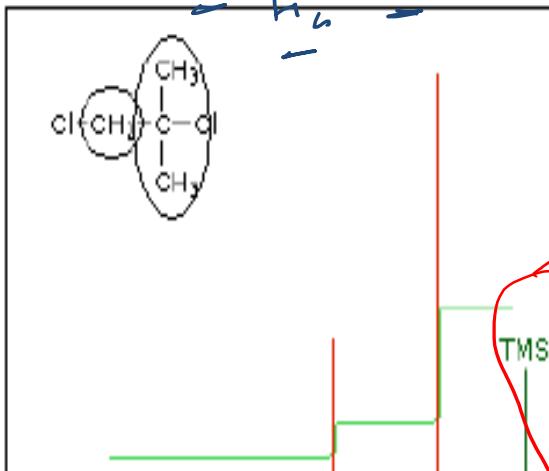


equivalent protons



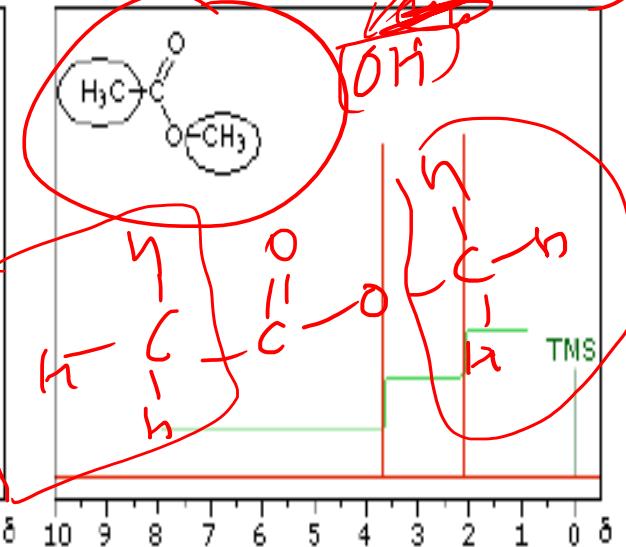
(A)

4 H's are on a plane of symmetry with each other. CH_3 are also on a plane of symmetry so 2 signals



(B)

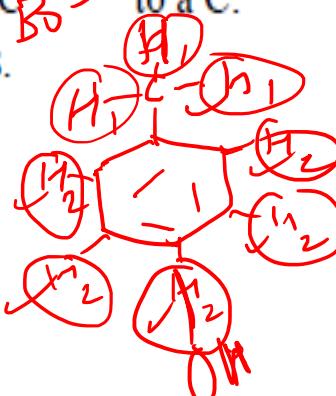
The CH_2 H's are attached to a C that's attached to a Cl. The CH_3 H's are attached to the same C and have the same neighbors.



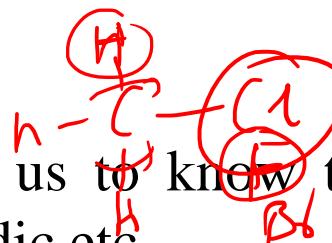
(C)

One CH_3 is attached to an O, while the other CH_3 is attached to a C.

Non equivalent

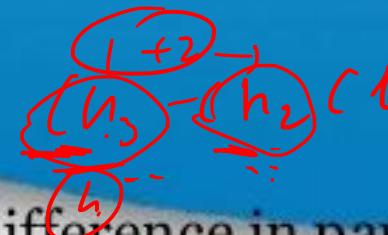


2) Position of signals (chemical shift):



- The position of proton in the spectrum helps us to know the type of proton viz. aromatic, aliphatic, alicyclic, aldehydic etc.
- The horizontal frequency scale at which the equivalent proton signals occur (δE) is called a chemical shift (measured in δ ppm). The chemical shift depends only on the varying local magnetic fields from the neighboring protons.
- The chemical shift parameter δ is defined $\delta = (H_s - H_{tms})/H_o \times 10^6$ ppm [where H_o , H_s and H_{tms} are field strengths corresponding to resonance for a particular nucleus in the sample (H_s) and TMS (H_{tms}) and H_o operating frequency of NMR instrument]
- As spectra are usually calibrated in cycles per second (cps), the equation can be written as: $\delta = \Delta v \times 10^6 / \text{Oscillator frequency (cps)}$
- where Δv = Difference in absorption frequencies of the sample and the reference in cps; oscillator frequency is the characteristic of the instrument: For a 60 MHz instrument, the oscillator frequency is 60×10^6 cps. The factor 10^6 has been included for convenience.

Chemical shift



A **chemical shift** is defined as the difference in parts per million (ppm) between the resonance frequency of the observed proton and tetramethylsilane (TMS) hydrogens.

TMS is the most common reference compound in NMR, it is set at $\delta=0$ ppm

$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^6$$

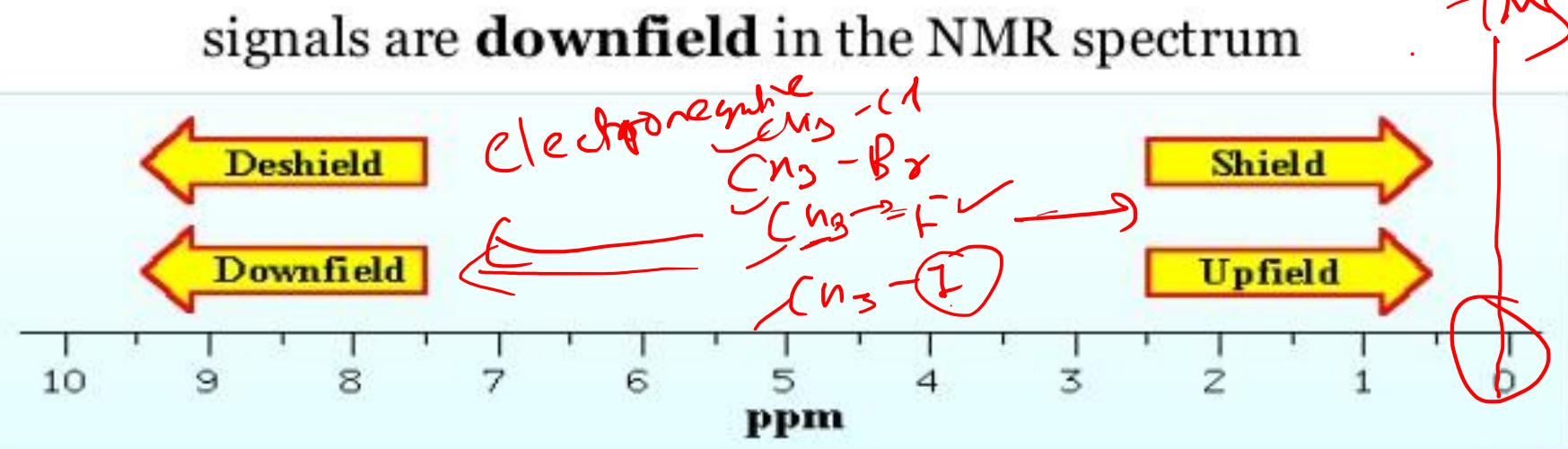
The term "frequency of signal" is circled in red. The term "TMS" is circled in red.

Shielding of protons:-

High electron density around a nucleus **shields** the nucleus from the external magnetic field and the signals are **upfield** in the NMR spectrum

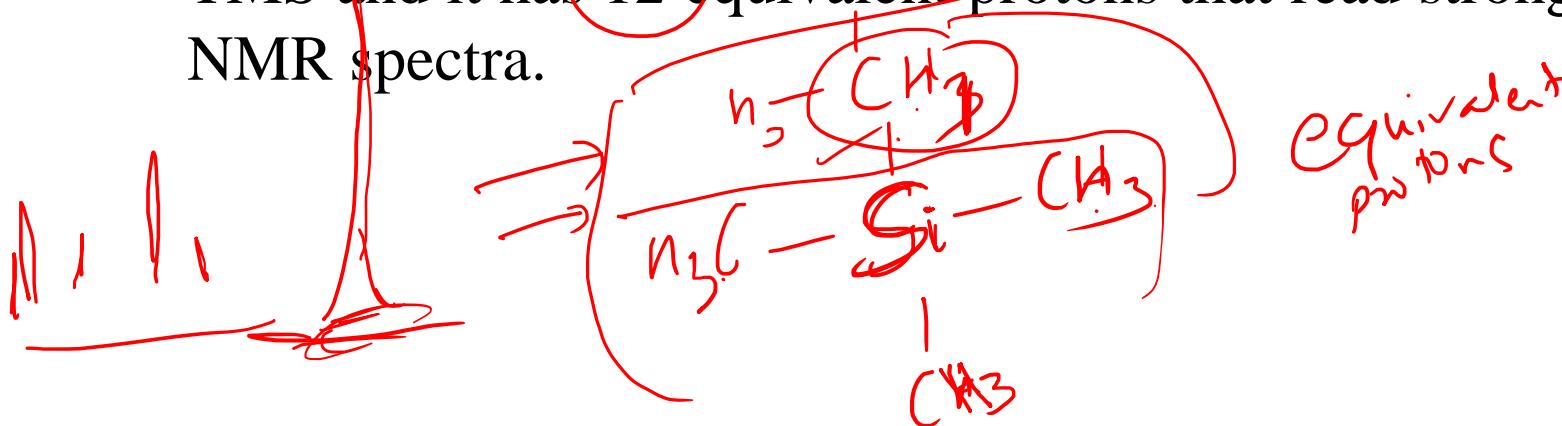
Deshielding of protons:-

Lower electron density around a nucleus **deshields** the nucleus from the external magnetic field and the signals are **downfield** in the NMR spectrum



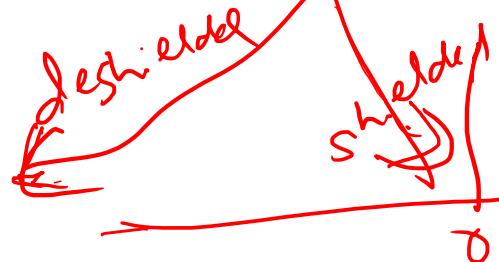
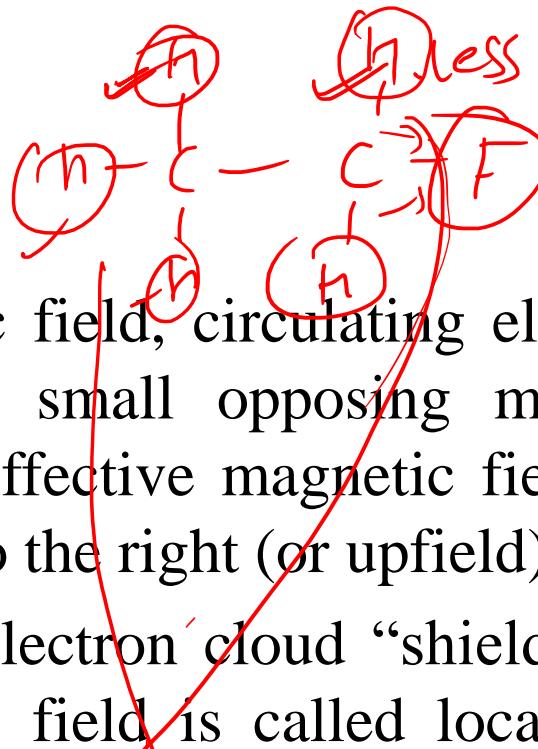
3) Reference compound: Tetramethylsilane (TMS)

- In order to standardize the NMR spectra, the chemical shifts are positioned in relation to a reference proton set at 0.00 ppm.
- Tetramethylsilane, $(\text{CH}_3)_4\text{Si}$, is the standard for ^1H NMR.
- TMS is practically used as a reference compound because of its inert quality that prevents it from reacting with the sample and its highly volatile nature that makes it easy to evaporate out of samples.
- Very few compounds have a lower frequency reading than TMS and it has 12 equivalent protons that read strongly on the NMR spectra.



4) Shielding effects:

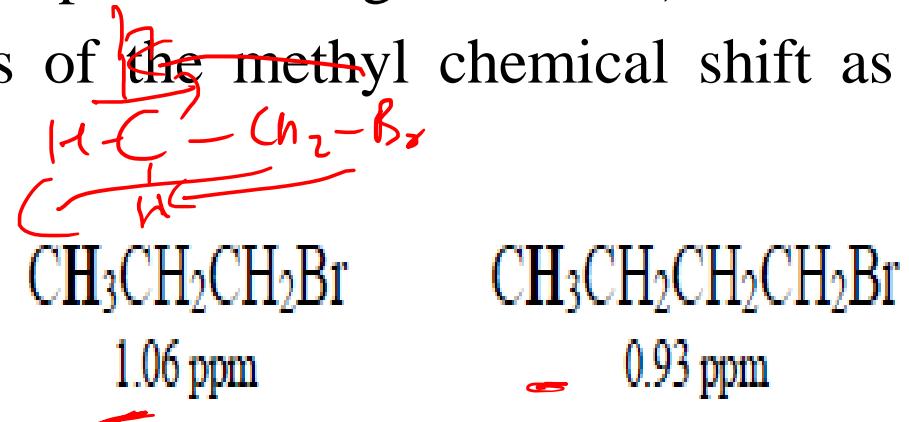
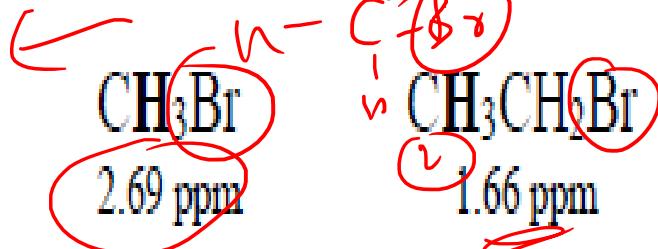
- Under an applied magnetic field, circulating electrons in the electron cloud produce a small opposing magnetic field, ultimately decreasing the effective magnetic field felt by the proton, shifting the signal to the right (or upfield).
- This effect, in which the electron cloud “shields” the proton from the applied magnetic field is called local diamagnetic shielding.



$$\delta =$$

5) Electronegativity and de-shielding:

- Hydrogen atoms that are attached to more electronegative atoms experience higher chemical shifts.
- Electronegative atoms also remove electrons from the electron cloud, which decreases their density and results in less shielding; hence electronegative atoms are said to deshield the proton and cause it to have a higher chemical shift, moving it to the left (or downfield).
- The magnitude of the de-shielding effect, however, rapidly decreases as the distance between the proton and electronegative atom increases (refer to NMR spectrum diagram above).
- Examples:** Literature values of the methyl chemical shift as it moves away from bromine.



① Equivalent from equivalent protons
② Splitting of signals

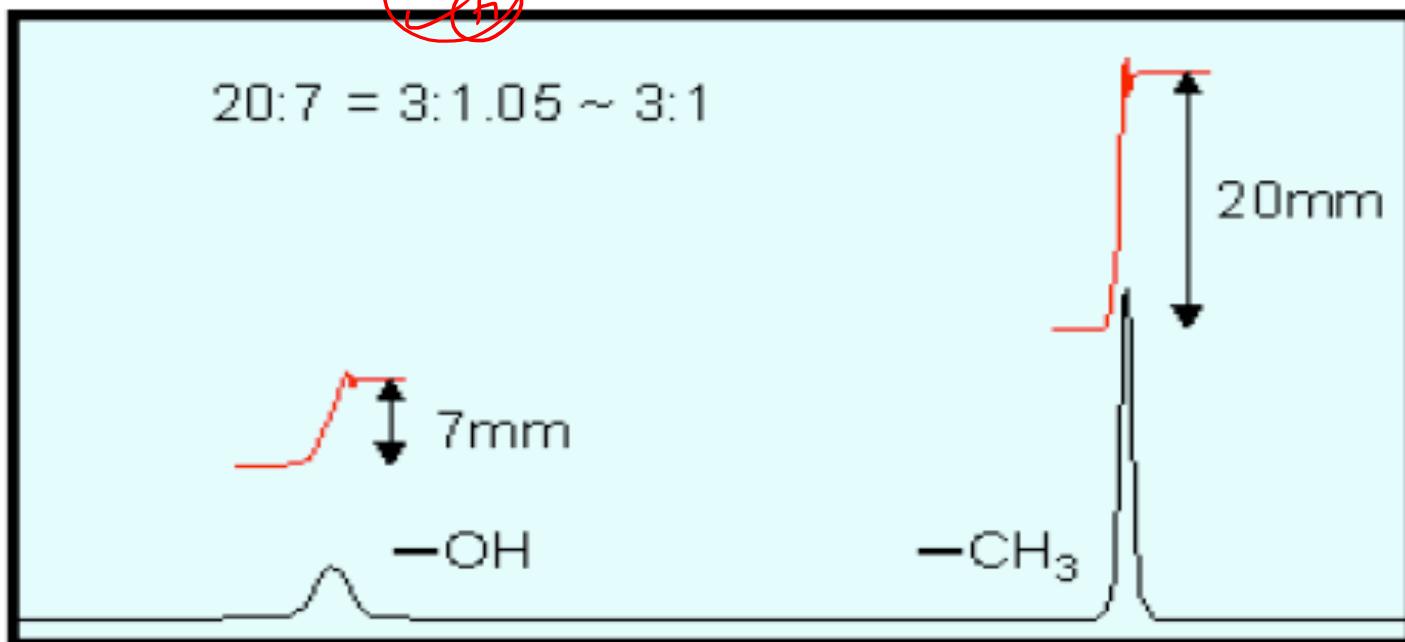
6) Relative Intensity of Signals (Integration):

- The area under the signals (integration) corresponds to the number of protons responsible for that signal.
- Therefore, the relative intensities of the signal are proportional to the relative number of proton equivalents.
- It is important to remember that integration only provides ratios of protons, not the absolute number.
- For convenience in calculating the relative signal strengths, the smallest integration is set to 1 and the other values are converted accordingly.

chemical shift
TMS (envelope)
Applications diagram



NMR
Signal
Strength

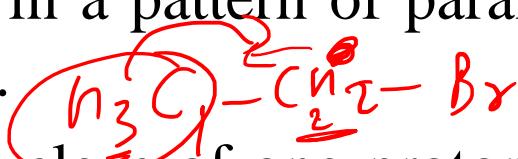


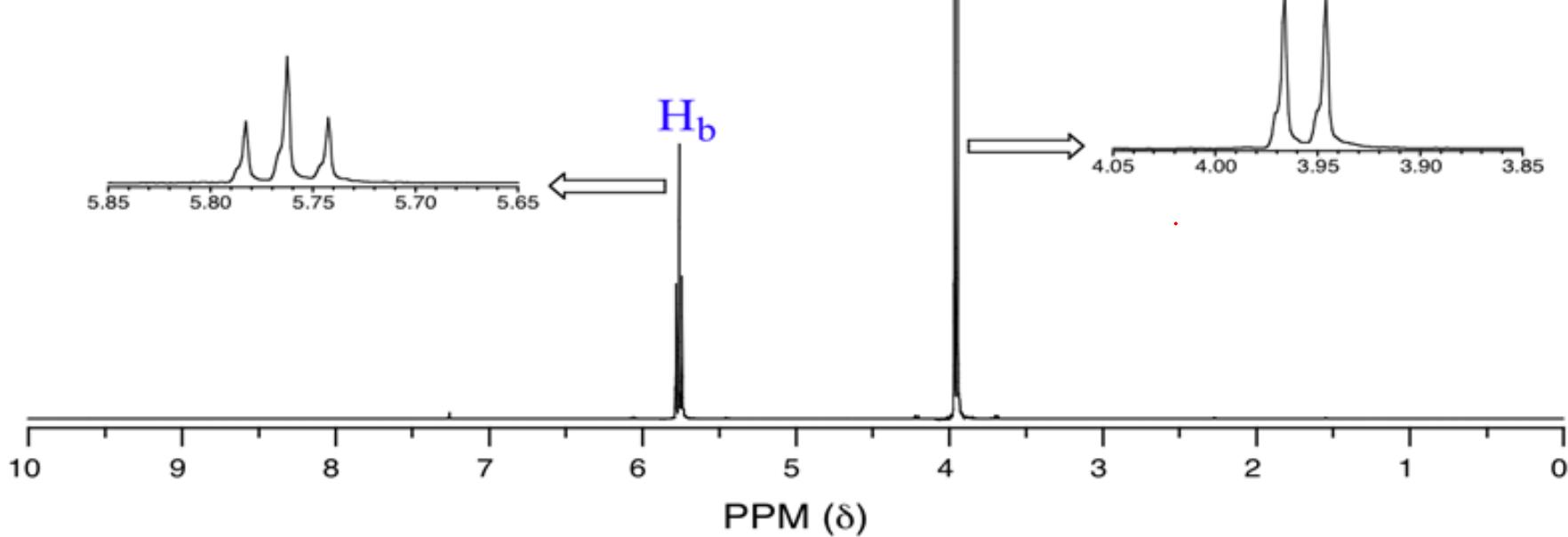
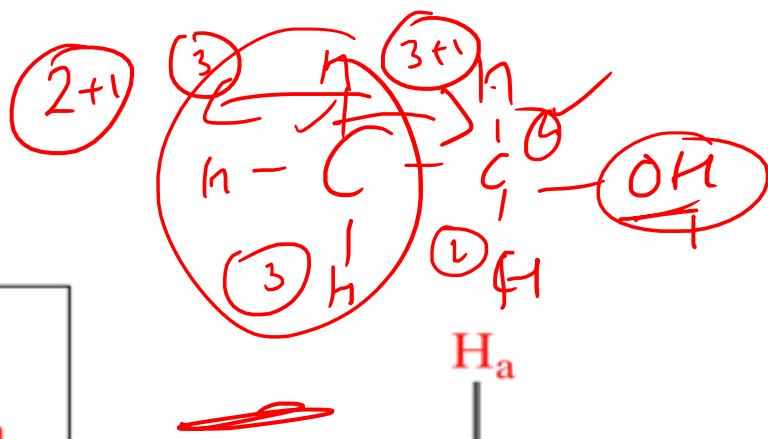
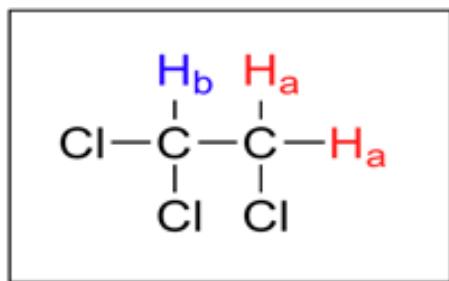
← ppm —

• Diagram 4¹²

*Integrals appear as lines on the spectra above the signals, in which their heights correspond to the integration ratios. In this spectra, the -OH H is correctly determined to be in a 3:1 ratio with the 3 CH₃ H's

7) Splitting of signals (Spin-Spin coupling):

- NMR signals are not usually single triangles, but a complex pattern of split triangles labelled as doublets (2 peaks), triplets (3 peaks), quartets (4 peaks), etc. 
- The distance between the split peaks are called coupling constants, denoted by J. 
- The interaction between nearby protons produce different spin flip energies (E) as they can orient themselves in a pattern of parallel or antiparallel to the applied magnetic force. 
- This phenomenon, where the spin of the nucleus of one proton is close enough to affect the spin of another, is called spin-spin coupling.
- Splitting is always reciprocated between the protons if H_a splits H_b , then H_b must split H_a and provides information on the neighbours of a proton within the molecule.



Hand-drawn integration curve:

- A red line starts at zero, rises to a peak at $\delta \approx 5.75$ ppm, stays flat until $\delta \approx 4.0$ ppm, then rises sharply to a second peak at $\delta \approx 3.95$ ppm.
- Labels include H_b at the first peak, H_a at the baseline between peaks, and OH at the second peak.
- The word "TMS" is written near the baseline.

Factors affecting the chemical shift:

Actually the chemical shift parameter δ is a function of electron density around the nucleus as the electrons are directly involved in the diamagnetic shielding which acts to attenuate the applied magnetic field. Hence following factors are responsible for influencing its value:

- Specific solvent,
- Bulk diamagnetic susceptibility effect,
- Temperature (only when change in temperature causes changes in some type of association equilibrium or changes in amplitude of torsional vibrations),
- Electron density,
- Inductive effect,
- Van der Waal deshielding, and
- Hydrogen bonding.

Factors affecting chemical shift:-

- Electronegative groups
- Magnetic anisotropy of π -systems
- Hydrogen bonding

Electronegative groups:-

Electronegative groups attached to the C-H system decrease the electron density around the protons, and there is less shielding (*i.e.* deshielding) and chemical shift increases

Compound	Chemical shift
CH_3I	2.16
CH_3Br	2.65
CH_3Cl	3.10
CH_3F	4.26

Magnetic anisotropy of π -systems:-

- The word "anisotropic" means "non-uniform". So magnetic anisotropy means that there is a "non-uniform magnetic field".
- Electrons in π systems (e.g. aromatics, alkenes, alkynes, carbonyls etc.) interact with the applied field which induces a magnetic field that causes the anisotropy.
- It causes both shielding and deshielding of protons.
- Example:-Benzene

Hydrogen bonding:-

- Protons that are involved in hydrogen bonding are typically change the chemical shift values.
- The more hydrogen bonding, the more proton is deshielded and chemical shift value is higher.

Applications of N.M.R. Spectroscopy:

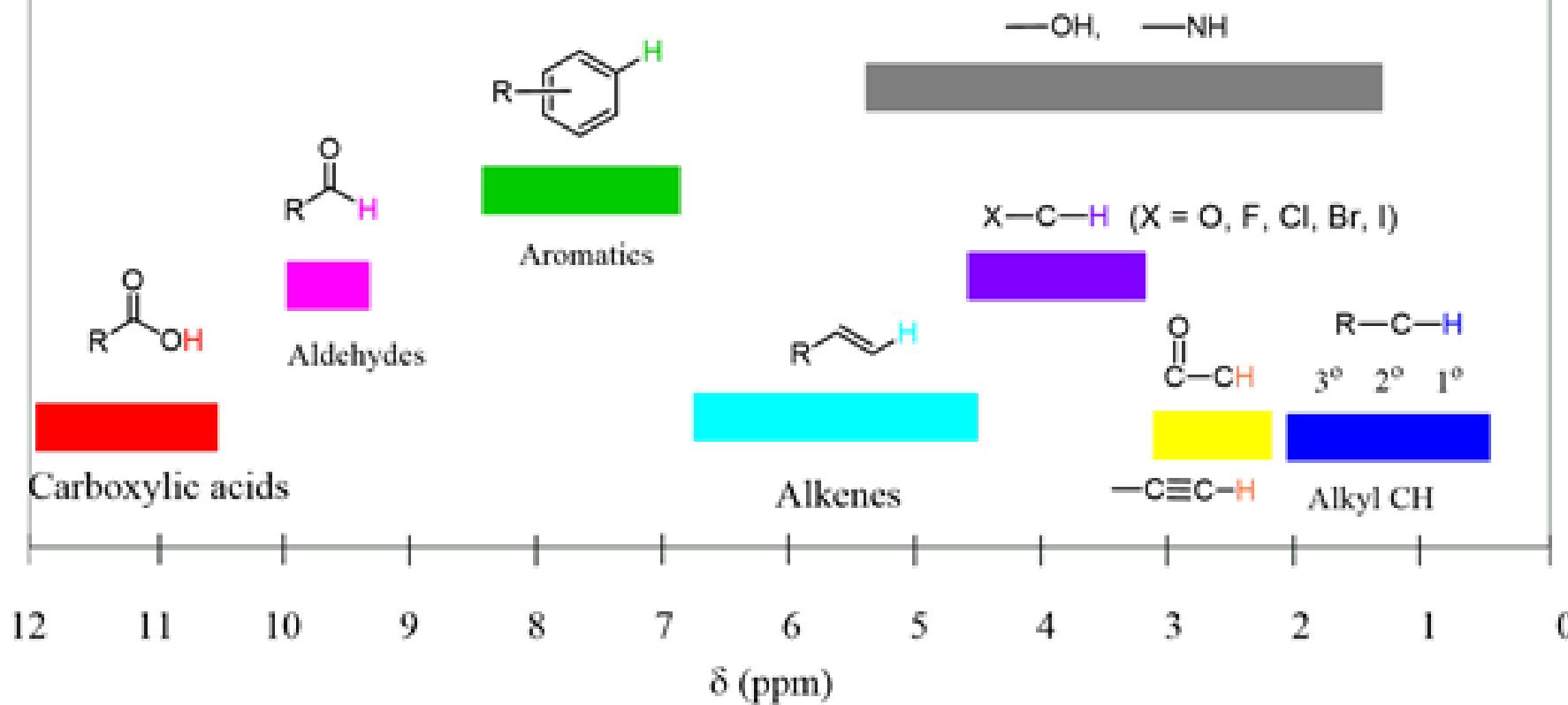
(1) Quantitative Analysis: The area of peak is directly proportional to the number of nuclei responsible for that peak. Thus the concentration of species can be determined directly by making use of signal area per proton. The signal area per proton can easily be calculated by use of a known concentration of an internal standard. Similarly, the concentration of new species formed during the reaction can also be calculated from the spectrum of parent compound.

(2) Qualitative Analysis: The qualitative analysis of the compound can easily be made by knowing:

- Chemical shift delta values of hydrogen containing groups,
- The presence of particular functional group,
- The relative position of these groups and
- The relative number of nuclei in these groups.

Downfield

Upfield



$\text{R} \equiv \text{H}$	1.7 - 2.7
$\text{R}-\text{N}-\text{C}-\text{H}$	2.2 - 2.9
$\text{R}-\text{S}-\text{C}-\text{H}$	2.0 - 3.0

$\text{R} = \text{H or alkyl}$	

NH and OH peaks are most often broad or may as well be missing completely unless the sample is very dry.

This is also true for any proton capable of making hydrogen bonding:

$\text{R}-\text{SH}$ 1.0 - 5.0

$\text{R} = \text{alkyl or aryl}$

$\text{R}-\text{NH}_2$ 1.0 - 5.0

1°, 2°

$\text{R}-\text{OH}$ 1.0 - 5.0

1°, 2°, 3°

4.0 - 7.0

5.0 - 9.0

1°, 2°

11 - 12

Downfield shifts more common

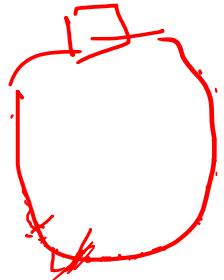
<https://www.youtube.com/watch?v=TJhVotrZt9I>

https://www.youtube.com/watch?v=x_uAtZIKIIA

Caustic embrittlement
NaOH

Hard water in the reactor

↳ steam generation



Deposits

Scale & sludge

lime + soda
 Na_2CO_3 + $\text{Ca}(\text{OH})_2$

200

soot line
T

100 l/h

Na_2CO_3 +

H_2O → NaOH

+ H_2O
 CO_2

precipitation

$2\text{NaOH} + \text{Fe} \rightarrow$
Steel reactor

$\text{Fe}(\text{OH})_2 + \text{H}_2\uparrow$

Corrosion
 $\text{MnO} + \text{O}_2 \rightarrow \text{MnO}_2$

$12\text{NaOH} \rightarrow 2\text{Fe}_3\text{O}_4$

Concentrated

NaOH

$2\text{Fe}_3\text{O}_4$
rust