

Spectroscopy

Interaction of matter and electromagnetic radiation:

× Help in structural analysis of Organic Compounds.

* a) Mass spectroscopy - Determine mass & MF.

b) IR :- Nature of functional group

c) NMR :- Determine nature of proton. So tells complete structure

× Better Methods as (1) Take less time for investigation and data can be stored in tabular or in chart form (2) Require small amount of sample (mg) (3) Results are correct reliable and may be repeated. (4) During process organic compound is not chemically affected and can be recovered (except mass spectroscopy) (5) Help in study of rxn mechanism & rates (6) Used for study of stereochemistry.

Electromagnetic radiations :- light radiations associated \vec{E} and \vec{B} field both.

× travel c velocity of light 3×10^8 m/s.

① Wavelength (λ) :- Distance b/w two crest or trough. ht of it is amplitude.

② frequency (ν) :- No. of waves which pass over a point in one sec. $\frac{\nu \times \lambda}{1}$ (unit cps $\frac{1}{s}$)

③ Wave no. ($\bar{\nu}$) :- Total no. of waves that are present in unit length. $\frac{\bar{\nu} \times \lambda}{1}$
Unit cm^{-1} or m^{-1}

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velocity (c): Linear distance travelled by a wave in one second. (m/s)

$$c = v \times \lambda$$

Characteristic: → ① E ⊥ B and propagate in direction ⊥ to both.

② Do not require any medium for propagation

③ Travel in vacuum at same velocity.

④ E (energy) associated with it is

$$E = h\nu$$

h = Planck Const (6.62 × 10⁻³⁴ Js)

ν = freq

Acc to Einstein $E = pc$

$$\frac{E}{c} = p$$

$$\frac{h\nu}{c} = p$$

$$\frac{h}{\lambda} = p$$

Types of Spectroscopy :-

a) Emission :- Used for study of atomic struc.

When EM rays having certain freq interact with atom then e⁻ jumps from one energy level to another by emission or absorption Spectroscopy

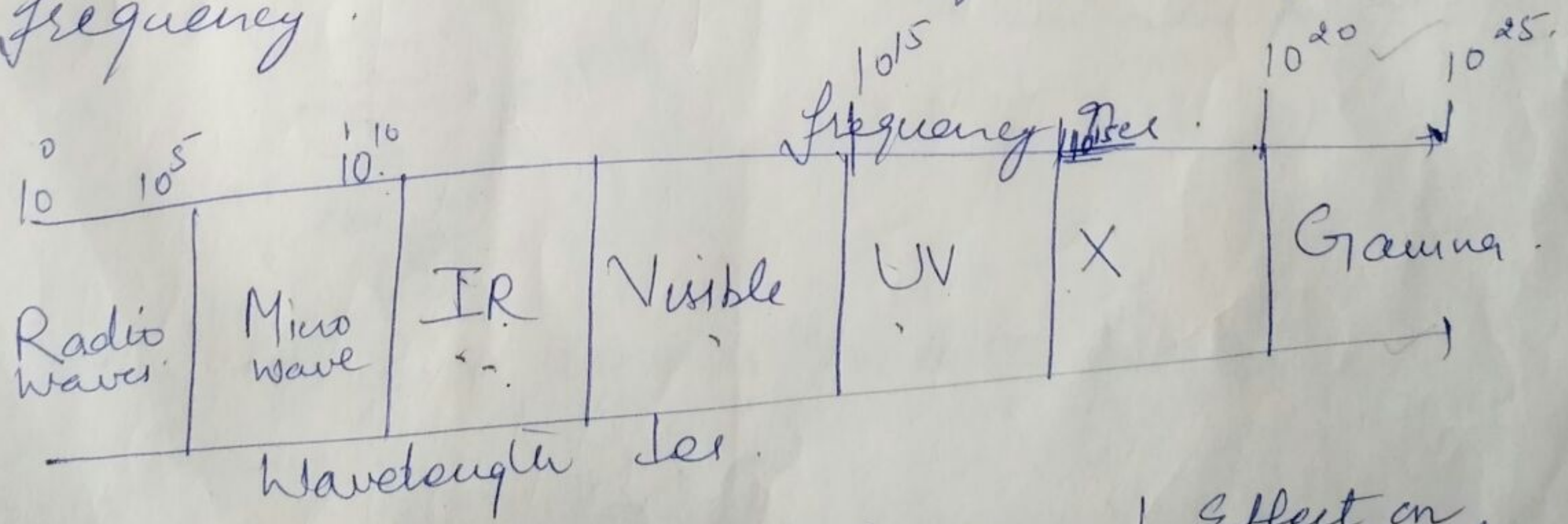
fact: E associated = equal to difference in energy (ΔE) b/w two energy levels

$$\Delta E = E_2 - E_1$$

Emission Spectroscopy :- Analysis of light source such as flame or an electric arc. Spectrum obtained due to excitation of atoms by thermal/electrical means. In ~~Absorption~~ ^{the case} e^- in ground state is to be promoted to excited state but life of e^- in this metastable state is short and they return to some lower level and the absorbed energy is released.

* Fluorescent lights & colours obtained by heating salts of certain elements in flame are eg of emission spectra. In some cases excited states may have appreciable life time such that emission of light continues after excitation has ceased — phosphorescence.

Absorption spectrum is obtained by placing the substance b/w spectrometer and some of the energy that provides EM radiations in the frequency range being studied. The spectrometer analyses the transmitted energy relative to incident energy for a given frequency.



S.No.	Type of Spectra	λ	Energy kcal/mol	Effect on molecule.
1.	Ultra Violet	200-400 nm	143.82	Changes in electronic energy level
2.	Visible	400-800 nm	82-36	"
3.	IR (Infra Red) and Microwave	2-16 μ m 1cm-100 μ m	14.3-1.8	Changes in vibrational and rotational movement of molecule.
	Radio waves	10m-1cm	12 Joules	changes in magnetic level

length of visible range from 400 nm (violet) to 700 nm (Red). Visible region is v. small part of EM spectrum. Shorter than visible falls into Ultra Violet. While longer than visible falls into Infra Red.

Remember :- $1 \mu\text{m} = 10^{-6} \text{m}$, $1 \text{\AA} = 10^{-10} \text{m}$, $1 \text{nm} = 10^{-9} \text{m}$.

Lambert's Law :- ^{Acc to Lambert} when monochromatic light is passed through solution, decrease in intensity of light I is directly proportional to Intensity of incident light (I_0) with thickness (x).

$$I = I_0 e^{-kx} \quad \text{--- (1)}$$

I = Intensity of transmitted light.

I_0 = Intensity of incident light.

k = Absorption coefficient.

Lambert

Beer's Law : An extension of Lambert law states that when monochromatic light is passed through a solution I in intensity of light with thickness of solⁿ is directly proportional to intensity of incident light as well as concentration of solⁿ.

$$I = I_0 e^{-\epsilon'cx} \quad \text{--- (2)}$$

ϵ' = Molar Absorption coefficient.

C = Concentration of solⁿ.

$$\frac{I}{I_0} = e^{-\epsilon'cx}$$

$$\log \frac{I}{I_0} = -\epsilon'cx$$

When $\frac{I}{I_0}$ is transmittance T and $-\log \frac{I}{I_0}$ is absorbance.

$$A = -\log T$$

Violet Spectroscopy:

spectrum is subdivided into two spectral

- a) Near UV 400 to 400 nm.
- b) Far UV or Vacuum UV } 10 to 200 nm.

Origin - from transition of electrons within the molecule of ion from lower electronic energy level to higher electronic energy level. For a radiation to cause "excitation", it must be in UV region of electronic spectrum. When a molecule absorbs UV radiations of frequency $\nu \text{ sec}^{-1}$, the e^- in that molecule undergoes transition from lower to higher energy level.

The difference in energy is given by

$$E = h\nu \text{ erg.}$$

The actual amount of energy required depends on diff in energy b/w ground state (E_0) and excited state (E_1) of e^- .

$$E_1 - E_0 = h\nu$$

The total Energy of a molecule is the sum of electronic energy (E_{elec}), vibrational energy (E_{vib}) and rotational energy (E_{rot}).

$$E_{elec} > E_{vib} > E_{rot}$$

When UV energy is quantised, the absorption spectrum arising from single electronic transition is expected to consist of single discrete lines. But this does not take place because electronic transition is ~~expected to consist of~~ ~~long~~ is superimposed upon vibrational and rotational sub-energy levels. That is why spectra of simple molecules in gaseous state contain narrow absorption peaks, wherein each peak represents a transition from particular combination of vibrational and rotational levels in electronic ground state to a corresponding combination in the excited state.

in polyatomic complex molecules, broad absorption bands are obtained due to coalescence of discrete bands.

When energy is absorbed by molecule in the UV region, it brings about some changes in the electronic energy of the molecule resulting in transition of valance e^- . The following 3 types of electrons are involved in organic molecules.

(a) π electrons:- The electrons (e^-) responsible for double bonds are called πe^- . These are involved in unsaturated hydrocarbons like dienes, trienes and aromatic compounds. In unsaturated systems πe^- predominantly determine the energy state of e^- which are excited by the absorption of UV or visible light.

(b) σ electrons:- Electrons forming single bonds. These are involved in saturated bonds such as $C-H$ in paraffins. Also called σ bonds. As the energy required for exciting σ bonds is much more than that obtained by UV radiation so compounds containing σ bonds do not absorb UV radiations.

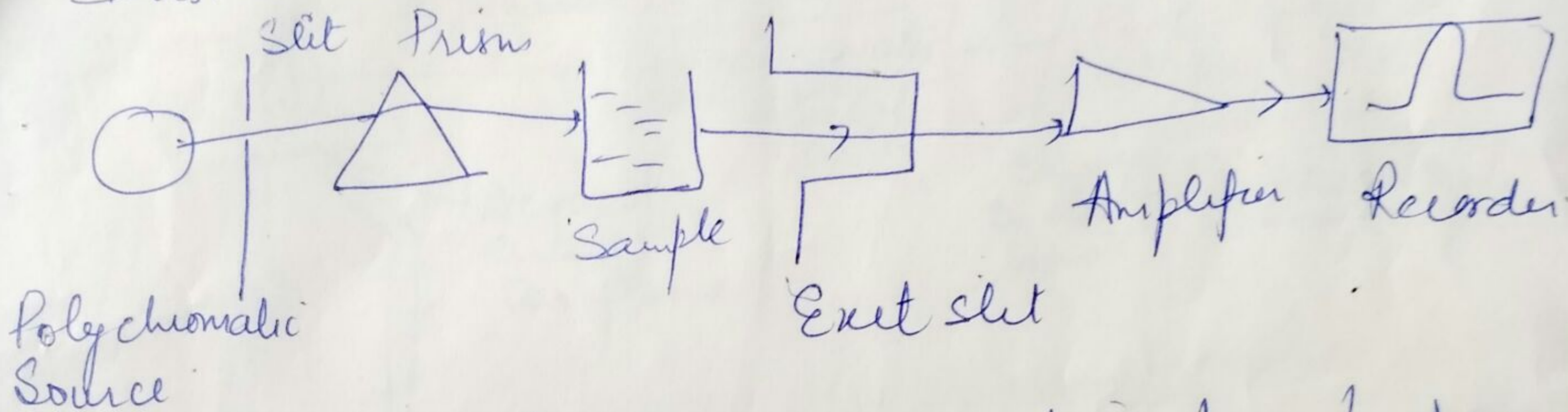
(c) n electrons:- These are unshared/nonbonded e^- and are not involved in bonding b/w atoms. Eg Organic compounds containing N, O or halogen $n e^-$ can be excited by UV radiations and hence compounds containing atoms like N, O, S, halogen may absorb UV.

$s e^-$ are more strongly held than $p e^-$.

Electronic Transitions

$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$
As per selection rule $n \rightarrow \pi^*$ transition is forbidden while remaining three are allowed.

Instrumentation



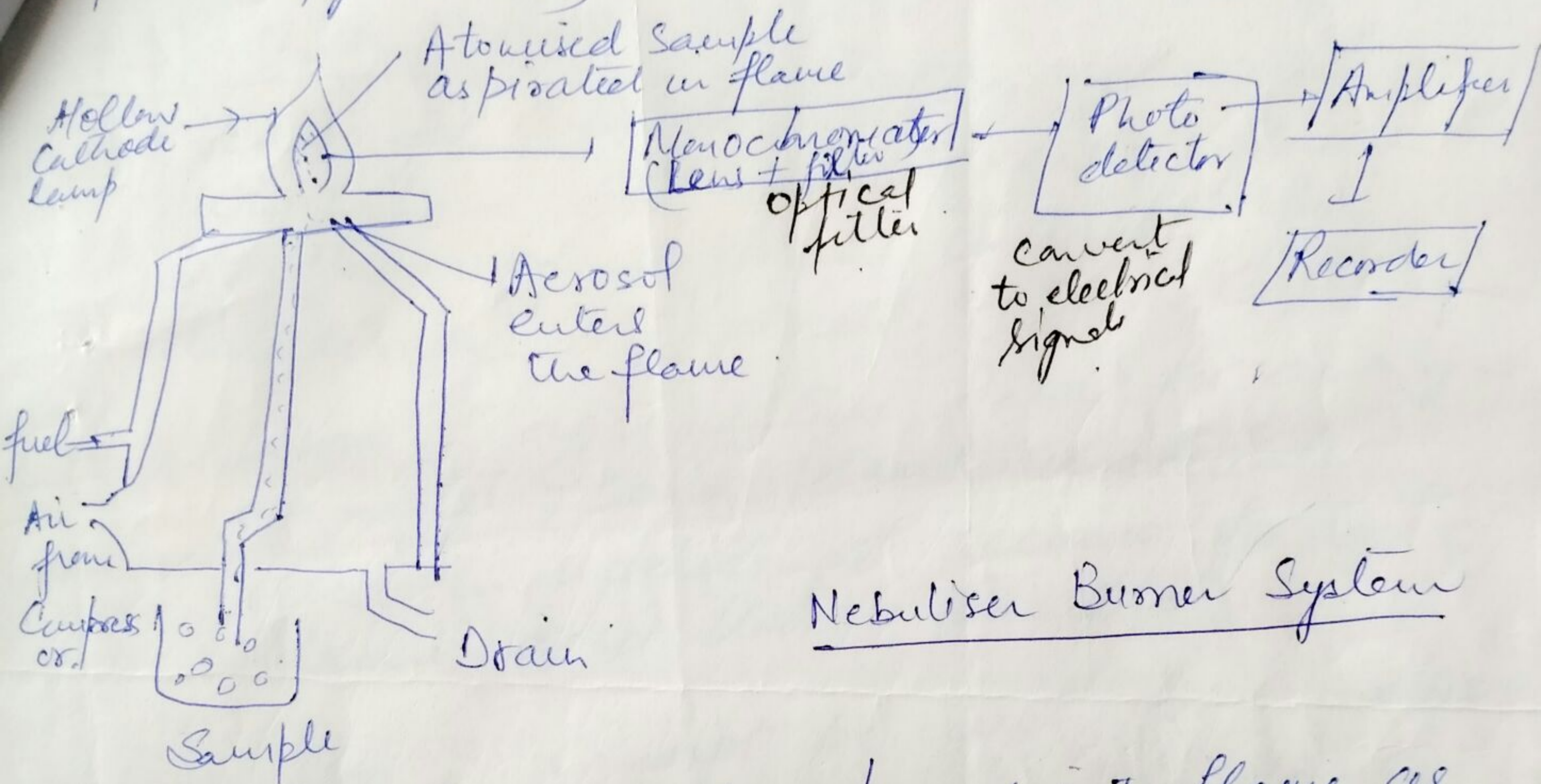
Radiation Source for UV range is high press hydrogen or deuterium discharge lamp, which covers the range of 200-375 mμ. A Xenon arc or mercury lamp provides a more intense radiation. The source for visible range is 6 or 12V tungsten automobile head lamp bulb. UV plot is of absorbance vs wavelength:

Application of UV Spectroscopy

1. In determining structure of several vitamins.
2. Determination of unknown concentration.
3. " of dissociation constant of acid & base.
4. " of molecular weight.
5. Detect Steric Hindrance.
6. " impurity.
7. Study rate of rxn.
8. For characterization of aromatic compounds and conjugated diene ⇒ predict relation b/w diff group especially. Conjugation b/w a) C-C & C=O double bonds.
b) two or more C-C multiple bonds.

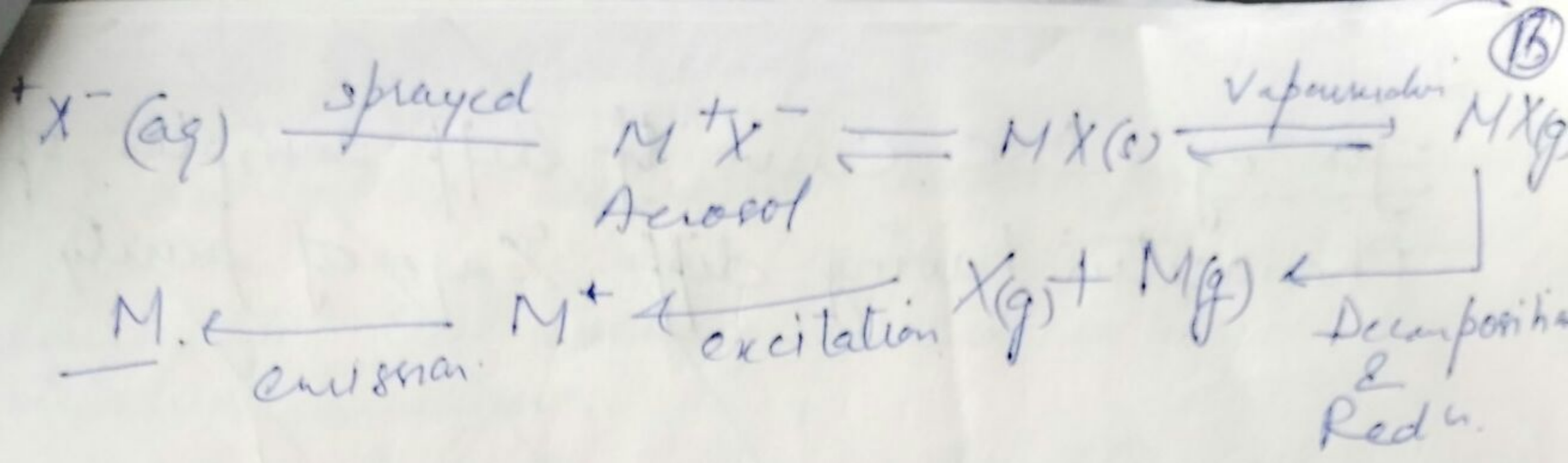
Photometry or flame emission spectroscopy

Characteristic colour imparted to the flame by the emission of radiation from alkali metals excited in flame is the basis of flame emission spectroscopy (FES)



Nebuliser Burner System

- Theory:
- (1) Sample solⁿ is sprayed into flame as aerosol by atomiser.
 - (2) Air is mixed with it and the mixture is passed to burner along with fuel gas.
 - (3) Molecules/ions of sample are reduced to free atoms: $\text{Na}^+ + e^- \rightarrow \text{Na} \dots$
 - (4) Heat of flame causes excitation of some atoms into higher electronic states.
 - (5) Excited electron revert back to ground state by emission of light energy (hv) measured by detector.
 - (6) Radiation is then passed via ~~lens~~ and then filter which permits only the radiation characteristic of element under investigation to pass via photocell. Output is measured in Recorder.



Application:

- (1) Used for analysis of those elements which have an easily excited flame spectrum of sufficient intensity for detection by a photocell. eg Na, K, Ca, Li
- (2) Used in agriculture field for analysis of water, soil, plant materials.
- (3) Used in medicinal science for testing urine and blood samples.

Limitation: Cannot be used for analysis of those metal which have tendency for incomplete vaporization.

DSC: Differential Scanning Calorimetry:
 Heating is done in such a way that Reference and sample material remains at same temperature. So, heat is added either to sample or Reference. This added heat is recorded as a function of temperature.

- heat supplied to Sample \rightarrow +ve sign. (1 mcal/s)
 - " " " Reference \rightarrow -ve sign.

Apparatus $A = K'm \Delta H$
 same as DTA. diff is it has individual heaters close to sample & reference

Infra Red Spectroscopy

(15)

powerful analytical technique useful for chemical identification and when coupled with intensity measurements, this technique can be used for quantitative analysis.

This spectra originate from absorption of energy by a molecule in IR region and transition occurs b/w two vibration levels.

- By measuring molecular vibrational frequencies, useful information regarding molecular structure can be obtained.

- Vibrational spectra, therefore are considered as molecular finger prints.

- IR region which extends from red end of visible spectrum to microwave region is divided into three regions.

1) Near IR (Overtone region) 0.8 to $2.5 \mu\text{m}$
($12,500$ to 4000 cm^{-1})

2) Middle IR (Vibration-rotation region) 2.5 to $50 \mu\text{m}$
(4000 to 200 cm^{-1})

3) Far-Infrared (Rotational region) 50 to $1000 \mu\text{m}$
(200 to 10 cm^{-1})

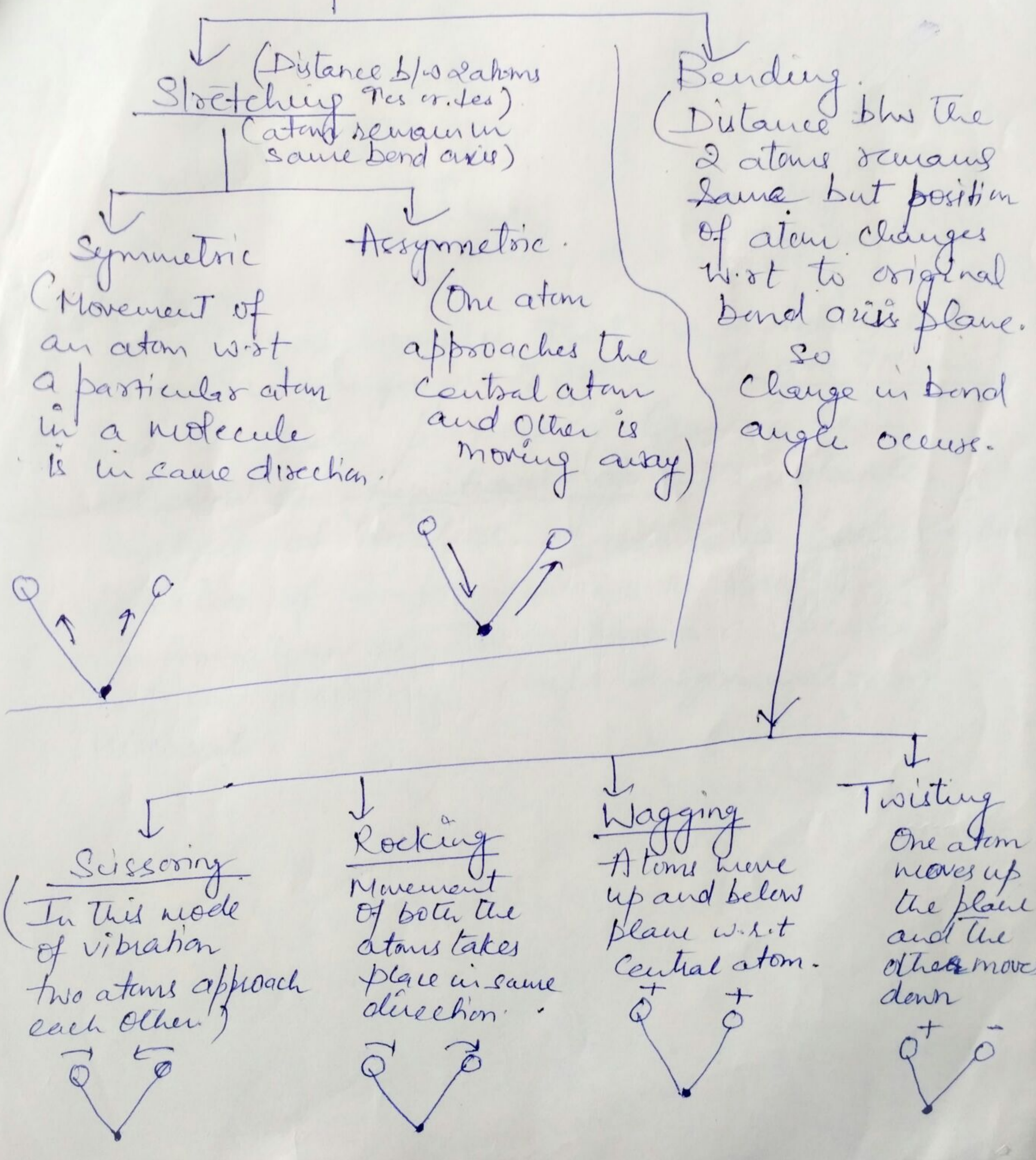
Imp region of interest for analytical part is 2.5 to $25 \mu\text{m}$ (4000 to 400 cm^{-1}). IR spectra originate from diff modes of vibration and rotation of molecule.

Do types also

Vibrational mode of Polyatomic Molecules:-

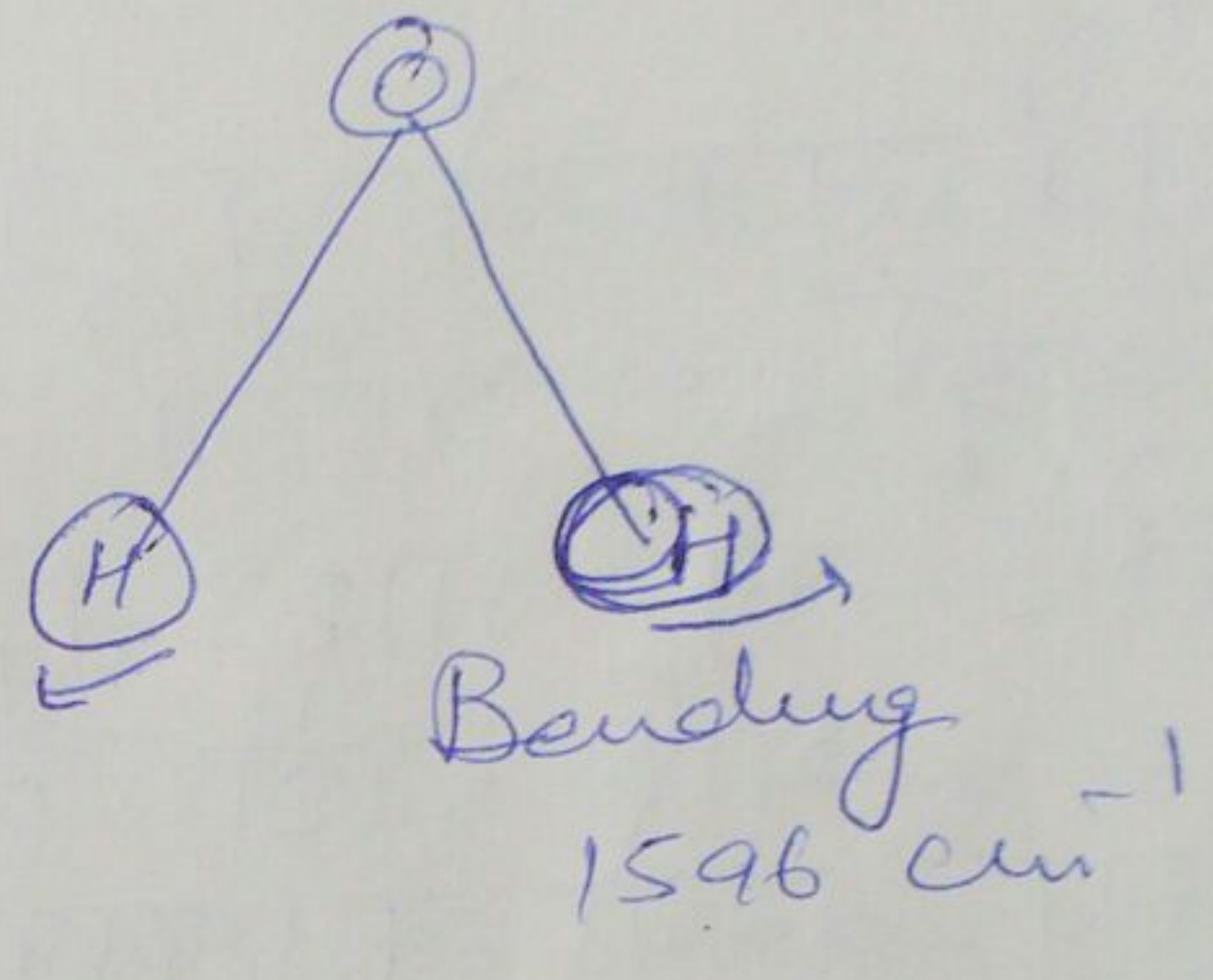
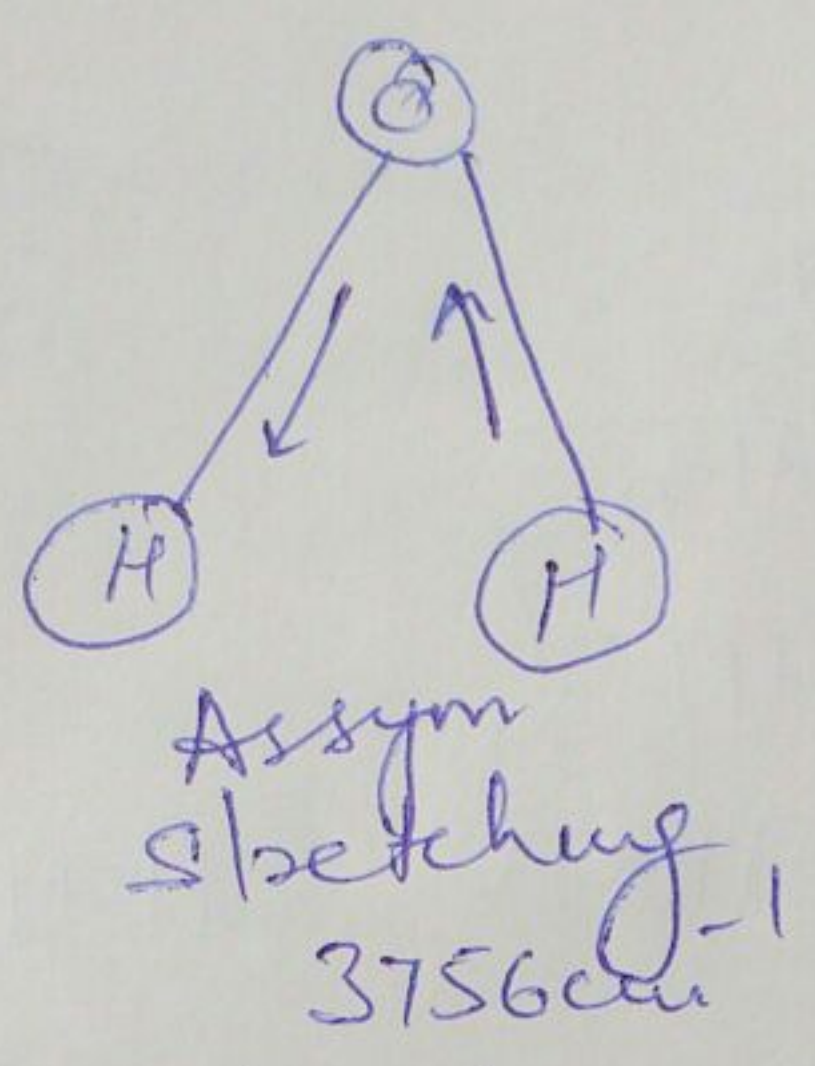
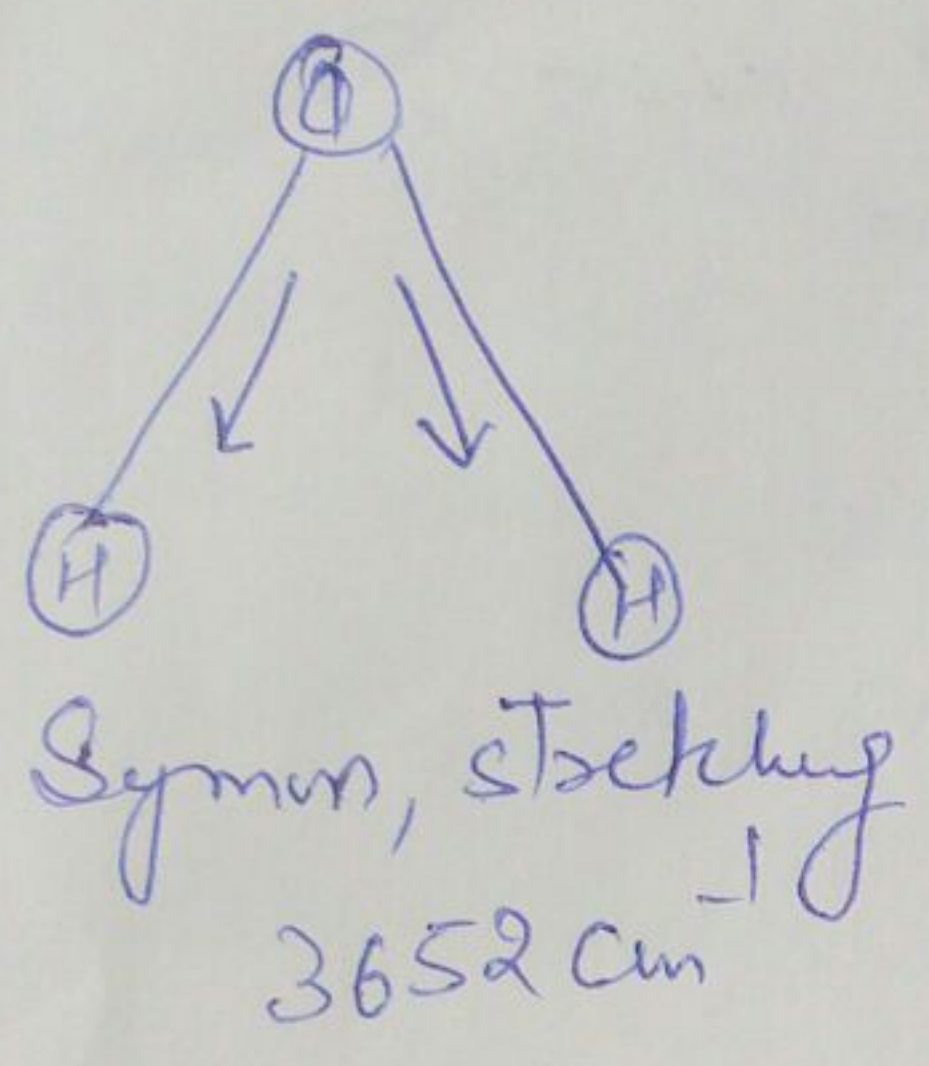
Degree of freedom in non linear polyatomic molecule is $(3N-6)$ and in linear $(3N-5)$. N is no. of atoms present.

Vibrations of a molecule



g H₂O and CO, case:

H₂O is triatomic ie n=3 so 3n-6 = 3x3-6 = 3 modes of vibration. All involve change in dipole moment so IR active. spectrum consist three bands at 3652, 3756 and 1596 cm⁻¹



Applications:

- ① Identify two samples that have identical spectra, in finger print region 1430 - 910 cm⁻¹
- ② Used to study progress of Organic rxⁿ.
- ③ Detection of functional gp in a molecule.
- ④ Analysis of mixture of aromatic hydrocarbons
- ⑤ Detection of Impurities in a sample.
- ⑥ Information of IR + Raman spectra help in deciding shape & symmetry of molecule.

NMR (Nuclear Magnetic Resonance)

any nucleus having odd number of protons or an odd number of neutrons or both has the property of nuclear spin eg ^1H , ^{13}C , ^{19}F possess spin but ^{12}C , ^{16}O do not.

Here we are concerned with nuclear spin associated with proton (^1H). Spinning proton generates electric current which produces magnetic field so spinning proton behave as tiny magnets. When such a proton is placed in magnetic field (B) two possible orientations

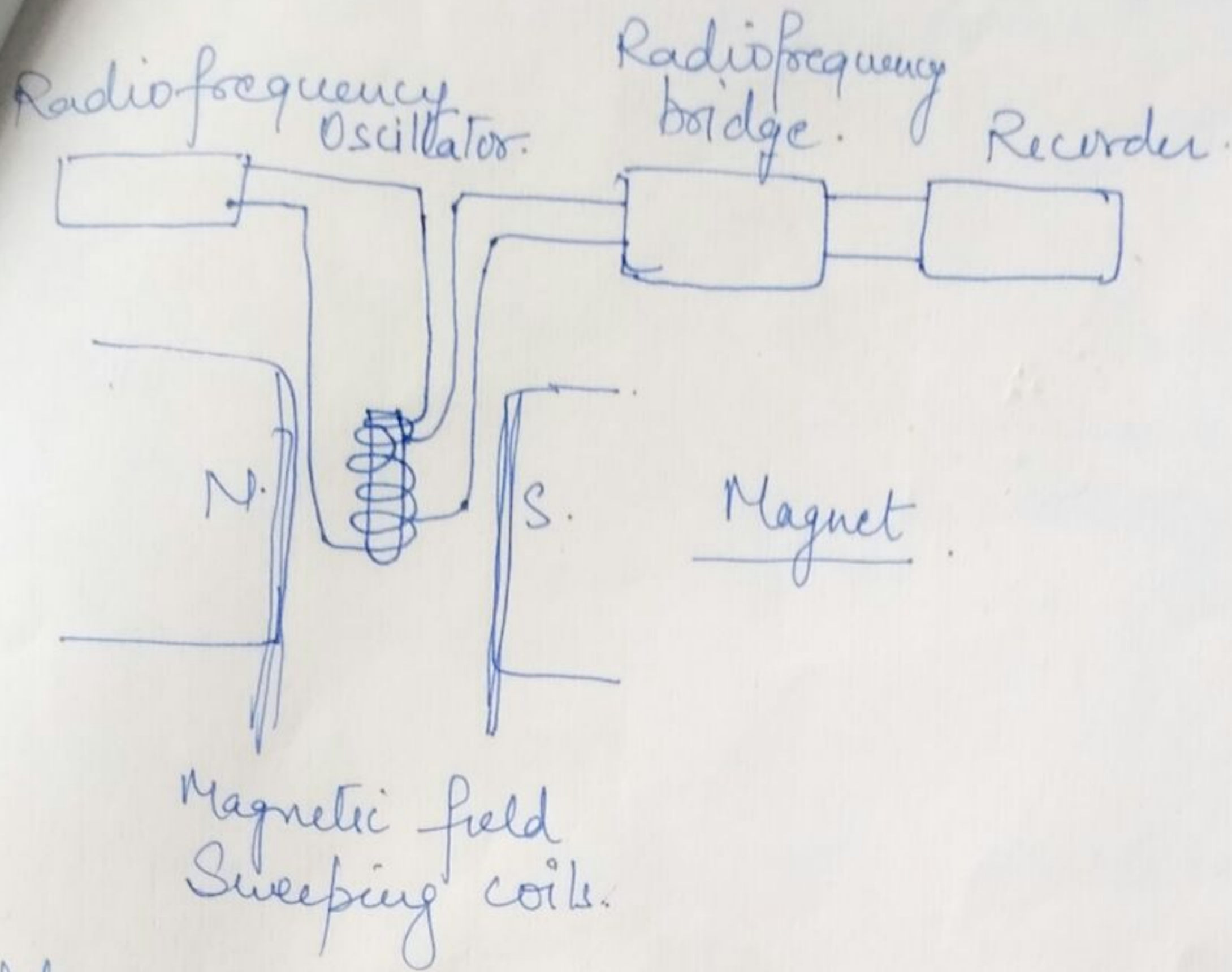
- (i) Low energy alignment of nucleus: Both applied and nucleus B are in same direction
- (ii) High energy alignment of nucleus: Both applied and nucleus B are in opposite direction.

if we provide energy = to diff b/w the two states ~~that~~ then a transition from low energy state to high energy state can be obtained. which is supplied by EM radiations.

Usually a field of 2.3 T or 23000 Gauss results in absorption in radio frequencies of 10 MHz.

freq of absorption depends on the environment of nucleus also. eg $\text{CH}_3\text{CH}_2\text{OH}$ has 6 protons so NMR contains 3 peaks for 3 protons of CH_3 , 2 protons of CH_2 and one proton of OH.

Instrumentation \rightarrow Here freq of radiation is kept constant and B is varied, till the proton absorbs. The B is varied by passing current through wire coils, wrapped around two poles of magnet. Absorption is detected on radiofrequency bridge.



Shielding & Deshielding of protons

When a proton is exposed to radiofrequency (rf) proton, its spin changes its orientation from (↑) to (↓). As spin flips its energy from lower to higher energy level. All protons do not change their spins at the same applied field, as their energy depends on the chemical environment of the protons.

Secondly electrons also ~~induce~~ induce their own B. So the B sensed by protons is not the same as B_{applied}. It ^(induced) may oppose or reinforce the B_{applied}. So B_{proton} is the effect of B_{induced} & B_{applied}.

- ① If both reinforce then small energy is needed to flip the proton. Such proton is said to be deshielded & absorbs lower magnetic field strength.
- ② When both oppose each other, a higher B must be applied to flip the proton. Such proton is said to be shielded and absorbs at higher B.

σ (shielding constant) $\Rightarrow \sigma = \sigma_d + \sigma_p$

\swarrow diamagnetic contribution
 \searrow paramagnetic contribution.

(B_{applied} generate orbital motion of electrons) which opposes it

current is also induced in the nearby atoms (Neighboring gp effect) in NMR. The protons of HC≡CH are shielded by the currents induced in triple

= this effect on shielding/deshielding also depends on the magnetic anisotropy of the group. for eg anisotropy of benzene ring, is the ability of the field to induce a ring current

Chemical Shift δ .

Shift in the position of spectrum peak due to small changes in chemical environment.

When a molecule is placed in B, its e⁻ are caused to circulate, thereby giving rise to induced magnetic field

(i) opposes the applied field :- Proton experiences field diminished field \Rightarrow shielded \rightarrow which shift the absorption position upfield. this is diamagnetic shift. eg acetylic proton

(ii) Reinforces the applied field :- proton experiences enhanced field \Rightarrow deshielded \rightarrow which shift the absorption position downfield. :- this is paramagnetic shift. eg CH=CH, aldehydes.

(3) Chemical shift is measured w.r.t same standard TMS [(Tetra Methyl Silane) (CH₃)₄Si] is taken as standard.

$$\delta = \frac{V_s - V_0}{V}$$

V_s = freq of the sample.

V_0 = freq of TMS ; V = operating freq.

Values are from 0 to 10. TMS is assigned δ value 0. Earlier τ (tau) units were used.

$$\boxed{\delta = 10 - \tau} \quad \boxed{\tau = 10 - \delta}$$

δ is dimensionless, independent of B_{applied}; $\delta = +ve$ means freq of gp of nuclei is higher than that of the standard, TMS.

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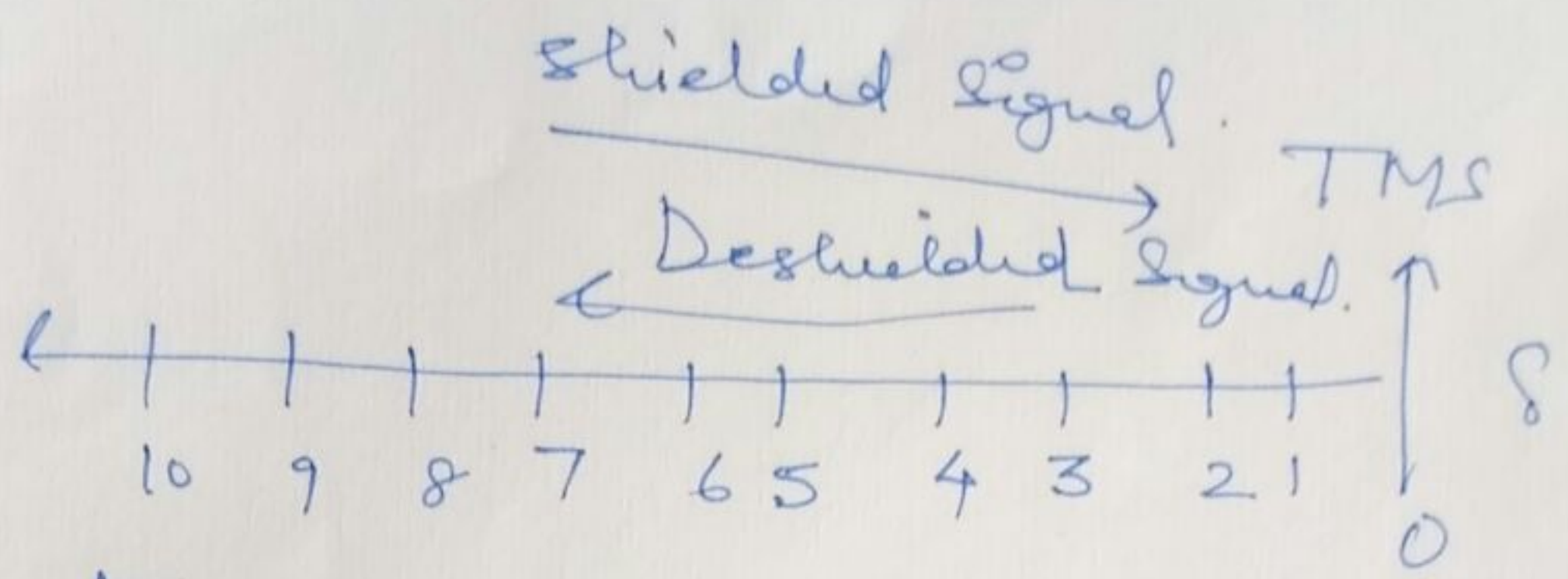
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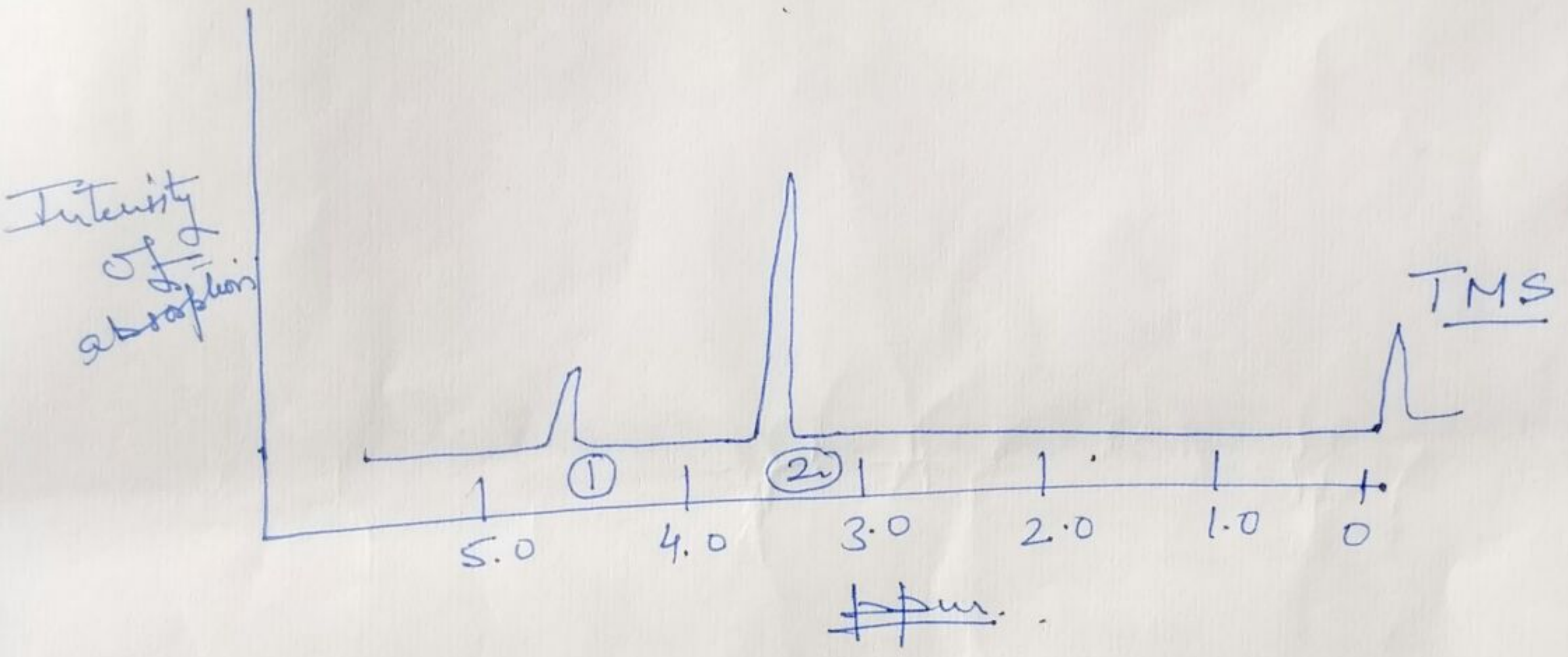
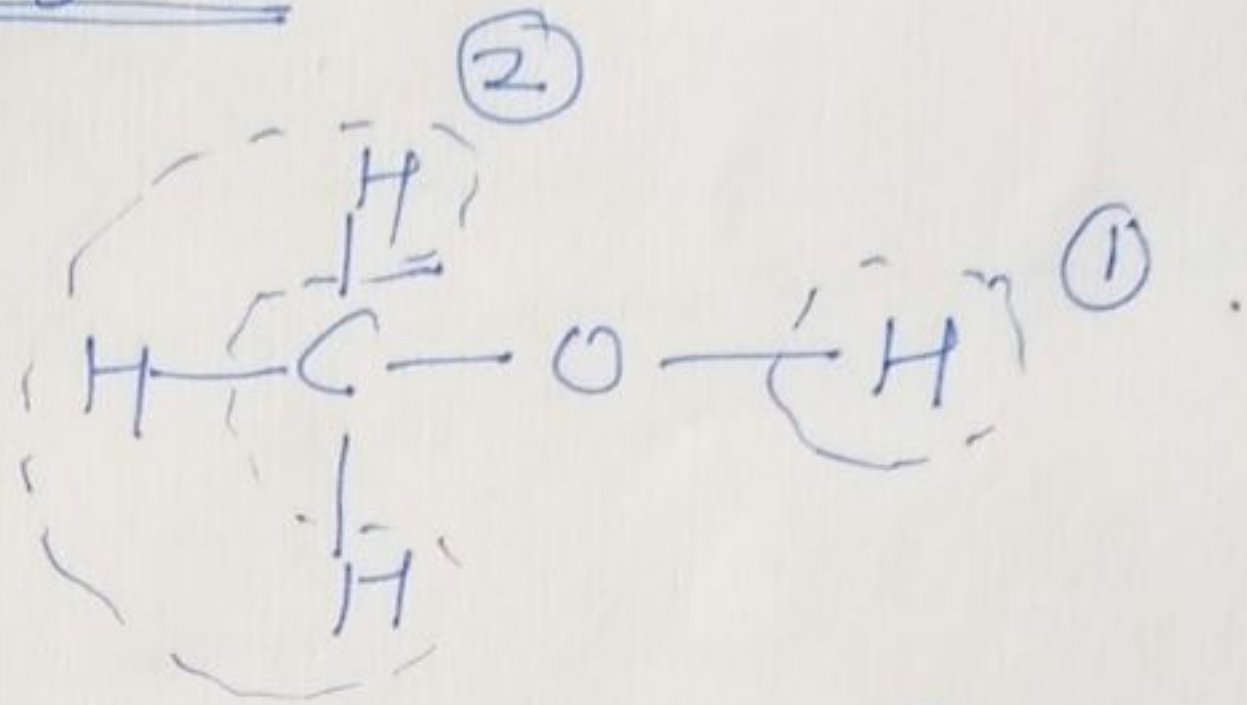
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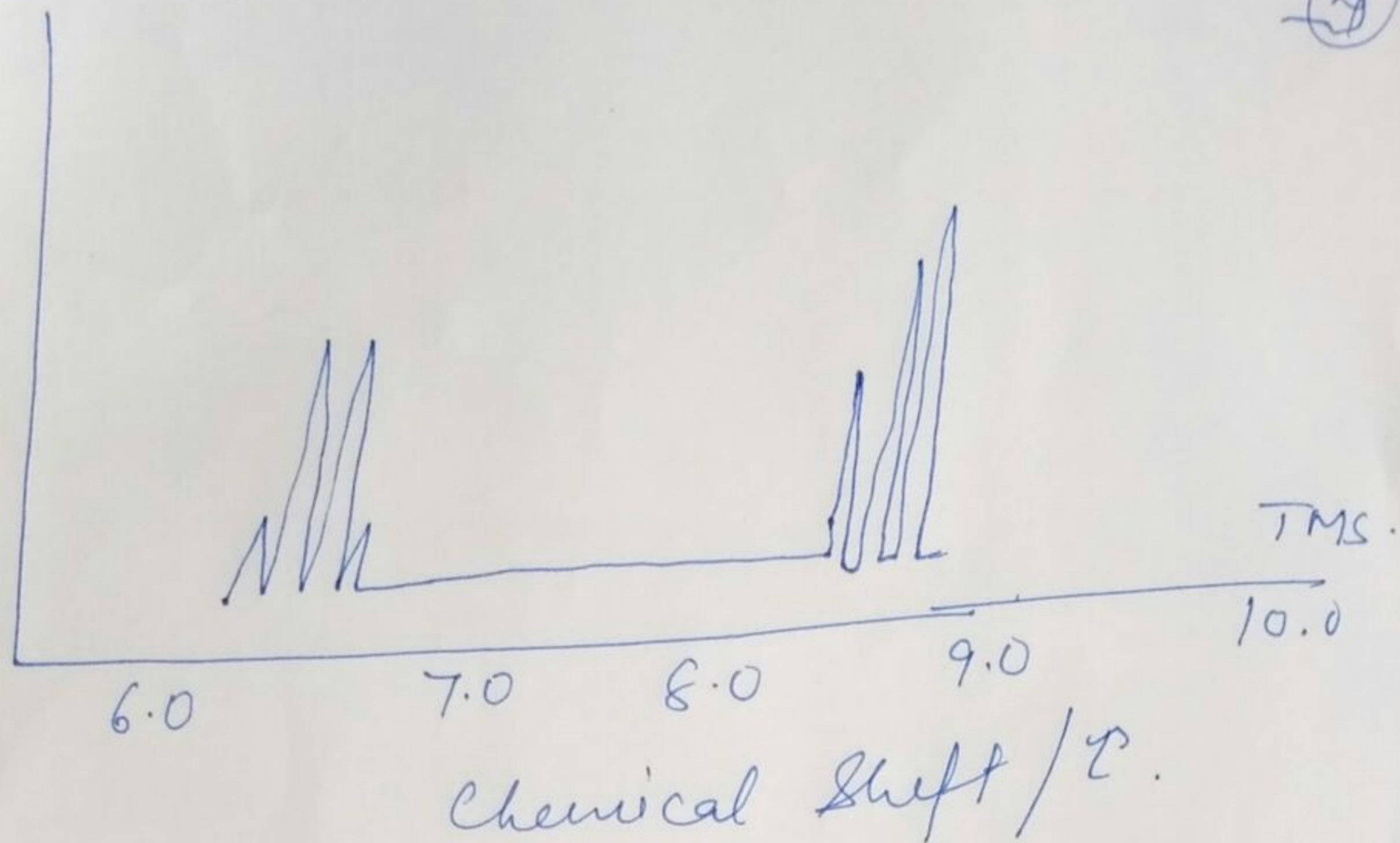
eg NMR spectra of CH₃OH

The areas under two types of peaks are in ratio of 3:1. So it confirms methanol has 3 protons of one type and one proton of another type. (OH)

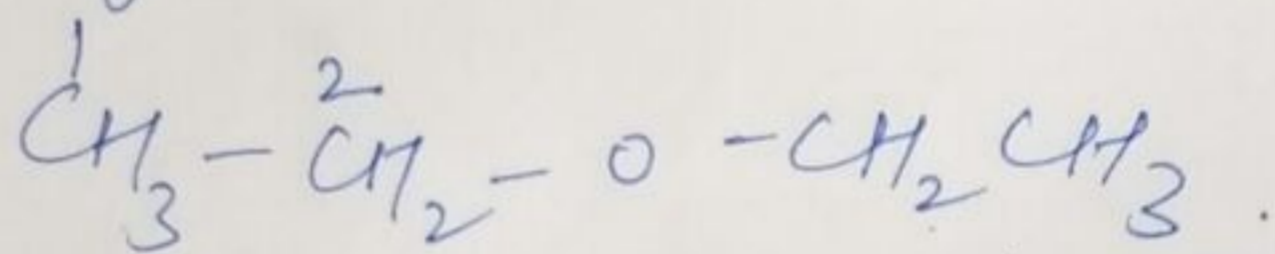


When homogenous magnetic field is applied to the substance, it is found that spectrum ^{does not} consist of a single peak but some of the peaks are split (resolved) into several parts. For eg. the high resolution spectrum of ethoxyethane (CH₃COCH₂CH₃) or (CH₃CH₂COCH₂CH₃) has two main peaks centered at 6.6τ and 8.85τ respectively. 6.6τ is split into (quartet) while 8.85τ into (triplet).

Absorption of Energy.



Splitting of peaks is due to interaction between protons on adjacent atoms



The B experienced by the protons of C1 will depend on the way in which B of proton on C2 are aligned with respect to the applied field.

There are three possible alignments

- (a) $\uparrow\uparrow$ (1) B of both protons arranged in the direction of applied field.
- (b) $\downarrow\downarrow$ (1) opposite.

- (c) $\uparrow\downarrow$ $\downarrow\uparrow$

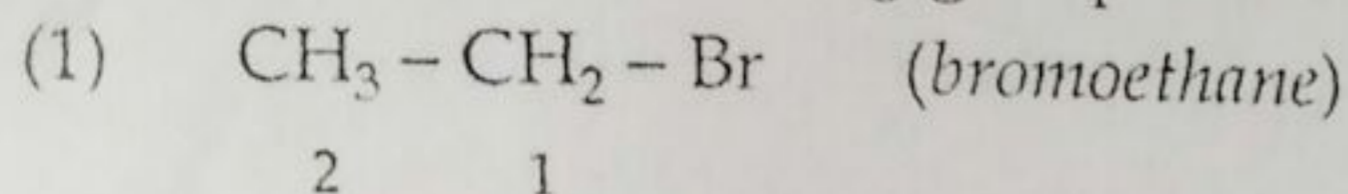
So the three equivalent protons on C1 experience three slightly diff field (above) strength. One of the field will be twice as probable as either of the other two so triplet is attained of intensities 1:2:1.

for Quartet. 1:3:3:1

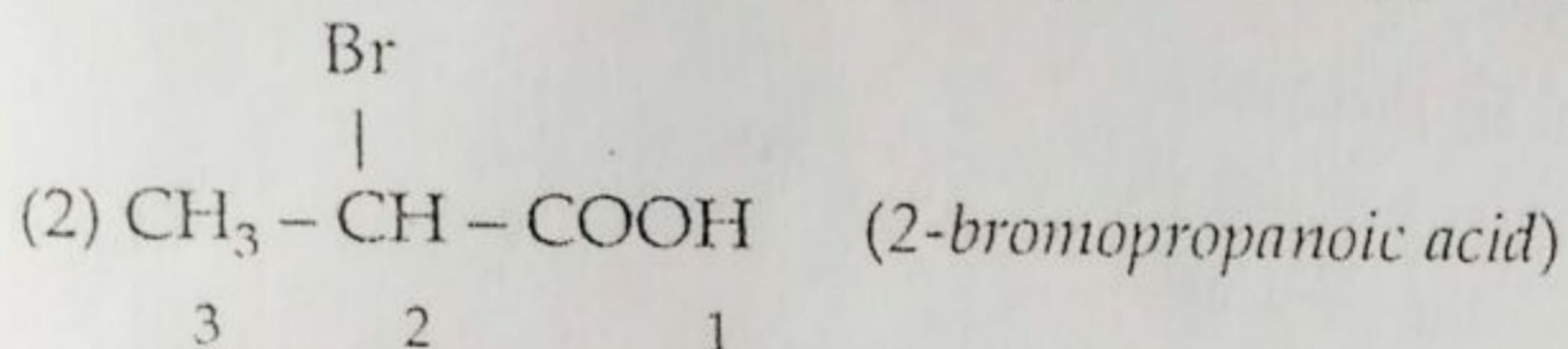
Application of NMR : (1) No. of signals indicate the type of protons in the compound. (2) Chemical shift tells the type of structure associated with particular protons. (3) Position of peaks tell the type of electronic environment of each kind of protons. (4) Splitting \rightarrow No. of protons on atoms adjacent to the group.

The protons on carbon atom '2' are surrounded by four adjacent protons, so a multiplet absorption pattern with relative intensities of 1 : 4 : 6 : 4 : 1 should appear for the $-\text{CH}_2-$ resonance. Similarly, the two sets of equivalent protons on carbon atoms '1' and '3' will give an absorption peak, split into triplet of intensities 1 : 2 : 1 by protons on the central carbon atom.

The multiplicity of the signal from a group is equal to $(n + 1)$, where n is the number of protons present in neighbouring group. Let take some examples :



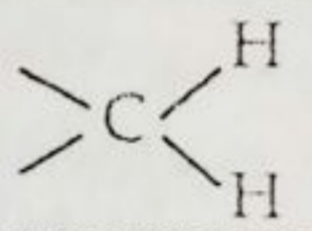
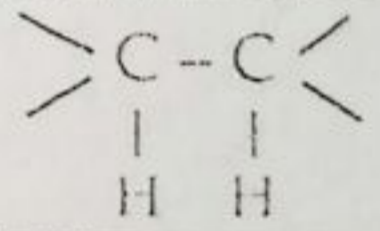
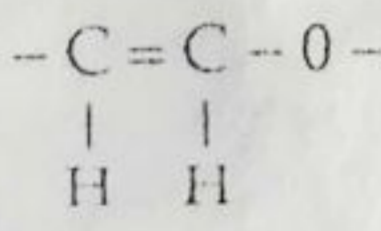
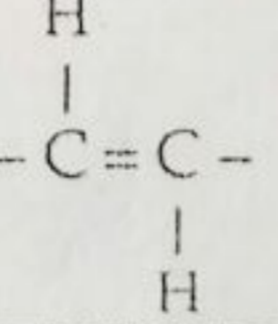

Here '1' is a 1 : 3 : 3 : 1 quartet, since there are three neighbouring protons (in CH_3) and '2' is a 1 : 2 : 1 triplet, since there are two neighbouring protons (in CH_2)



Here '1' is singlet, since there is no neighbouring proton ; '2' 1 : 3 : 3 : 1 is a quartet, since there are three neighbouring protons (in CH_3) and '3' is a 1 : 1 doublet, since there is one neighbouring proton (in $-\text{CH}-$).

Spin-spin coupling constant (J) : In the NMR spectrum, each magnetic nucleus contributes to the local field experienced by the other nuclei and hence, modifies their resonance frequencies. This in-turn leads to splitting between the lines of a given multiplet. The strength of spin-spin interaction is expressed in terms of the *spin-spin coupling constant (J)* and is reported in hertz.

Table 6. Spin-spin coupling constants.

System	H - H	H - C	H - F		
J (Hz)	276 ✓	120 - 160 ✓	521 ✓	-20 to -6 ✓	5.5 to 7.5 ✓
System					
J (Hz)	7 to 10		12 to 19		6 to 9 (ortho), 0.5 to 4 (meta), 0 to 2.5 (para)

The magnitude of J falls off with increasing number of bonds intervening between the nuclei involved and is related to the geometrical relationship of the bonds over which the coupling is transmitted. Coupling constants of some of the systems is given in Table 1. It may be pointed that coupling constants are independent of the strength of the applied field, since they do not depend on the latter's ability to generate local fields.

13 HOW TO INTERPRET ^1H NMR SPECTRA ?

Following points may be considered for the interpretation of NMR spectra :

(1) Number of signals tells the number of different environments in the molecule.

(2) The relative areas of different peaks corresponds to the number of protons present in different environment in the molecule. In other words, area under each NMR signal is proportional to the number of H-atoms present in that environment.

(3) Multiplicity of lines in an NMR signal (high resolution) for a group of protons is dependent on hydrogen atoms present in the neighbouring groups. If there are n neighbouring protons, then multiplicity of signal = $(n + 1)$.

(4) The intensities of signals are asymmetric about the mid-point of the group. Pascal's triangle gives the relative intensities of various signals in the NMR spectrum.

14 APPLICATIONS OF NMR SPECTRUM

Information obtainable from NMR spectroscopy are given below :

(1) The number of signals in the spectrum indicate types of proton in the compound.

(2) Integration of trace of spectrum gives the relative number of protons of different types.

(3) Chemical shifts give the type of structure associated with particular protons.

(4) Positions of the peaks indicate the type of electronic environment of each kind of proton.

(5) The splitting patterns give the number of protons on atoms adjacent to the group, which contains proton(s), whose resonance is being measured.

(6) The intensities (relative height) of signal give the number of protons of each kind. For example, if three signals recorded on NMR spectrum are of relative heights 3 : 2 : 1, then there are 3 protons of one type, 2 protons of other type and 1 proton of another type.

15 USE OF NMR SPECTROSCOPY IN INORGANIC CHEMISTRY

Although the major uses of NMR are in organic chemistry, yet it is also employed in the determination of inorganic structures. For example, ^{19}F has a nuclear spin and compounds containing this atom exhibit nuclear magnetic resonance effects. Bromine pentafluoride (BrF_5) has a spectrum consisting of two main peaks of relative intensities 4 : 1, with the more intense peak split into a doublet (1 : 1) and the other peak split into a quintet (1 : 4 : 6 : 4 : 1). The molecule thus contains one unique fluorine atom and a group of four equivalent ones. Similarly, the spectrum of sulphur tetrafluoride (SF_4) consists of two triplets, i.e., the molecule contains two pairs of non-equivalent fluorine atoms. The spectra of these two compounds are consistent with the structures shown in Fig. 42.

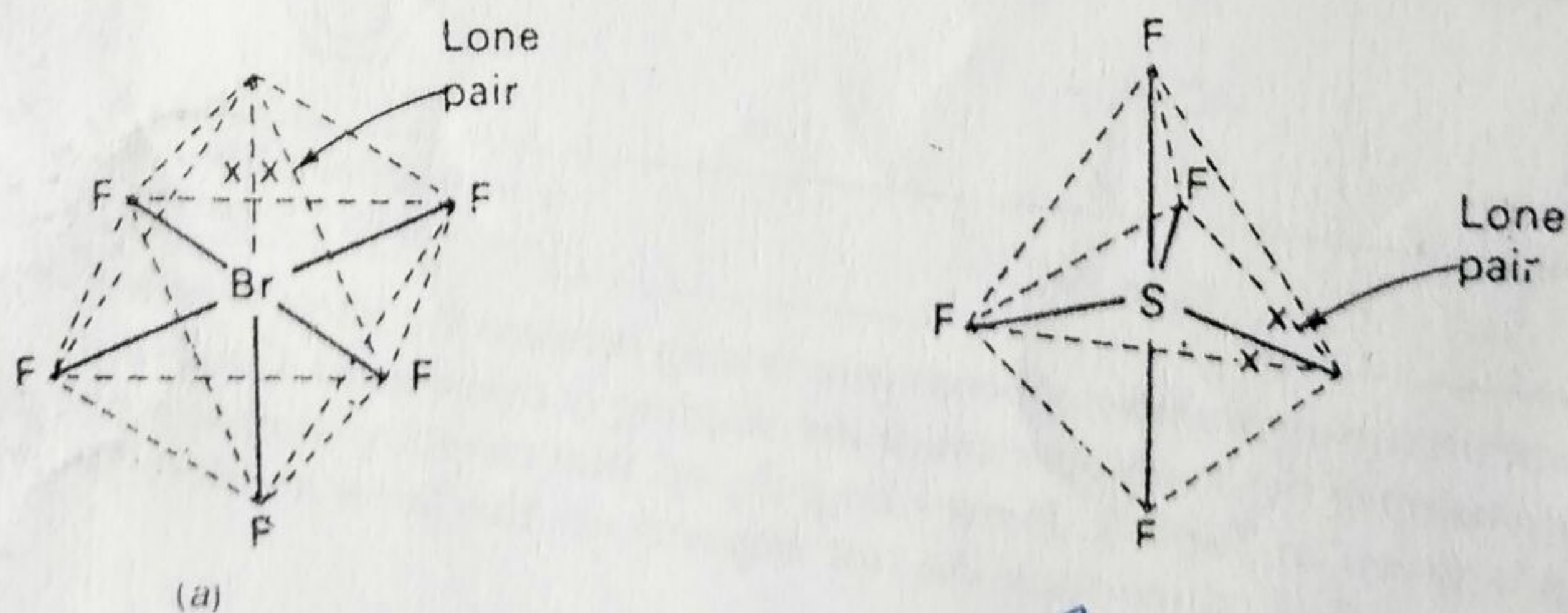


Fig. 42. Structure of : (a) BrF_5 , (b) SF_4 .

16 MAGNETIC RESONANCE IMAGING (MRI)

Magnetic resonance imaging employs nuclear magnetic resonance of protons to produce proton-density maps (or images) of the human body. Thus, MRI can be utilized to discriminate between healthy

and diseased tissues of body. It is based on the fact that the protons present within water, lipids, fats, etc. resonate at a given frequency. Since human body contains about 75% water, and each water molecule (H_2O) has two hydrogen nuclei, so images of the different parts of the body can easily be taken. In a diseased condition of body part, the distribution of water, fats, lipids, etc. alters, and by using MRI, one can detect the diseased part(s) of the body.

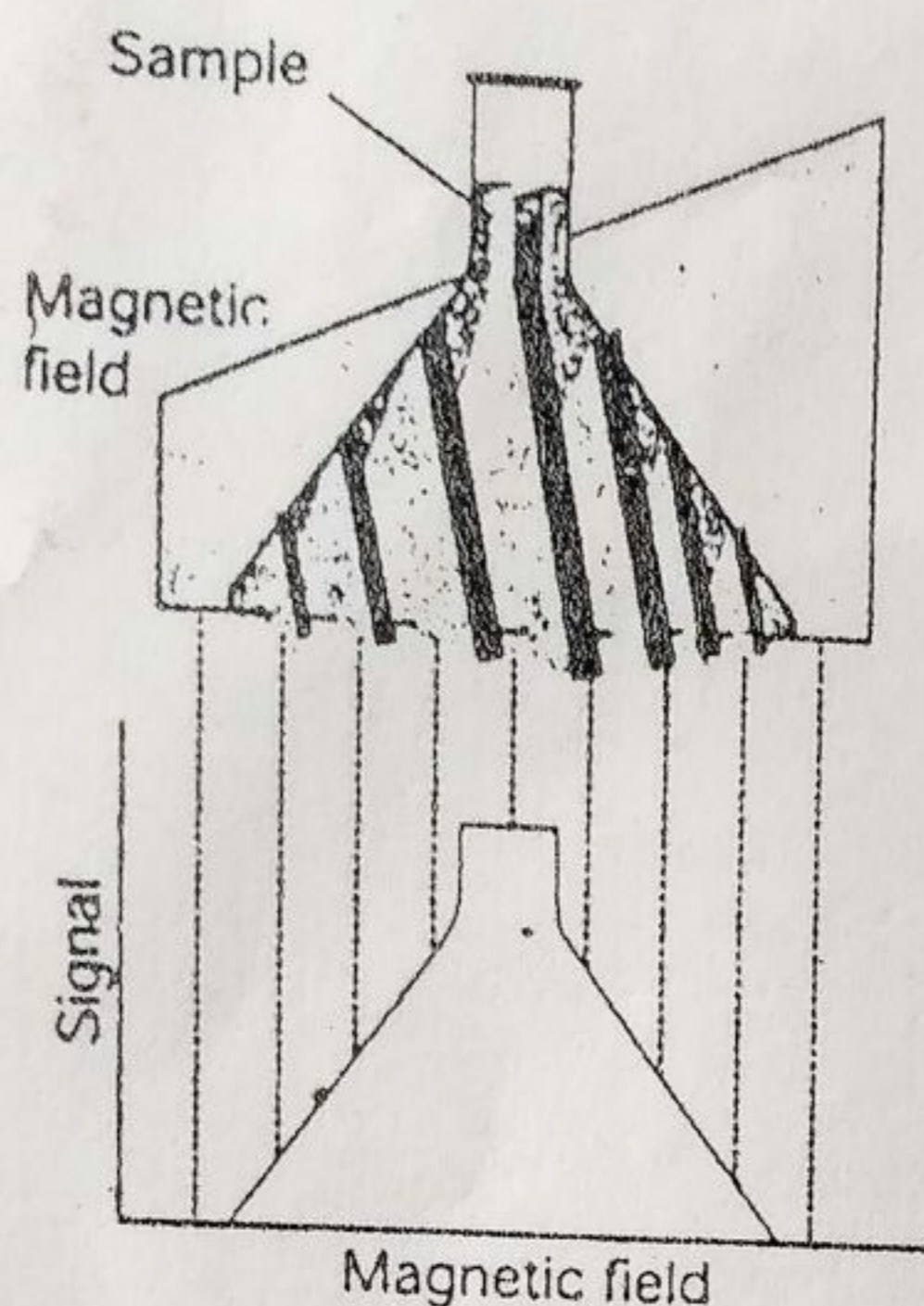


Fig. 43. Arrangement for MRI.

Procedure : For getting an image in MRI, a varying magnetic field is applied across the body part under consideration. The protons in various regions of body come to resonance at different frequencies and the intensity of signal is proportional to the number of protons at that magnetic field. The body part is then rotated into a different orientation and another projection is made. Finally, the data obtained from different projections is combined by computer to get three-dimensional image of the body part. MRI requires very small time for scanning a particular body part.



Fig. 44. Cross-section of a patient's head (displaying soft tissues) obtained by MRI.

Applications : (i) For investigating the functioning of myocardium, heart, etc. (ii) To identify the regions of excessive fat deposition in different body organs, blood vessels, etc. (iii) For the analyses of blood, by using (^{23}Na) MRI. (iv) For estimation of fluorine concentration in different body parts, by using (^{19}F) MRI.

Note : X-ray can be used to generate a two or three - dimensional image of an object such as human body. Such an imaging procedure is known as X-ray tomography. Unfortunately, the soft tissues of the body show little contrast to X-rays and moreover, the exposure to X-rays is detrimental to health. On the other hand, NMR is very sensitive to changes in the physical and chemical environments of the nuclei, especially the protons, which are the most abundant and widely distributed in the human body, and the energy involved in NMR imaging techniques is so low that health risks are eliminated. Consequently, NMR imaging methods for the human body are now being rapidly developed and improved and are widely used.

The absorption spectrometer consists of :

- (a) a suitable source of electromagnetic radiation ;
- (b) a system to analyse the radiation or a monochromator and
- (c) an appropriate detector to detect the intensity of the radiation absorbed.

The final absorption spectrum is displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength (or frequency or wave number).

INFRARED (IR) SPECTRA

Electromagnetic radiation in the *infrared* region of the spectrum (3×10^{12} to 3×10^{14} Hz or 100 cm^{-1} to 10^4 cm^{-1}) results in changes of the *vibrational energy* of molecules. The energy change required for molecular vibrations is of the order of 1 to 100 kJ mol^{-1} . The changes in vibrational energy levels are accompanied by transitions between rotational levels also. Consequently, each line in vibrational structure is accompanied by the rotational fine structures. Evidently, such a spectrum, is known as *vibrational-rotational spectrum*. However, if the rotational fine structure is not considered, then absorption, is known as *vibrational spectrum*.

Requisite for IR spectra : All type of molecules cannot interact with IR radiation. *Only those molecules which exhibit change in dipole moment during a vibration* can exhibit infrared (IR) spectra. Evidently, *homonuclear diatomic molecules* (e.g., H_2 , O_2 , N_2 or Cl_2) do not show change in dipole moment during vibration. Consequently, these do not exhibit infrared spectra.

The quantum theory predicts that permitted vibrational energies (E_{vib}) are governed by the expression :

$$E_{\text{vib}} = \left(v + \frac{1}{2} \right) h\nu_0$$

where v is the vibrational quantum number, with possible values of 0, 1, 2, etc. and ν_0 is the fundamental frequency.

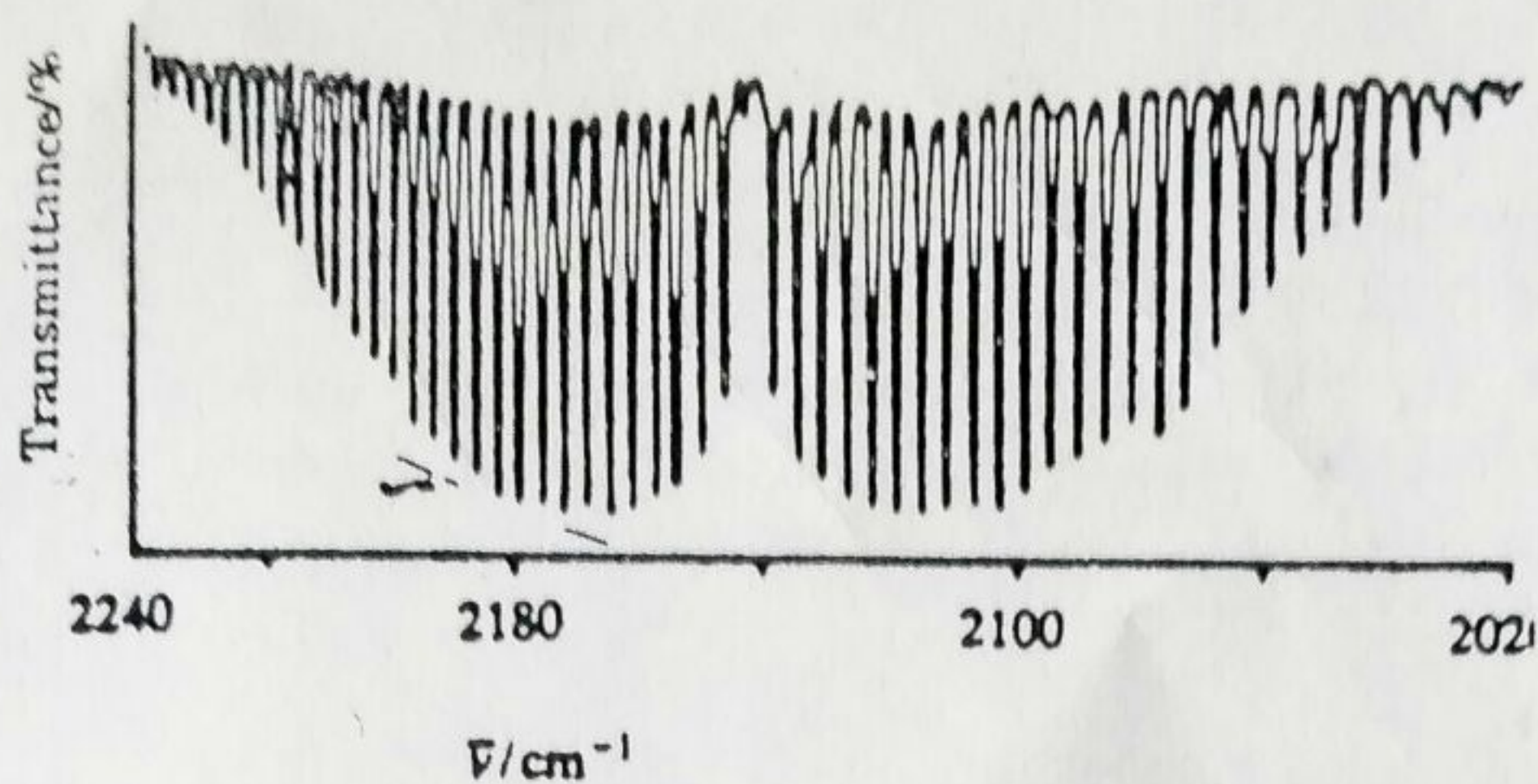
The lowest two energy levels, $v = 0$ and $v = 1$, possess E_{vib} values of $1/2 h\nu_0$ and $3/2 h\nu_0$, respectively, and the difference between them (i.e., the energy of the $v = 0 \rightarrow v = 1$) transition) is $h\nu_0$. The appropriate frequency of the electromagnetic radiation associated with this energy change, is the *fundamental frequency* (ν_0). It may be noted that even in the ground vibrational state, the molecule has the vibrational energy $= 1/2 h\nu_0$. This is called the *zero point energy*, which signifies that a molecule must always vibrate and can never be at rest. It may be pointed that *the vibrational energy levels are much more widely spaced than the rotational energy levels*.

When a molecule absorbs energy in the infrared region of electromagnetic spectrum, it can change its vibrational and rotational levels and these energy changes account for the features of IR spectrum. However, such a spectrum is much complicated, due to the rotational fine structure [see Fig. 6(a)]. But this complication can be avoided by taking IR spectrum for liquid or in solution or solid sample. Under such conditions, the rotational fine structure becomes buried and consequently, a broad peak [see Fig. 6(b)] is observed for a vibrational change only. Consequently, the interpretation of the IR spectra is made simple, even for polyatomic molecules.

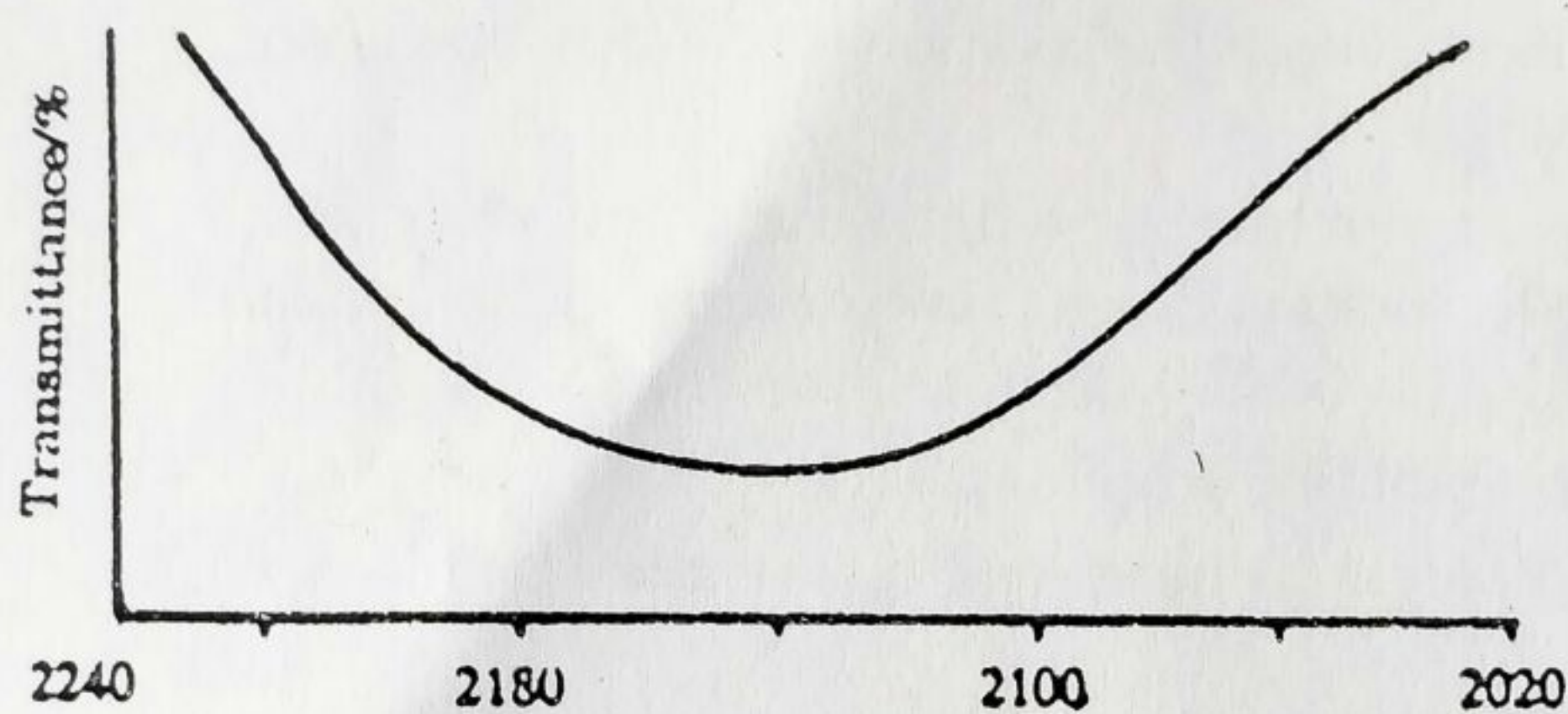
Vibrational spectra of a diatomic molecule : The vibrational motion of a diatomic molecule is akin to vibration of simple harmonic oscillator, whose restoring force (F) is proportional to the displacement x (Hooke's law), i.e.,

$$F \propto -x$$

$$F = -kx \quad \dots (i)$$



(a)



(b)

Fig. 6. IR spectra of CO :
 (a) in the gas phase,
 (b) in CCl₄ solution.

The frequency (ν) for the simple harmonic motion is given by :

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ s}^{-1} \quad \text{(ii)}$$

where k = force constant and μ = reduced mass.

In spectroscopy, the unit commonly used is wave number ($\bar{\nu}$). So dividing Eq. (ii) throughout by velocity (c), we get :

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad \text{(iii)}$$

Like all other molecular energies, vibration energy is *quantized*. Permitted vibrational energies can be calculated by using Schrodinger equation. Accordingly the energy associated with any vibration state is given by :

$$E = h\nu_0 \left(v + \frac{1}{2} \right) \text{ joules} \quad \text{(iv)}$$

where v is vibrational quantum number and ν_0 is fundamental vibrational frequency.

Suppose there is a transition from lower frequency vibrational level (v) to higher vibrational level (v'), then :

$$\begin{aligned} \Delta E_{vib} &= E' - E = \left(v' + \frac{1}{2} \right) h\nu - \left(v + \frac{1}{2} \right) h\nu \\ &= (v' - v) h\nu = \Delta v \cdot h\nu. \end{aligned} \quad \text{(v)}$$

For transitions between adjacent vibrational energy levels, we get by applying *selection rule*, $\Delta v = \pm 1$.

$$\therefore \text{Eq. (v) becomes : } \Delta E = h\nu \quad \dots(vi)$$

From Eqs. (iv) and (v), we get :

$$h\nu_0 = h\nu$$

$$\nu = \nu_0 \quad \dots(vii)$$

ie the frequency of the absorbed infrared radiation (ν) should be the **same** as the fundamental frequency (ν_0) of the molecule.

Selection rule for a harmonic vibrational transition : From the solution of Schrodinger equation, we get $\Delta v = \pm 1$, i.e., the increase or decrease in the vibrational quantum number is by one unit only. In other words, the energy difference between two vibrational levels involved in a transition would always be equal to spacing ($h\nu_0$). Consequently, all lines in the spectrum fall in the same place. (see Fig. 7)

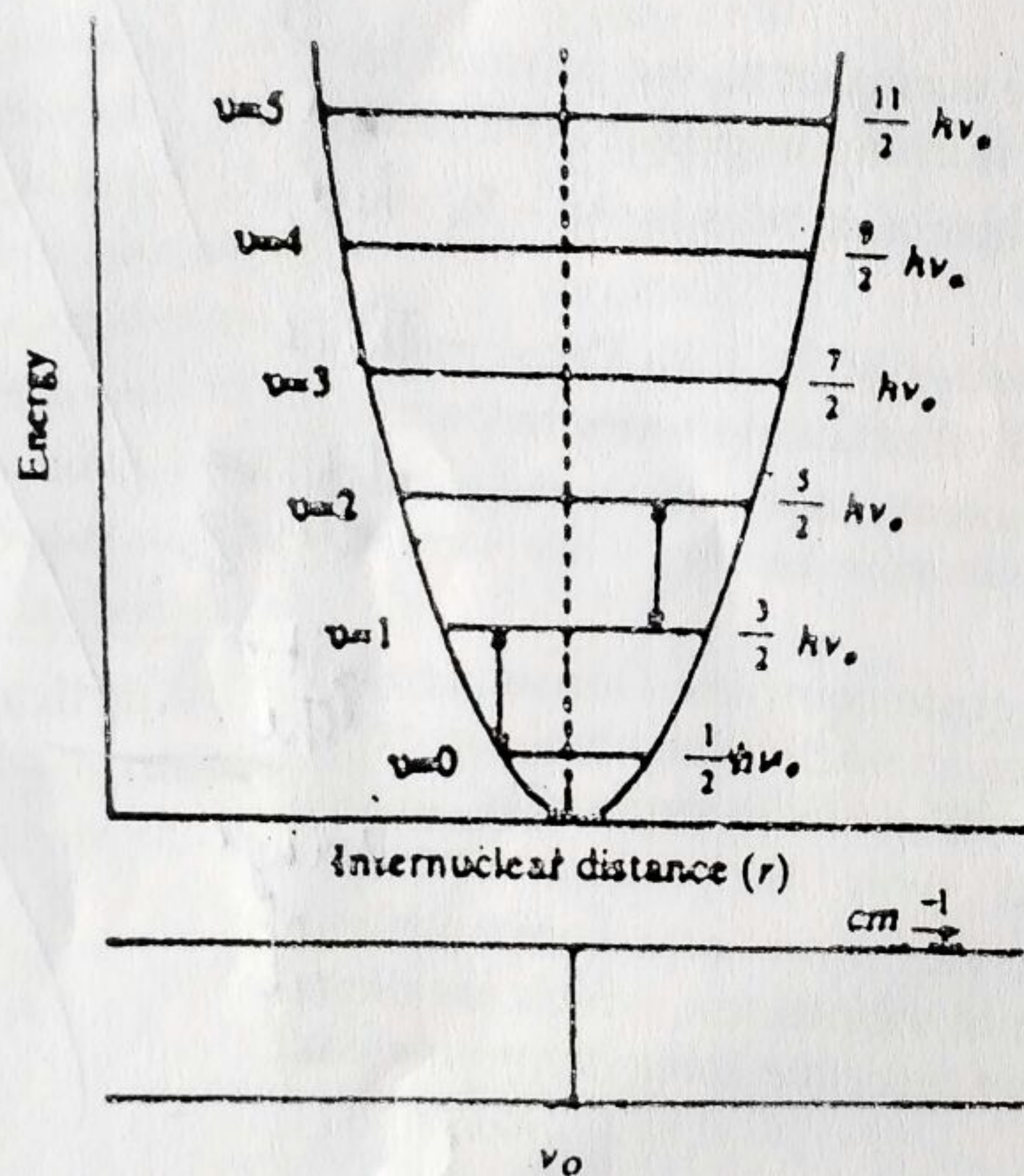


Fig. 7. The allowed vibrational energy levels and the transitions between them.

IR spectra of polyatomic molecules : For polyatomic molecules, the bonds can vibrate in several possible ways. These are known as *vibrational modes* and each vibration has an associated fundamental frequency (ν_0). For example, for linear molecule CO_2 , there are three fundamental frequencies :

- (i) ν_1 , the *symmetric stretching* mode involves no dipole change, so is "inactive" in the IR region, so no corresponding absorption of energy. In symmetric stretching, both bonds (a and b) are shortened or elongated to the same extent simultaneously.
- (ii) ν_2 , the *asymmetric stretching* mode involves variation of bond length, (i.e., involves dipole moment change). In asymmetric stretching, one of the bonds (a and b) is shortened ; while the other (b or a) elongated. The value of $\nu_2 = 2,349 \text{ cm}^{-1}$.

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(iii) ν_3 , the bending mode involves variation of bond angle (i.e., involves dipole moment change). The value of $\nu_3 = 667 \text{ cm}^{-1}$. The value of $\nu_3 < \nu_2$, because it is easier to bend a spring than to stretch.

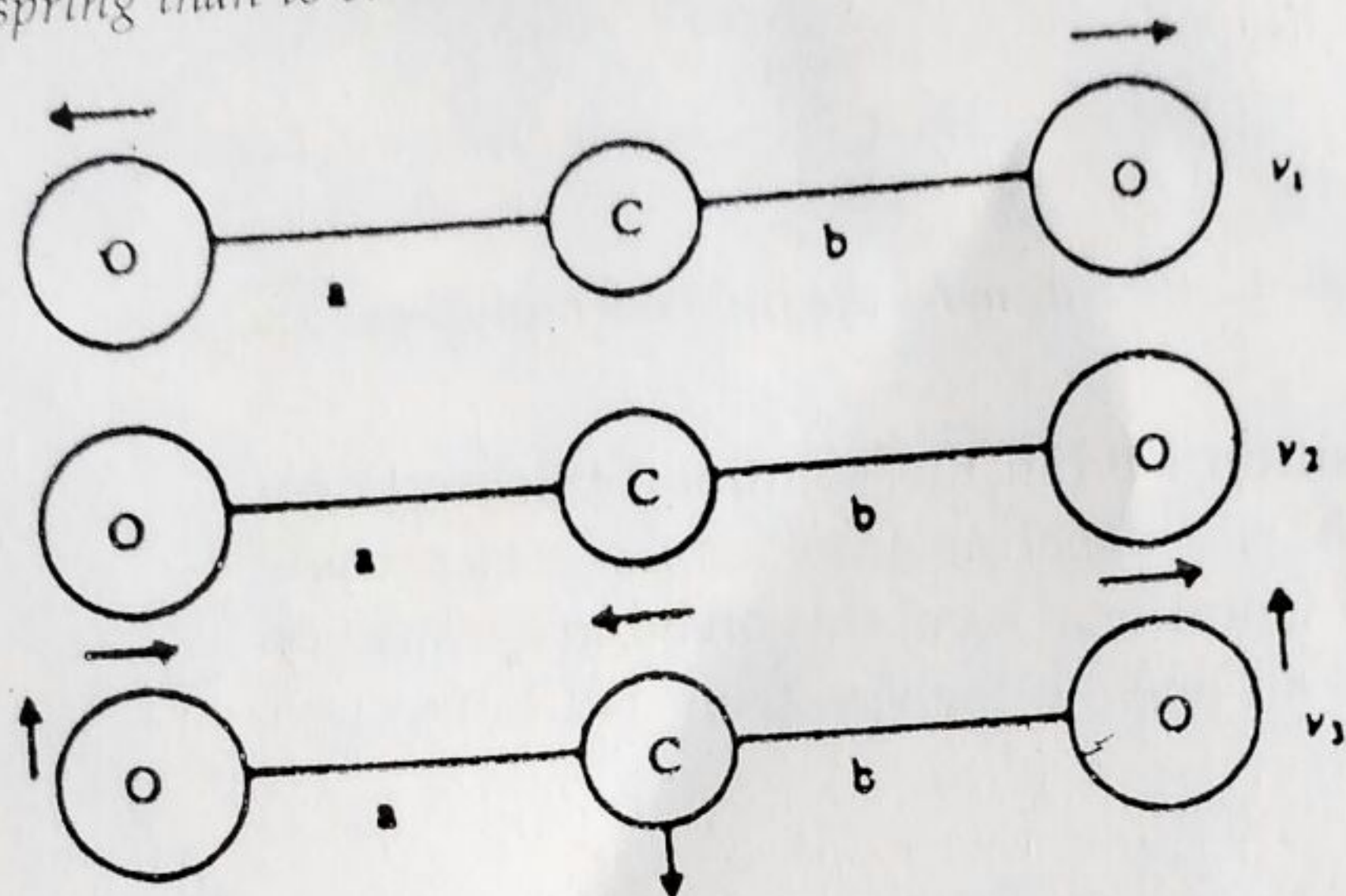


Fig. 8. Vibrational modes for carbon dioxide ($\text{O}=\text{C}=\text{O}$).

If it may be pointed that IR spectra for molecules become more complex as we proceed from diatomic to triatomic to polyatomic molecules, due to the increased number of possible vibrations.

(i) For a linear molecule, theoretically the number of vibrational modes is $(3n - 5)$, where n is the number of atoms in the molecule.

(ii) For a nonlinear molecule, the number of vibrational modes is $(3n - 6)$. Thus, methane ($n = 5$) and ethane ($n = 8$), theoretically possess 9 and 18 vibrational modes respectively.

Note: Actual number of observed vibration bands for a molecule is, generally, different from the calculated number. This is because overtone or combination of overtones may increase the number of vibration bands; while some bands may be obscured by other bands.

Group frequencies: IR spectra for polyatomic molecules is quite complex. Consequently, it may not be easy to assign mode for every vibration band. However, in such a case, we can get the most important information by recognizing the group frequencies. Organic compounds, usually show complex spectra in which many bands are spread over the wide scan-range ($4,000 - 600 \text{ cm}^{-1}$), but each band is associated with a particular vibration (or a combination of vibrations). The complexity of the spectra reflects a large number of vibrations, which are dependent on the structure of the molecule. To a certain extent, we can associate some absorptions

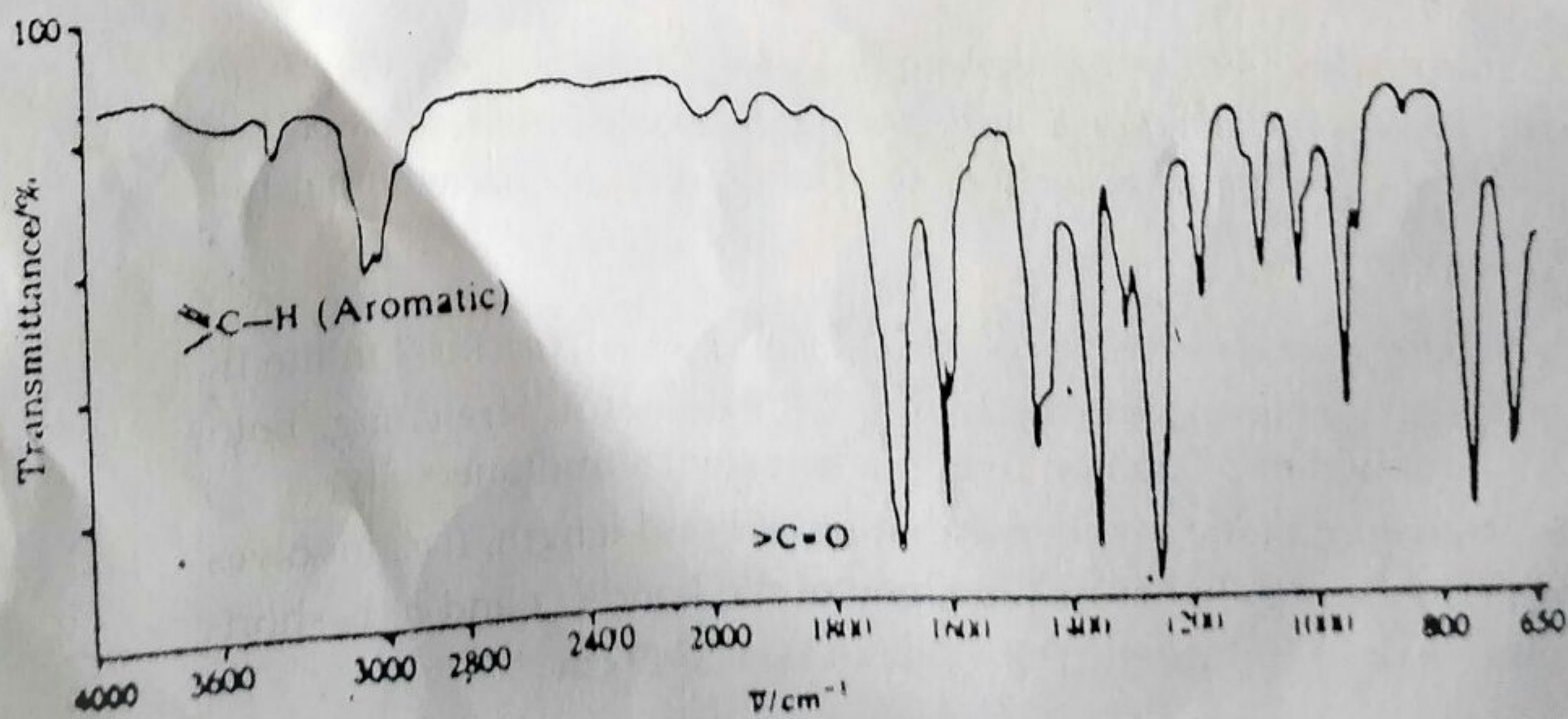


Fig. 9. IR spectrum of acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$).

stretching or bending vibrations characteristic of particular functional group in any molecule. Such frequencies, are known as group frequencies. For example, the absorptions at $3,050\text{ cm}^{-1}$ and $1,700\text{ cm}^{-1}$ in the IR spectrum of acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) are typical of the stretching modes of C-H (aromatic) and C=O groups respectively. Thus, the IR spectra permits recognition of the types of functional groups present in organic molecules.

Note : The group frequencies remain constant from molecule to molecule, because : (a) the value of force constant for a particular bond is constant, and (b) the reduced mass (μ) is nearly constant in big organic molecules.

Table 4. Characteristic infrared absorption frequencies for different groups.

Bond	Type of compound	Frequency (cm^{-1})	Bond	Type of compound	Frequency (cm^{-1})
C-H	Aliphatic	2,800 - 3,000	C=O	Esters (aromatic)	-1,230 - 1,650
C-H	Aromatic (Ar-H)	3,000 - 3,100	C=O	Acids	- 1,650
C-H	Cycloaliphatic	2,920 - 3,100	C=O	Amides	1,790 - 1800
C-H	Olefinic	3,000 - 3,100	O-H	Acid chloride	- 3,045
C-H	Acetylenic	- 3,300	O-H	Primary alcohols	- 3,630
C-C	Open chain aliphatic	750 - 1,100	O-H	Secondary alcohols	- 3,620
C=C	Aromatic	1,460 - 1,600	O-H	Tertiary alcohols	- 3,610
C=C	Olefinic	1,620 - 1,670	N-H	Phenols	- 3,500
C≡C	Acetylenic	2,100 - 2,250	N-H	Primary amines	- 3,450
C=O	Aldehyde (aliphatic)	1,720 - 1,740	C-N	Secondary amines	1,180 - 1,360
C=O	Aldehydes (aromatic)	1,495 - 1,715	C=N	Amines	1,650
C=O	Ketones (aliphatic)	1,705 - 1,705	C≡N	—	2,210 - 2,260
C=O	Ketones (aromatic)	1,720 - 1740	-NO ₂	Nitro compounds	1,565 - 1,585
C=O	Aldehydes (aliphatic)	1,720 - 1,740	C-Cl	—	600 - 700
C=O	Aldehydes (aromatic)	1,695 - 1,715	C-Br	—	500 - 600
C=O	Esters (aliphatic)	1,725 - 1,745	C-F	—	1,000 - 1,350

Applications for IR spectroscopy : (1) In establishing the identity of the compounds : The IR spectrum of the compound is compared with that of known compounds and from the resem-

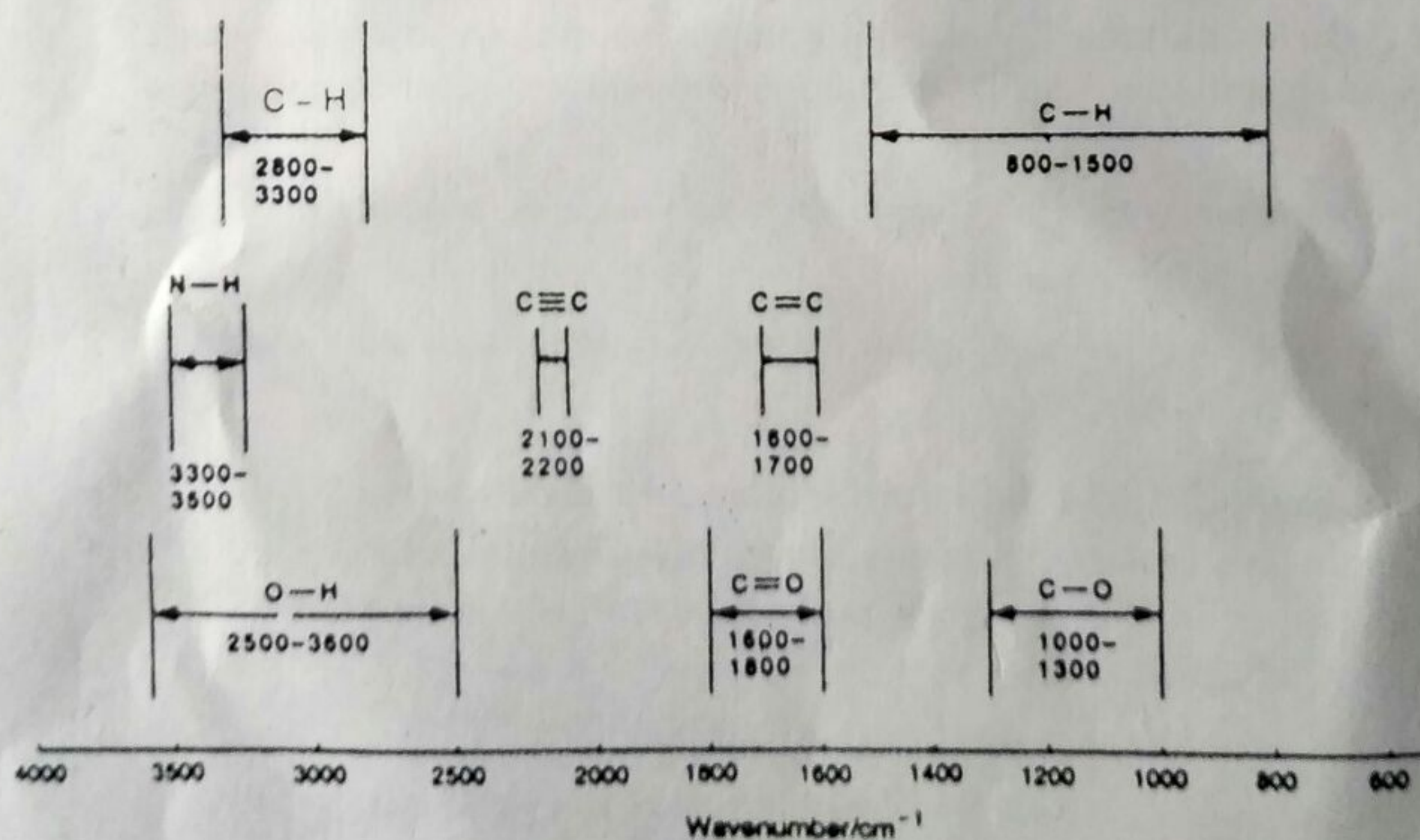


Fig. 10. The diagram shows where some of the most common groups appear on an infrared spectrum.

blance of the two spectra, the nature of the compound can be established. This is because a particular group of atoms give rise to characteristic absorption bands in the IR spectrum, i.e., a particular group strongly absorbs light of certain wavelength in IR spectrum, no matter to which compound it belongs. For example, IR spectra of both benzaldehyde and phenyl methyl ketone show pronounced absorption peak at $1,700\text{ cm}^{-1}$. This is indicative of the presence of $\text{C}=\text{O}$ group in both the compounds.

(2) *In detecting impurities in a sample* : IR spectra of impure sample will show some extra absorption bands. By comparison with IR spectra of pure compound, presence of impurity can be detected.

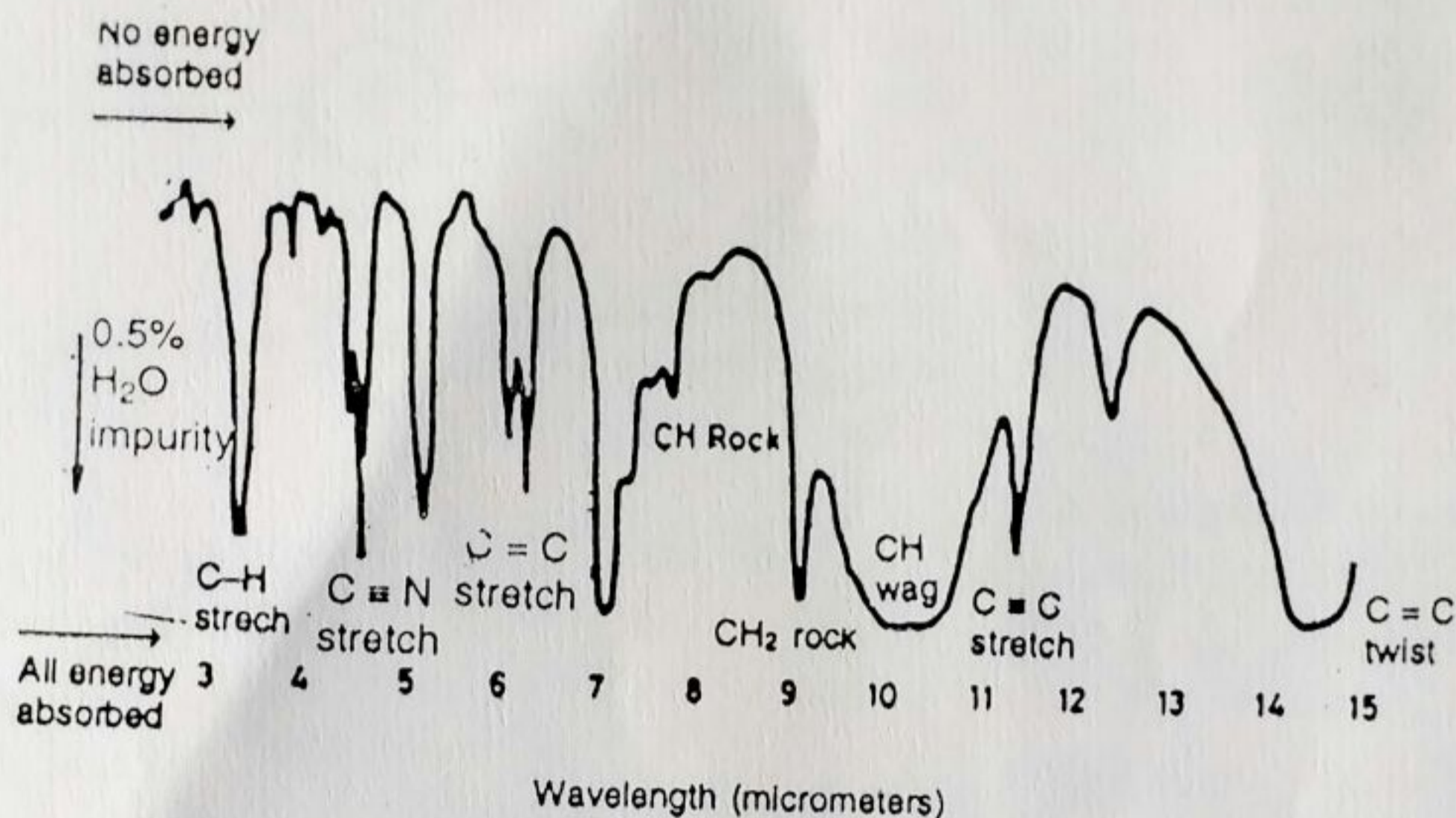


Fig. 11. Infrared spectrum of acrylonitrile, $\text{CH}_2 = \text{CHCN}$, absorption bands occurs at those wavelengths, where the frequencies of infrared radiation correspond to the natural vibrational frequencies of the acrylonitrile molecule.

(3) *To ascertain hydrogen bonding in a molecule* : Generally, it is not possible to distinguish between *intra* and *inter* molecular hydrogen bonding. This can be ascertained by taking a series of IR spectra of the compound at different dilutions. As the dilution is increased, the absorption band due to intermolecular hydrogen bonding diminishes ; while that due to intramolecular hydrogen bonding remains unchanged.

(4) *Provides valuable informations of molecular symmetry, dipole moments, bond lengths.*

(5) *Distinguishing positional isomers of a compound.*

(6) IR spectra may also be employed for rapid quantitative analysis of a mixture of compounds, in pollution detection, in milk analysis, etc.

Examples of IR spectra : (i) *Benzene (C_6H_6)* : Spectrum of benzene is shown in Fig. 12, which is fairly complex, because absorption due to the the benzene molecule as a whole occur in addition to those characteristics of particular bonds. Various peaks in the spectrum of certain vibrations of the molecule and the major one have been marked.

Note : IR spectra are normally plots of percentage transmittance and *not* absorbance (the two are related *inversely*). In addition, the wavenumber ($\bar{\nu}$), which is the reciprocal of the wavelength (in cm), is employed and this quantity is related directly to the *energy of the transition* (i.e., $\bar{\nu} \propto E$).

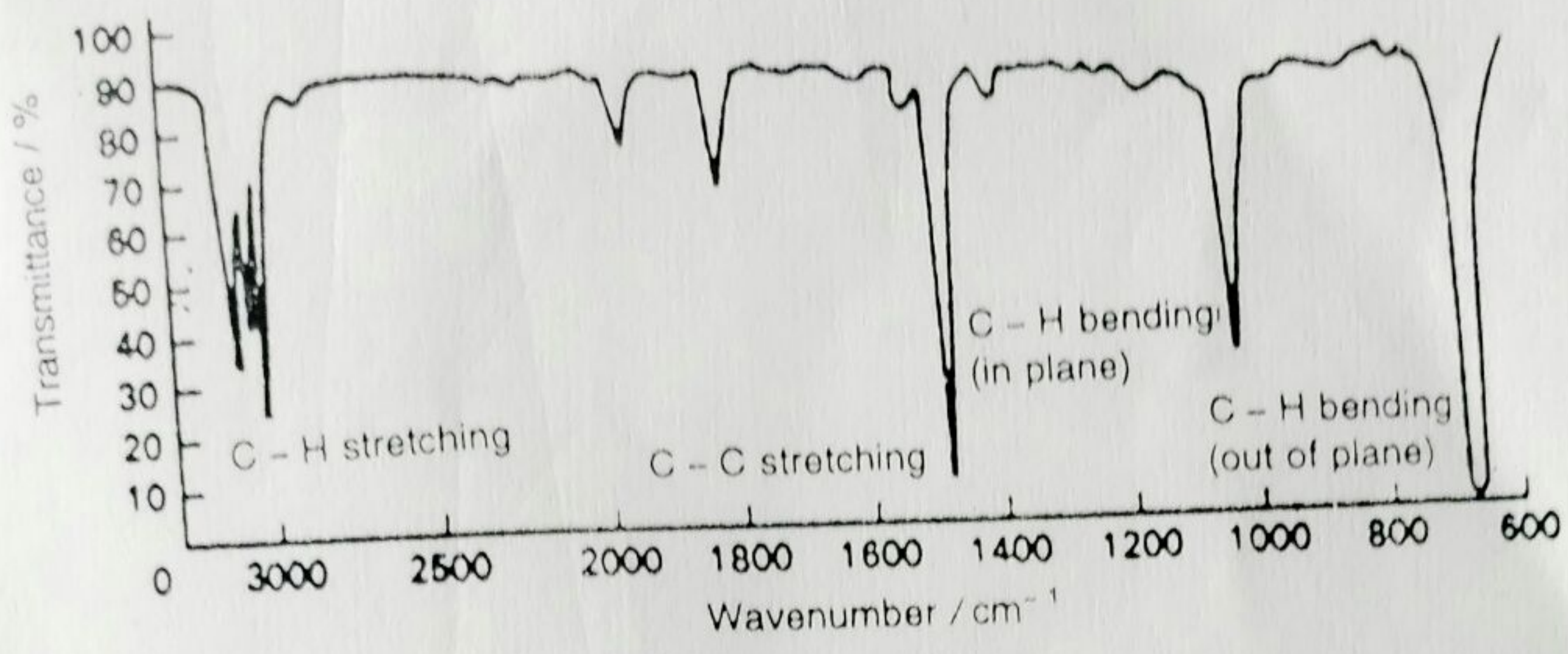


Fig. 12. IR spectrum of benzene (in liquid film)

(ii) Propanone (CH_3COCH_3) spectrum is shown in Fig. 13, with characteristic peaks marked.

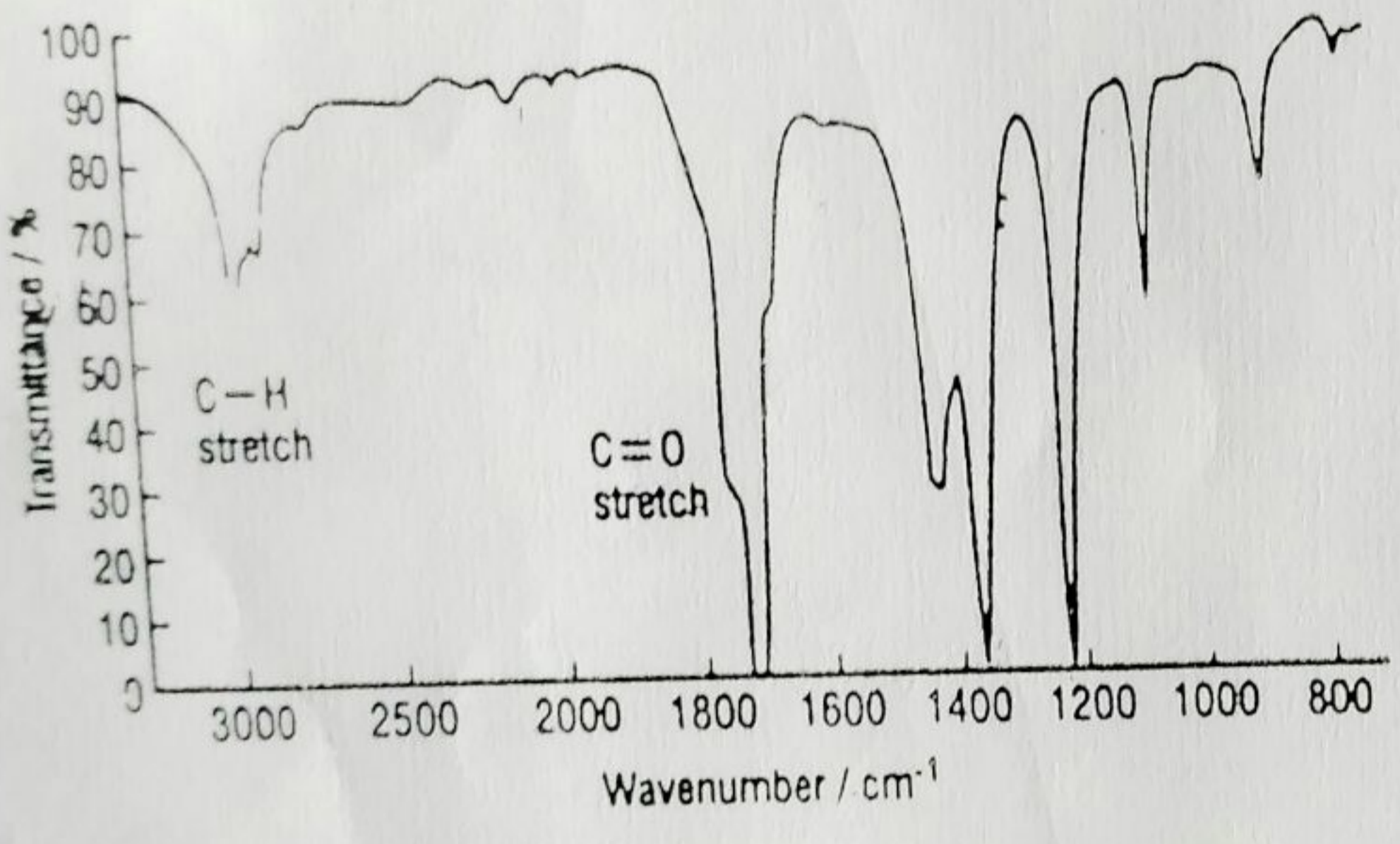


Fig. 13. IR spectrum of propanone.

(iii) Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) spectrum is shown in Fig. 14 with three characteristic peaks.

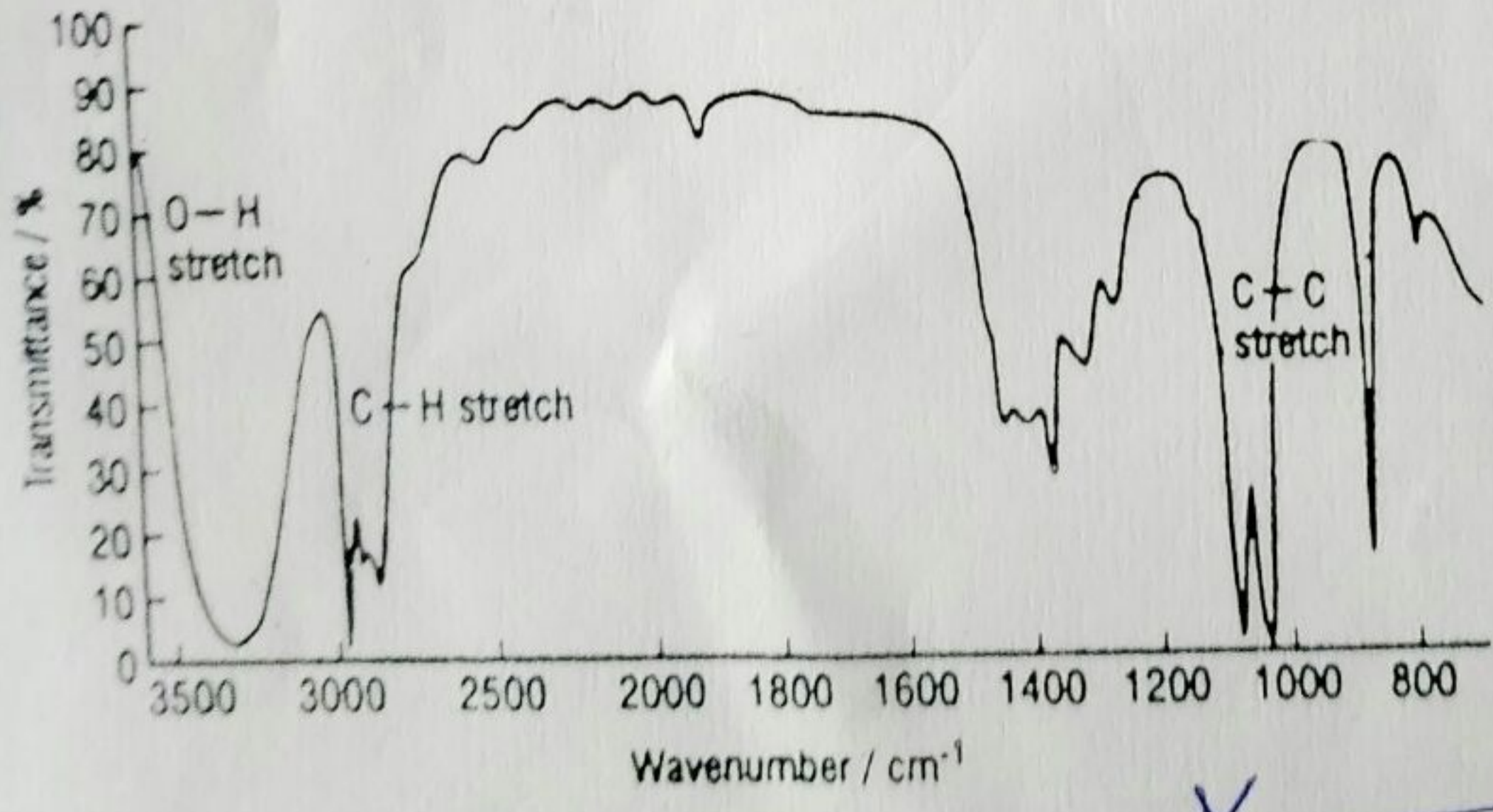


Fig. 14. IR spectrum of ethanol.

(iv) Pent-1-ene ($\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}_2$). The bands appearing at 3080 cm⁻¹, 2950 cm⁻¹ and 1640 cm⁻¹ are due to =C-H, -C-H and -C=C- stretching, respectively. (see Fig. 15)