Chapter # 24

ANALYTICAL CHEMISTRY

Modern Methods of Analysis

Spectroscopy

is the branch of science which describes. the interactions of electromagnetic radiation with matter is known as spectroscopy.
It involves instrumentation to examine the radiations emitted or absorbed by chemicals giving information about their molecular structure.

Electromagnetic Radiation

- It is form of energy commonly known as radiation energy such as light energy.
According to quantum mechanics, electromagnetic radiation has properties of both a wave and a particle, like discrete packet of energy, called quanta or photons.

- Cosmic rays, gamma rays, X-rays, ultraviolet, visible light, infrared rays, microwaves and radio waves, all are EM radiation.
- Electromagnetic spectrum include wide range of wavelengths each having different characteristics.
- The whole EM spectrum can be divided into regions by following parameters :
  - Wavelength
  - frequency
  - wave number
  - energy.

Spectrum region	Wavelength	Frequency (Hz)	Wavenumber (cm^{-1})	Energy (J)
Cosmic rays	10^{-4}-10^{-3} A°	3×10^{22} - 3×10^{21}	10^{12}—10^{11}	2×10^{-11}
Gamma rays	10^{-1} - 10^{-4} A°	3×10^{19}	10^{9}	1.3×10^{-12}
X-rays	100 A°	3×10^{16}	10^{6}	2×10^{-17}
Ultraviolet	400 nm	7.5×10^{14}	2.5×10^{4}	5×10^{-19}
Visible	800 nm	3.8×10^{14}	1.3×10^{4}	2.5×10^{-19}
Infrared	10^{3} μm	3×10^{11}	10	2×10^{-22}
Microwave	10^{6} μm (1m)	3×10^{8}	10^{-2}	2×10^{-25}
Radio wave	10^{3} m	3×10^{5}	10^{-5}	2×10^{-28}

Principle of Spectroscopy

Different molecules absorb different amount of radiations when they interact with them.

★ Lower energy radiation may cause;

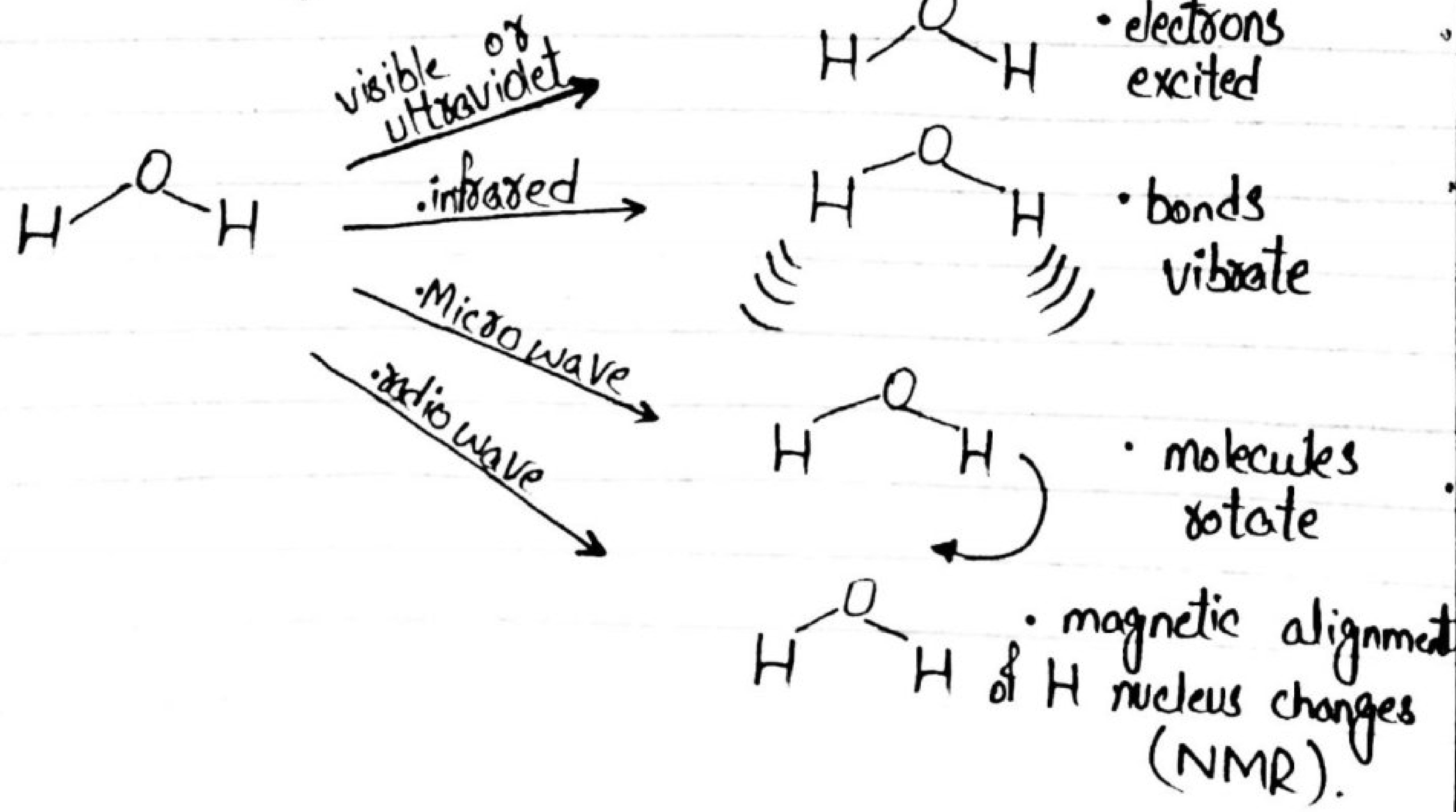
i) Molecular rotation

ii) Bond Vibration

★ Higher energy radiation may cause;

i) Electronic excitation

ii) Bond cleavage



★ The absorption of radiation is selective for a particular transition is selective for a particular transition which depends upon the structure of molecule.

→ The wavelength of absorption spectra of known compound (reference compound) are correlated with the wavelengths of absorption spectra of unknown compounds. The information is then used to determine structure of unknown compounds.

Spectrophotometer

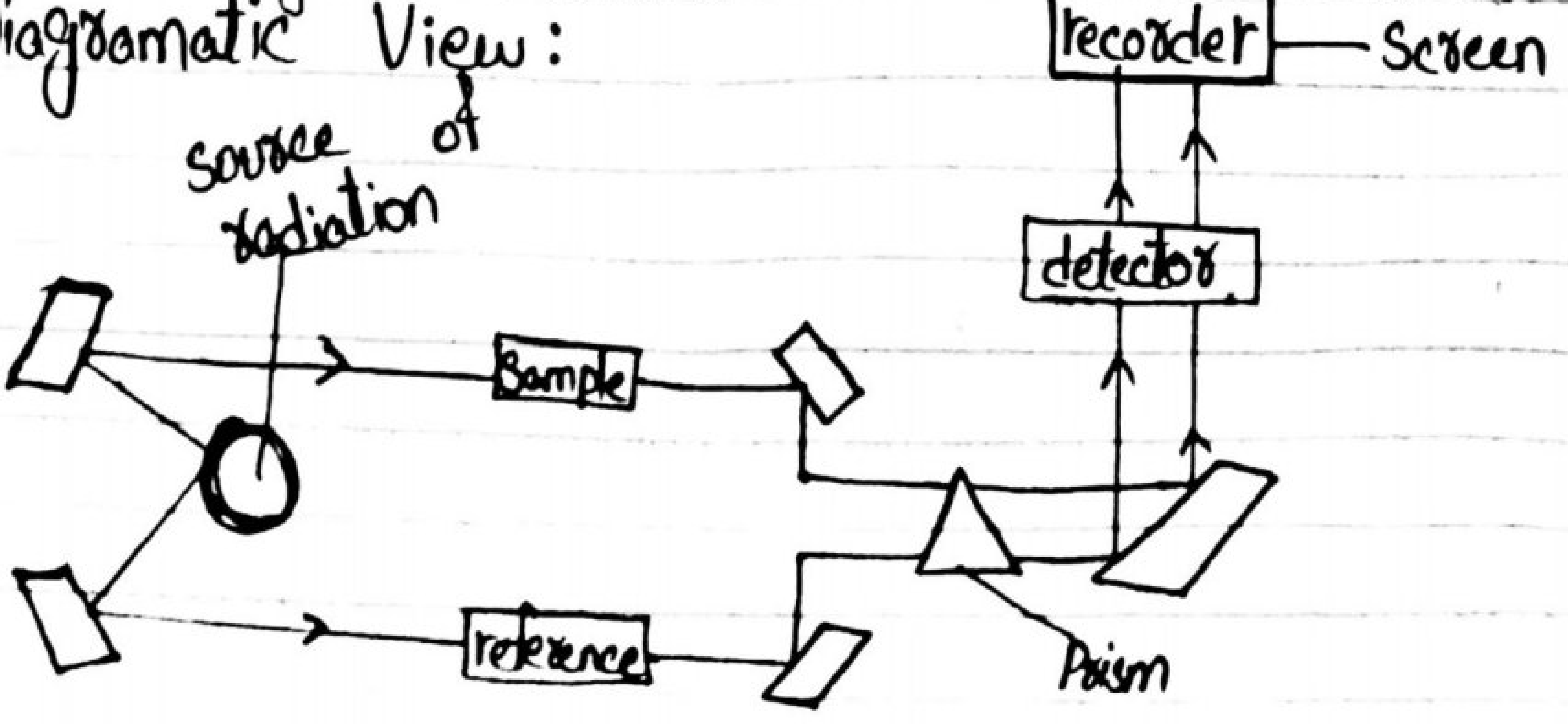
is a instrument that is used to measure the amount of electromagnetic radiation absorbed by a compound.

Construction:

It consists of;

- A light source of radiation
- A sample cuvette
- A monochromator (prism) to select the desired wavelength of radiations.
- A detector to detect the radiation absorbed by sample.
- The result is recorded on a spectograph against the wavelength or wave number.

Diagramatic View:



Infrared Spectroscopy (IR)

This technique or process involves the use of Infrared radiations.

- IR radiation have sufficient energy to vibrate bonds in a molecule.

★ Their wavelength ranges from : 2.5 - 16 μm (4000 to 625 cm^{-1}).

A molecule is made up of atoms that undergo continuous vibration and rotation. IR radiations having low energy affect the vibrational kinetic energy of atoms in a molecule. During vibration small displacement of atoms from their mean position occurs and causes a change in dipole moment of a molecule. This changed dipole interacts with electric field of IR radiations and increase the rate of vibration and rotation. Different bonds absorb radiations of different frequencies.

→ Polar molecules are IR active.

IR absorption spectrum is used to;

- Identify bonds and functional groups.
- Identify structure of organic compounds.

Types of Vibrations:

There are two types of vibrations.

(i). Stretching vibrations:

In this type of vibration:

→ Bond angle does not change.

→ Bond length changes.

(ii) **Bending vibrations:**

In this type of vibration:

→ Bond angle changes.

→ Bond length remains same.

Interpretation of IR Spectrum:

IR spectrum shows downward peaks which correspond to absorbance (A) or percent transmittance (% T) as ordinate (y-axis) against wavelength (λ) or wave no. ($\bar{\nu}$) in cm^{-1} as abscissa (x-axis).

★ The strength of peak is the characteristic of the bond itself, not of number of bonds.

Types of IR Regions:

These are two important absorption regions in IR spectrum:

1. Finger print region (600 to 1500 cm^{-1})

The absorption in this region is a characteristic of a compound. Different compounds will give different absorption peaks in this region. Hence this region is called fingerprint region.

→ This region is used to identify the structure of organic compounds.

2. Functional group region (1500 to 4000 cm^{-1})

Different functional groups show absorption in this region.

Bond	Compound it is in	Absorption/ cm^{-1}	Intensity (M= Med, Strong)
C—H	Alkanes, alkenes, arenes	2840 to 3095	M/S
C=C	alkenes	1610 to 1680	M
C=O	Aldehydes, ketones, acids,	1680 to 1750	S
=	esters		"
C—O	Alcohols, ethers, esters	1000 to 1300	S
C≡N	nitriles	2200 to 2280	M
C-Cl	Chloro compound	700 to 800	S
O-H	free	3580 to 3670	S
	Hydrogen-bonded in alcohols, phenols	3200 to 3550	S(broad)
	Hydrogen-bonded in acids	2500 to 3300	M(broad)
N—H	Primary amines	3100 to 3500	S

For example:

The IR spectrum of propanone.

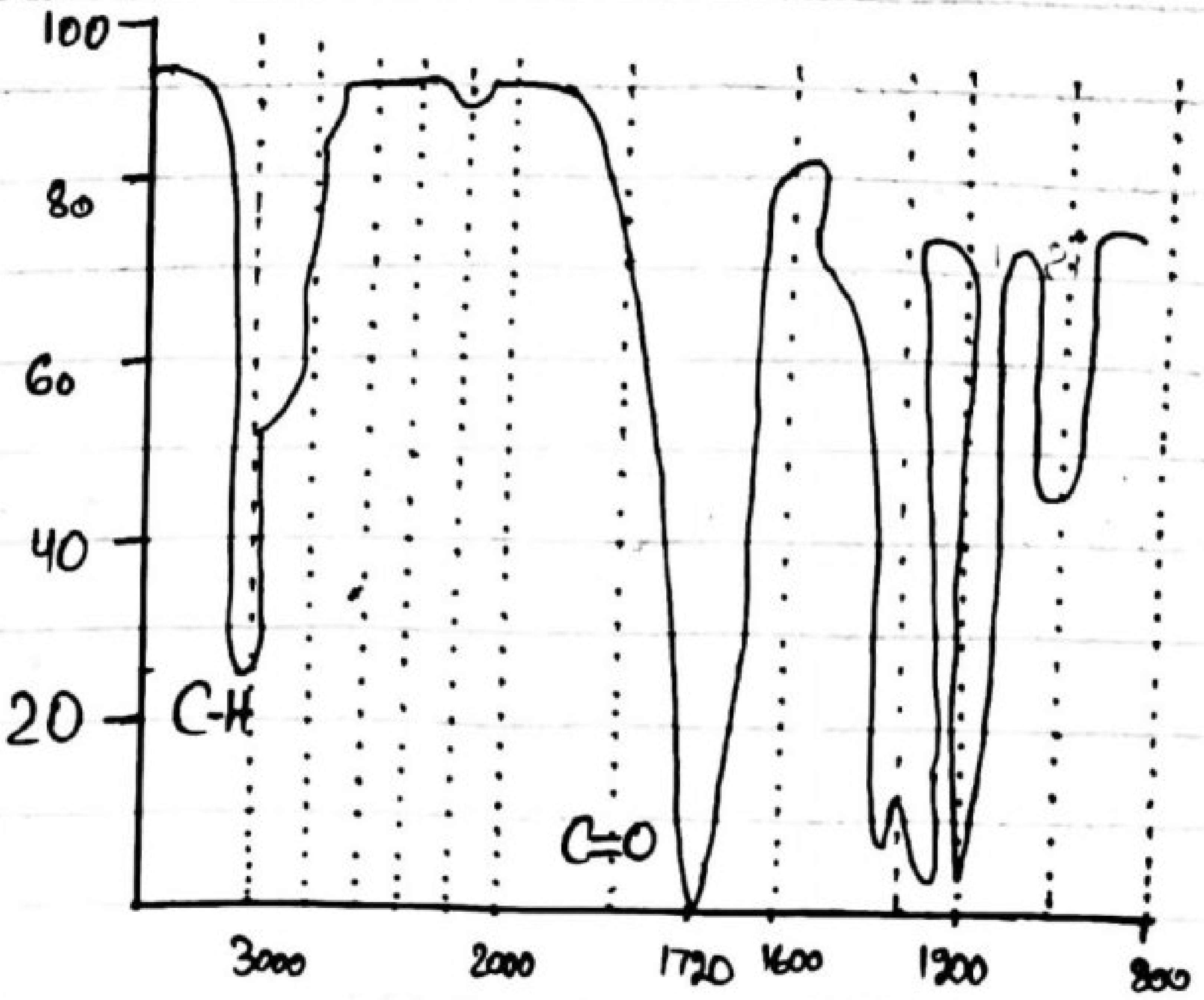


Fig: The infrared spectrum of propanone

In the spectrum of propanone the strong peak at 1720 cm^{-1} corresponds to the C=O bond. The weaker absorption at 3000 cm^{-1} corresponds to the C-H bond. This peak is weaker even though there are more H atoms in the molecule.

Visible and Ultraviolet Spectroscopy

- It is also known as *electronic spectroscopy*.
- It involves the use of UV & visible radiations having range of **200 to 800 nm** in the EM Spectrum.
- It involves the transition of electrons with in the molecule or ion from lower to higher energy levels or vice versa by absorption or emission of UV/visible radiation.

Importance:

It determines the following:

- presence of unsaturation
- extent of conjugation in a molecule.

Principle:

Absorption of UV-radiation causes the excitation of electrons from lower energy level to higher energy level. (from HOMO to LUMO).

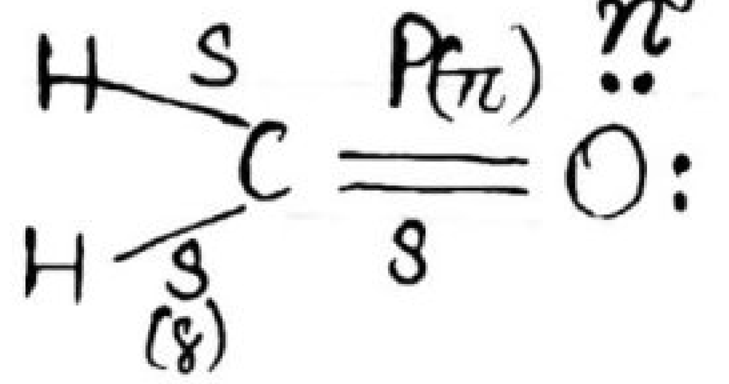
Kinds of electrons

There are **three** kinds of electrons

(i) σ electrons (ii) π electrons

(iii) Lone pair of electrons (non-bonding pair denoted by n)

The higher energy levels are antibonding molecular orbitals. i.e π^* & σ^*



Types of electronic transition

i) $\sigma \rightarrow \sigma^*$ transition:

The UV radiation is not so energetic to excite electrons from σ to σ^*. Because these electrons are strongly held together.
Such transition (excitation of σ electrons) require energy in the range of **150 nm** which is not available in UV-region.

★ It occurs in vacuum UV region. The term vacuum UV region ranges below **200 nm**.

ii) $n \rightarrow \sigma^*$ transition:

This type of transition occurs in those compounds which contain **non-bonding electron pair.**

For example:

Compounds containing nitrogen, oxygen, sulphur and chlorine show type of transition.

iii) $\pi \rightarrow \pi^*$ transition:

This type of transition occurs in unsaturated organic compounds.

For example:

$$=C,\ C\equiv C,\ C\equiv N,\ N=N,\ C=O$$

etc show this type of transition.

iv) $n \rightarrow \pi^*$ transition:

This type of transition occurs in compounds containing non bonding electron pair on hetroatoms.

- These compounds must include unsaturation.

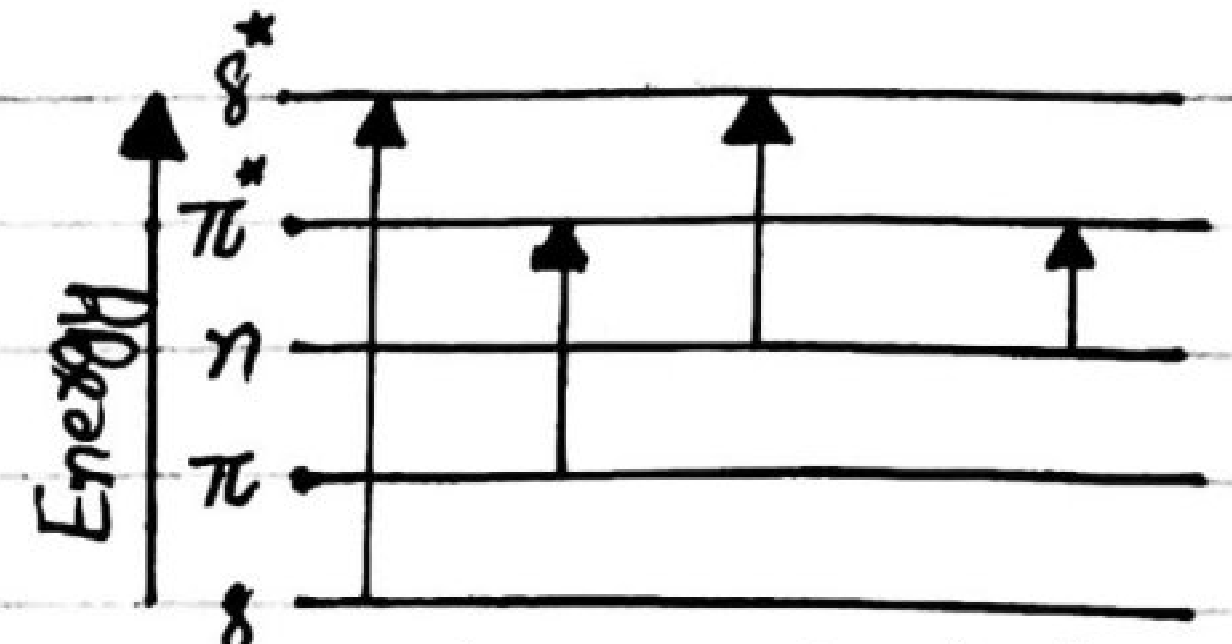
→ The electrons get excited to π^* antibonding orbitals.

→ This type of transition requires least energy and occurs at longer wavelength.

Relative energy Order

The relative energy for three electronic transitions detectable by UV spectrophotometer in order of increasing energy is:

$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^*$$



Relative energy changes involved in various electronic transitions.

Nuclear Magnetic Resonance (NMR)

There are two types of nuclei.

i) Nuclei which contain odd number of protons or neutrons or both have spin quantum number of $\frac{1}{2}$.

→ They are magnetically active.
→ Like electrons, these nucleus also spin about an axis.
→ They behave as tiny magnet.

Examples:

C^{13}, N^{15}, F^{19} and P^{31}.

ii) Nuclei having even number of protons and neutrons have zero spin and zero magnetic moment.

→ These nuclei are magnetically inactive.
→ They do not spin about an axis as they have zero spin.

Examples:

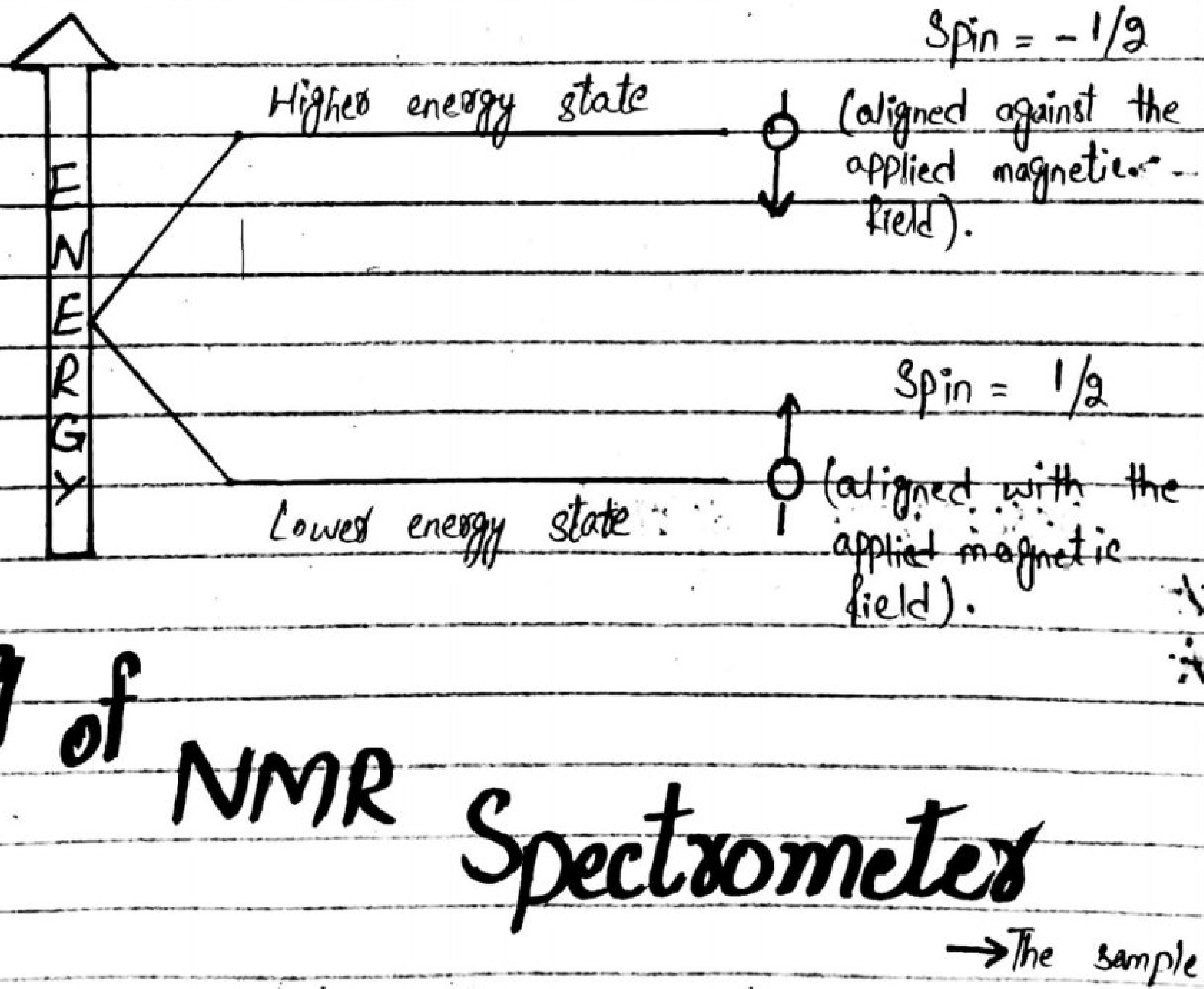
C^{12}, O^{16} etc.

The spin states of a nucleus have equal energies in the **absence of magnetic field**. When magnetic field is applied, the magnetic moments of different nuclei may either **align with** or **oppose** the applied magnetic field. As a result, the spin is split up into two energy levels having nuclear spin of $+\frac{1}{2}$ with low energy and $-\frac{1}{2}$ with high energy.

The energy difference between the two spin states is **very small** and lies within range of **radio frequency**.

Spin flipping:-

In NMR spectrometer, the sample is placed in an external magnetic field and radio waves swept across it. At particular combination of magnetic field and frequency of radio waves, **some protons change their spin state** i.e. **they "flip over"**. This is called spin flipping.



Working of NMR Spectrometer

→ The sample is dissolved in a solvent having no protons, such as tetrachloromethane (CCl_4).

→ A small amount of tetramethyl silane $(CH_3)_4Si$, commonly known as TMS, is mixed with sample to act as reference sample.

Scanned with CamScanner

★ TMS is used as a reference due to following properties:

• all 12 protons are equivalent (are in same enviroment).
• It produce a strong field due to combined effect of 12 equivalent protons.
• It has a chemical shift of zero (0).
• It producies peak at $\delta = 0$.

→ The tube containing this mixture is suspended between the poles of electromagnet.
→ When no energy is absorbed by the sample, the detector does not pickup any energy from the oscillator.
→ However, when the sample absorbs a definite amount of energy from the RF transmitter, the proton flip over. This induces a signal in the detector, which is indicated by an increase of current in the RF detector. This is recorded as resonance signal.
★ Only small amount of sample is enough to produce an NMR spectrum.

Proton (^1H) NMR spectra of organic compounds

- If all protons in a molecule are similar, as in CH_4 and C_6H_6, their spin states are equal and produce a single peak in NMR spectrum.
- Protons in different environments require slightly different magnetic field to resonate. So different protons show different peaks.

★ Area under the curve is proportional to number of protons involved.

Chemical Shift (δ):

The separation of absorption position of particular proton from the absorption position of the reference standard is called chemical shift.

→ Chemical shift is denoted by δ (delta).

→ Chemical shifts are quoted in parts per million of the applied field.

→ Protons of organic molecules have range of chemical shift between 0.0 – 10 δ.

★ Highly shielded protons require stronger field to resonate and have low chemical shifts.

e.g:-

NMR Spectrum of Ethanol

Low-Resolution NMR spectrum of Ethanol

NMR spectrum of ethanol consists of three peaks at different absorption and of different areas as shown.
The areas under the peaks are in the ratio 1:2:3.

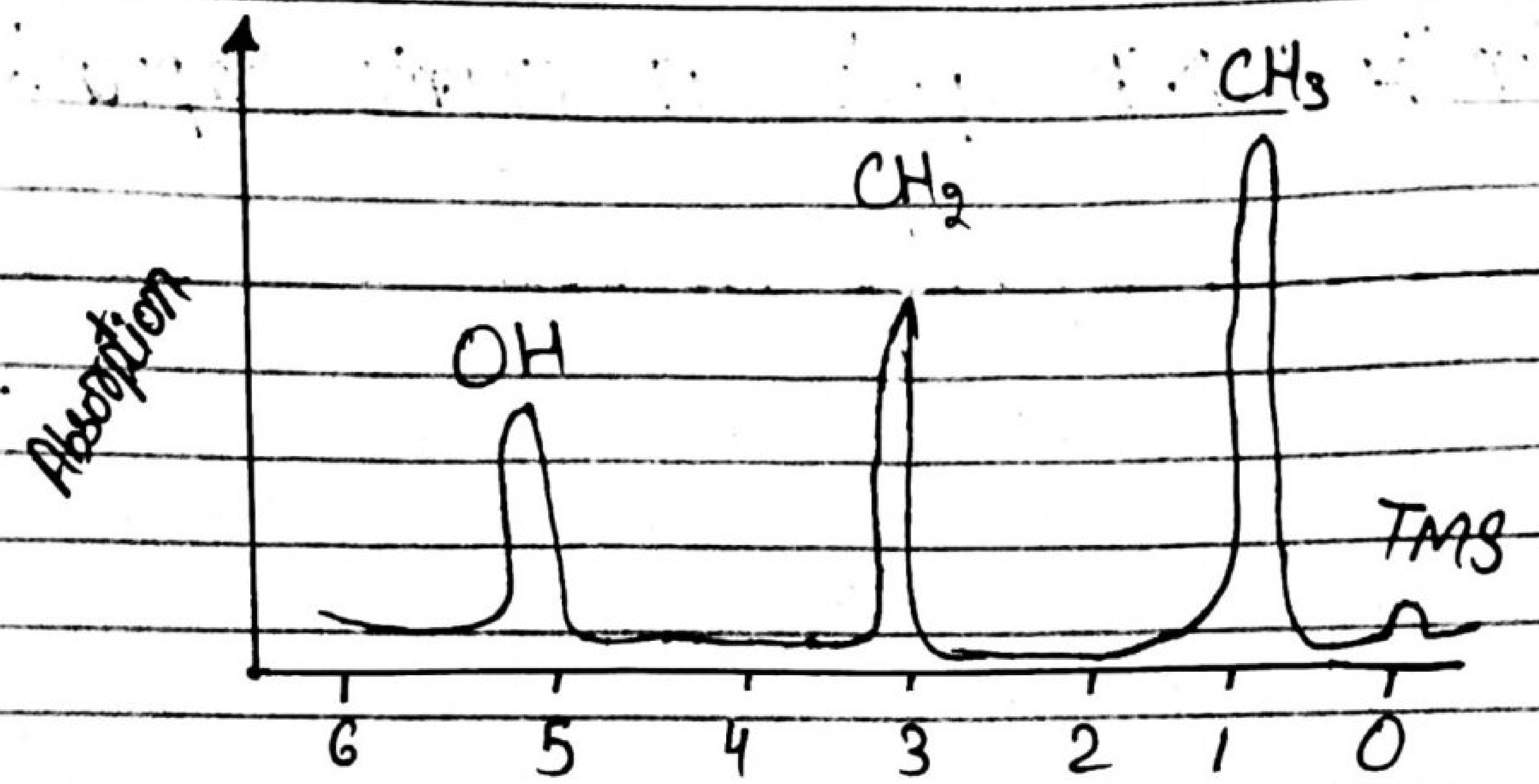


Fig: The proton NMR spectrum of Ethanol

The presence of three peaks is explained by the fact that one proton in the -OH group, the two protons in the CH_2 group and the three protons in the CH_3 group are in different chemical enviroments.
Hence, they require different strength of magnetic field to resonate.

Atomic Emission Spectroscopy

Introduction:

Atomic emission spectroscopy is related to electronic transitions in atoms which use an excitation source like flames, sparks.

- It is related to atoms.
- It is concerned with characteristic radiation that are produced by excitation of atoms.
- These excited atoms emit radiations in the form of discrete wavelengths of light called **spectral lines** while returning to lower energy states.

Principle

The source (sparks, flames etc) vaporizes the sample and causes electronic excitation of elementary particles in the gas.

- Excited molecules in the gas phase emit band spectra.

★ A molecule in an excited state of energy E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy $h\nu$ is emitted.

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

Types of Atomic or Line Spectrum

Spectrum may be classified as;

1. Atomic or Line Emission Spectrum
2. Atomic Absorption Spectrum

1. Atomic or Line Emission Spectrum

When an element is vaporized in a flame, or in an electric arc or in a discharge tube, it emits a characteristic colour.

- In Line emission spectrum, coloured lines are separated by dark spaces.

This type of separation is called line emission spectrum.

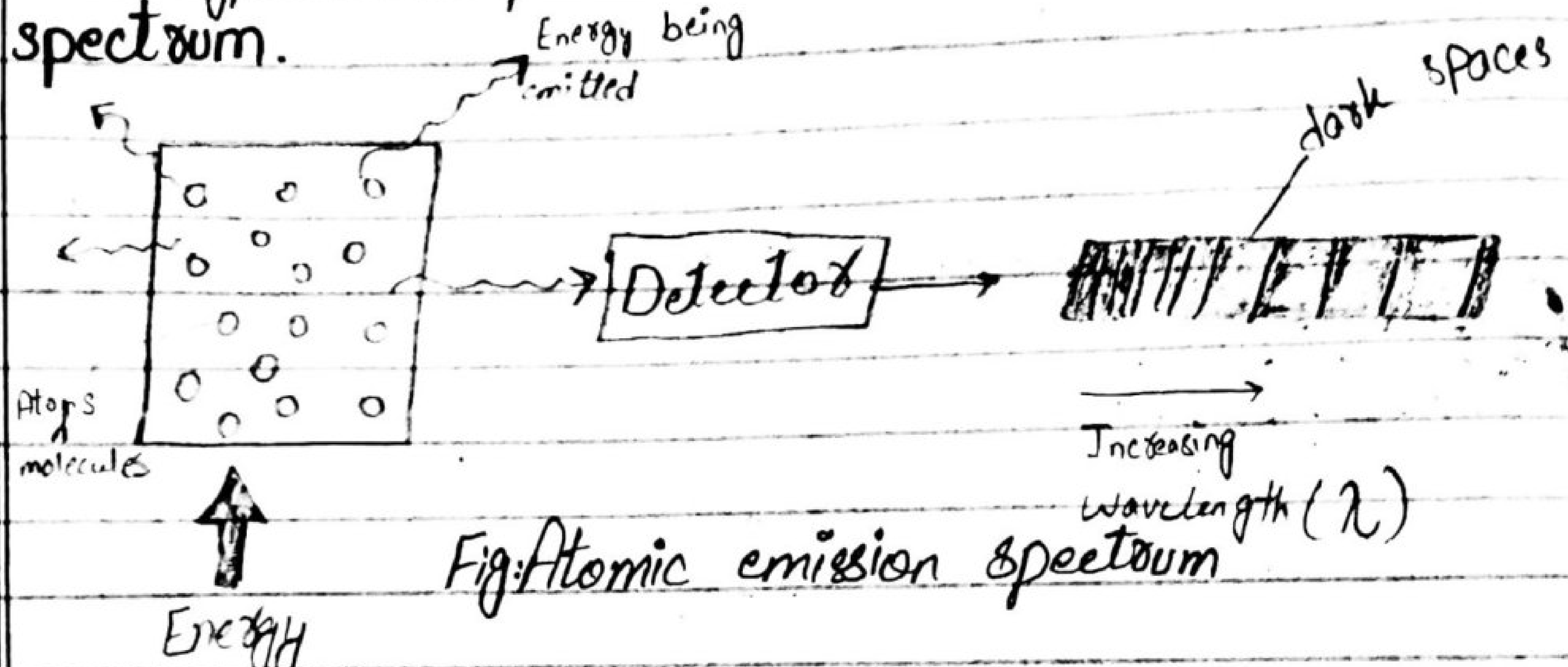


Fig: Atomic emission Spectrum

Colours imparted by Metals.

Each element has its own characteristic colour by which it can be identified.

→ Following Metals give colour in Bunsen flame;

- Na gives yellow colour.
- Sr gives red colour.
- K gives violet colour.

→ Following Gases give colour in discharged tube;

- Ne glows with Orange red colour.
- He glows with orange pink colour.
- H_2 glows with orange red or blue colour.
- Cl_2 glows with orange green colour.

The lines in spectrum are not haphazardly distributed but occur in series or group which become continuous by decreasing wavelength.
(wavelength $\propto$ separation b/w lines)

Applications of emission spectroscopy

Emission spectroscopy has been used to detect **40 elements**. The following materials have been analysed by emission spectroscopy:

i). Trace major constituents in ceramics.
ii). Traces of Co, Ni, Mo and V in Graphite.
iii). Trace metal impurities in analytical reagents.
iv). Trace of Ca, Cu, Zn in blood.
v). Zinc in pancreatic tissues.

2. Atomic Absorption Spectrum

When white light is allowed to pass through a sample of a substance, it may absorb radiation of a particular wave length.

• In Atomic Absorption Spectrum, dark lines are separated by coloured spaces.

This type of spectrum is called atomic absorption spectrum.

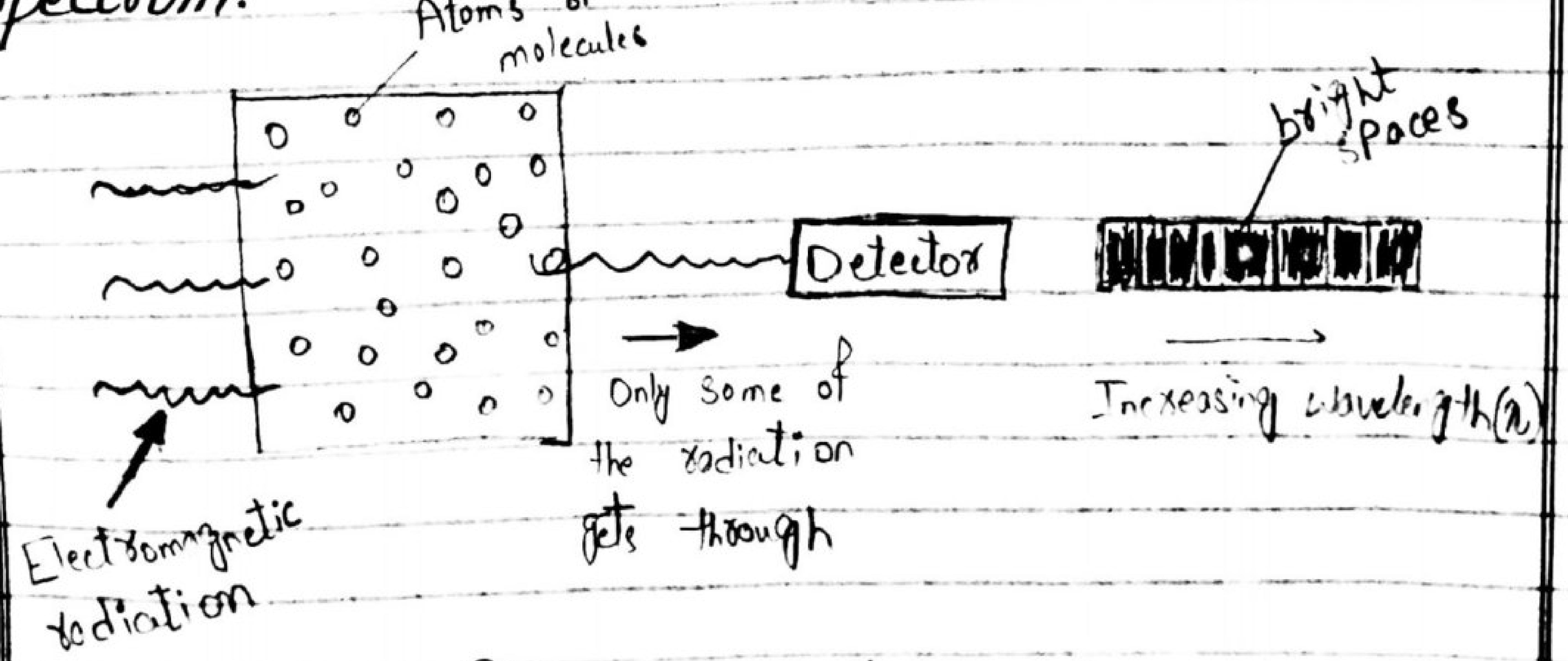


Fig. Atomic absorption spectrum

Applications of Atomic Absorption Spectroscopy (AAS)

- The AAS technique has become the most powerful tool of analysis because in this method **small concentration** of sample is used.
- AAS methods are **highly specific**, hence analysis of a metal from a complex mixture is possible and a high energy source needs not to be employed.
- The technique is used for the **analysis of substance** including ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.