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The Spectroscopy

الاطيـــــــاف

Contents:

Chapter one: Principles of spectroscopy science

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Definitions:

1-The spectroscopy science :

Represents important method to diagnosis the material types and to study the atomic and molecular structures.

2- Light and radiation :

When sun light pass through the prism , the light is analysis to seven colors ,this evident refer to the sun light contains some regions and the tools which make this analysis called spectroscopy .

The light represents the visible part from electromagnetic radiation and which have the particulate and wave properties . Many scientist study the light nature like Maxweel which was determined the light speed (2.9979×10^8 m/s).

3-Hertiz :

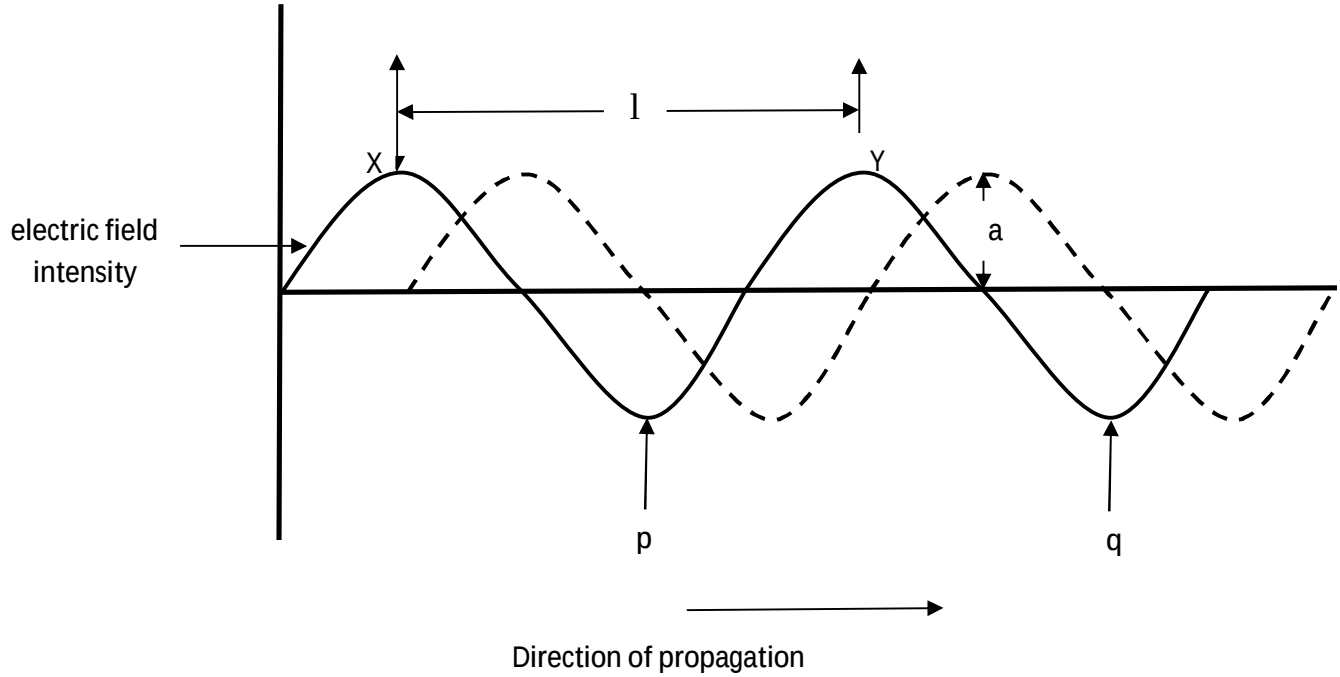
Generate the electromagnetic wave by used electric spark and noticed some of Light properties as reflection , refraction and polarization and after electron discovered became clearly that the light is product as move of electron inside atom and its have also magnetic nature , and the electric and magnetic field were oscillate together in two perpendicular planes with the path of wave .

This fact introduce the conclusion that the light is part of electromagnetic wave Range from (radio waves) up to cosmic waves as shown in the flowing table.

Radiation type	Wave length (A^o)	Wave number $\nu' = 1/\lambda\ (cm^{-1})$	Frequency (ν) $\nu = C/\lambda$ (Hz)	Energy (cal / mole)	Effects
Radio	10^{14} - 10^{12}	10^{-6} - 10^{-4}	$3x10^4$ - $3x\ 10^6$	10^{-6} - 10^{-4}	Spin orientations
Television	10^{10}	10^{-2}	$3x10^8$	10^{-2}	Spin orientations
Radar	10^8	10^{-1}	$3x10^{10}$	2.85	Spin orientations
Microwave	10^7	10	$3x10^{11}$	28.5	Rotational molecular trasitions
Far IR	10^6	10^2	$3x10^{12}$	285	Rotational molecular trasitions
Near IR	10^4	10^4	$3x10^{14}$	28 k	Vibrational
Red	$8x10^3$	$1.2x10^4$	$3.7x10^{14}$	35.7 k	Inner Shell / electronic transition
Violet	$4x10^3$	$2.4x10^4$	$7.5x10^{14}$	71.4 k	Inner Shell / electronic transition
Ultraviolet	$3x10^3$	$3.2x10^4$	$1x10^{15}$	96 k	Valence Shell / electronic transition
X-rays	1	10^8	$3x10^{18}$	10^8	Valence Shell / electronic transition
γ -rays	10^{-2}	10^{10}	$3x10^{20}$	10^{10}	Nuclear transition
Cosmic rays	10^{-4}	10^{12}	$3x10^{22}$	10^{14}	Nuclear transition

The Wave Nature of radiation :-

The radiation is defined as a transfer energy or motion energy . In motion energy the disturbances is transfer in medium, when the particles of medium oscillate to up and down or to back or forward, but not with wave. The center of disturbances generate another and series of wave and energies generate and transmitted to another particles ((can be considered that any point on front wave source of new disturbance)).



Electric component is more important for spectrometric studies over magnetic component .

X , Y
q , p
} Maximum disturbance in electric

a:- maximum amplitude of wave .

λ:-The wave length .

Spectral parameters and their units:-

The wave length: - is represent the length of single wave .

The wave number: - is represent the number of wave per unit length.

The frequency: - is represent the number of vibrations per unit time.

The units:-

- The wave length measured by Cm , ^{o}A ,nm and m.

  $^{o}A = 10^{-8}\ cm = 10^{-10} m$

  $nm = 10^{-7}\ cm = 10\ ^{o}A$

  In I.R the wave length measured by μm

  μ(micro) = 1000 nm

  $^{o}A = 10^{-1} nm$

  $cm = 10^{4}\mu m = 10^{7} nm = 10^{8}\ ^{o}A$

- The wave number measured by Cm^{-1}.
- The frequency measured by Hz.

$$Hz = \frac{1}{sec} = s^{-1}$$

$$\nu = \frac{c}{l} = \frac{cm/s}{cm} = s^{-1}$$

Then the freq. means the number of periods or vibration in one second which the wave was completed.

- The energy in Cal/mol , ev , and joul.

  joul conversion to ev divided by electron charge .

joul to cal divided by 4.18 and to cal/mol multiplying Avogadro No.

Avogadro No.=6.023×10^{23} atom / mole.

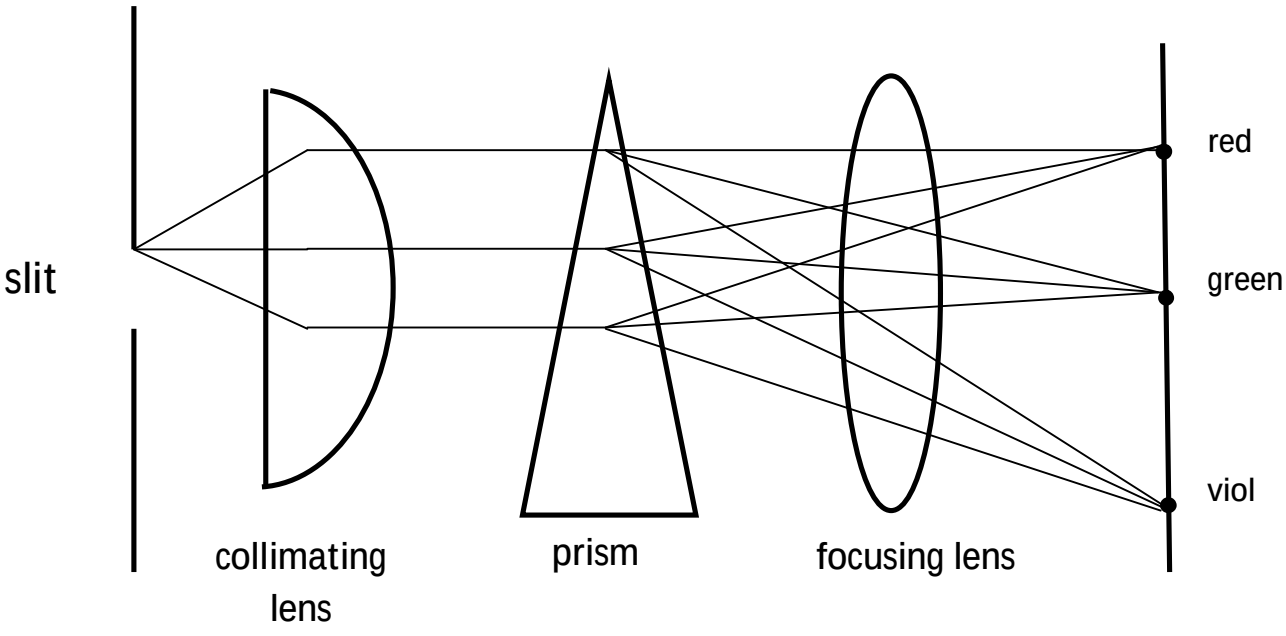
J , 4.18 ⟶ cal , 10^3 kal x N_A ⟶ K cal/mole

J , 1.602×10^{-19} ⟶ ev

Angular separation of waves to produce a spectrum:-

One of important methods to produce the spectrum: The dispersion of radiation to continuous bands from narrow wave length .This bands may be may be visible region or another region , the waves are transmitted in speed of 3×10^8 m/sec in space but this speed is reduced through the medium and proportional with the optical density of medium . this reduce will appear as a refraction when the light transfer from medium to another and the refraction depend on frequency or wave length of wave .

The reflection is increase when the freq. is increased or the wave length is reduced.



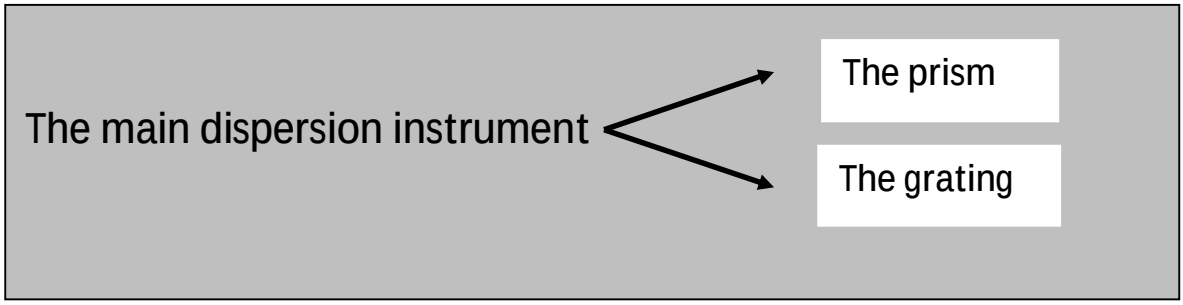
Arrangement of light dispersion

mono chromator :-

The normal light is polychromatic which contains No. of wave lengths, but the light in take from prism can be considers, but the light in take from prism can be considered monochromatic beam contains one color or single wave length.

The mono chromator consists of:-

1. Grating or narrow slit.
2. Lens or mirror to ensure the radiation (collimator).
3. Prism or grating diffraction.
4. Outer slit to pass the wave band.
5. Lens or mirror placed after dispersion tool to ensure the waves on detector.



The prism: - dispersion the rays by refraction.

The grating: - dispersion the rays by diffraction.

Grating: - transparence surface from glass or Al contains many parallel lines and more accurate , the distance between them is uniform . This make by small diamond head in the rang of 40000 line / inch and the width is 5-6 inch to conform 200000-240000 line. The Aluminum grating is better than glass if used in v.s , uv and IR regions .

Planck – Einstein Relation :-

One of the basic equation deals with the radiation Materials interaction.

$$E = h\nu$$

E: is the energy

h: planck constant $\cong 6.6 \times 10^{-34}$ (J.sec)

ν : The frequency (Hz) or (sec^{-1}).

Note:-

1. The energy of monochromatic radiation depend on freq. or wave length but independent on intensity of radiation .
2. The Intensity of radiation depend on number of photon per unit time or per unit area.

Ex:- Calculate energy of the following wave length

1. $\lambda = 3000^{o}A$.
2. $\lambda = 2\ \mu m$.

Photons – Materials interaction:-

The rays consist of stream from energy band transfer in same direction of band of 3×10^{8} m/sec and this concept is assist to study of spectrometric analysis for materials. Max planck discovered the concept of quantum or light quanta which represent the optical energy bands.

Enishtein used the planck concept to explained the photo electric effect and explained the corpuscular theory .represent the energy band

called photons and the relation connect between corpuscular and wave theory E=hn.

The spectroscopy science (for absorption) means study how the molecules of sample absorb the photons and which photons can be absorb , and from determine photons type , which absorb from molecules can be determine the shape , volume ,and atomic structure of molecules sample.

The molecules moving have four types of energy:-

1. Transition energy: - The molecule can be absorb quantity of energy when translate from place to another and the energy equal to $E_{tra.} = 1/2\ mv^2$.
2. The rotation energy: - it is kinetic energy which the molecule have when the molecule rotate around the certain axis.
3. Vibration energy: - represent the potential and kinetic energy when the molecules are vibrate.
4. Electronic energy: - represent the energy of molecule as result of potential and kinetic energy.

Type of spectrum:-

There are two types of spectrum

1. The absorption spectrum: - In this type of spectrum the material or sample absorbs apart of radiation source and the monochromater placed before sample in side source to protect the sample from source radiation.

2. The emission spectrum: - The sample emits the radiation by excitation of translate from case to another and the monochromater placed between the sample and detector.

The instrument of spectrum measurement :-

1. Spectroscopes:- the radiation is detect by eyes.
2. Spectrograph:- detect by photographic film.
3. Spectrophotometer:- detect by electric circuit (convert the radiation to electric pulse).

Ex:-Express the energy of a photon in electron volt in terms of its wave length given in meters, and then use the result to obtain the wave length of x-rays in terms of the accelerating voltage applied to an x-ray tube.

Solution:-

$E=h\nu$ and $\lambda\nu=c$ we have that

$E=hc/\lambda$ But

$hc = (6.6256\times10^{-34}\,J.s)\times(2.9979\times10^{8}\,ms^{-1})$

$= 1.9863\times10^{-25}\,J.m$

Remembering that $1\ ev = 1.6\times10^{-19}\,J$.

we see that $hc = 1.2397\times10^{-6}\ ev$.

H.W:-Drive the relation

$$E_n = \frac{-13.6}{n^2}$$ (For Hydrogen atom).

Hydrogen atom spectrum:-

The wave Numbers ($\bar{\nu}$) for Hydrogen atom spectrum wave determined by the relation:-

$$\bar{\nu} = \frac{n}{C} = R_\infty \left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$R_\infty = \frac{2\pi^2 m e^4}{ch^3} = \text{Rydberg constant} = 10973.7\ cm^{-1}$$

$C = 3 \times 10^8$ m/sec .

ν: Frequency .

n,m : Integer and m > n .

Bohr Hypothesis:-

The electron transition takes place according to Selection rules, and the conclusion of Bohr Hypothesis as follows:-

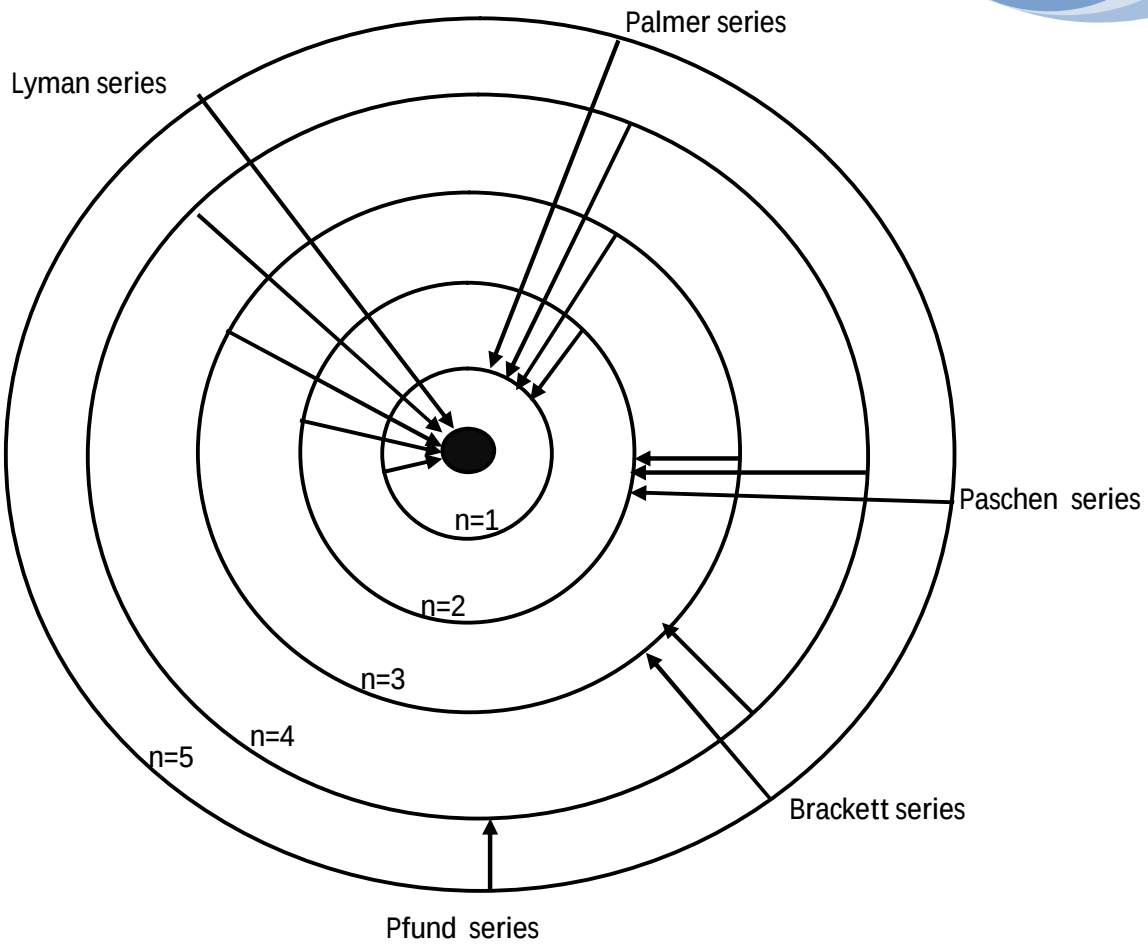
1- An electron in an atom may only be bound with certain energies which for one electron atom or ions are proportional to $\frac{1}{n^2}$ where n is integer

$$E \propto \frac{1}{n^2}$$

2- It may also only have certain angular moment a I = n h / 2π .

3- The transition of electron between these level may not be understood classically.

The Hydrogen atom consist of nuclear and one electron move around it in the one of stable orbit which define by n= 1,2,3,4,---------- .



1- Lyman series: from any orbit to $n_f = 1$.
2- Balmer series: from any orbit to $n_f = 2$.
3- Pashen series: from any orbit to $n_f = 3$.
4- Brackett series: from any orbit to $n_f = 4$.
5- Pfund series: from any orbit to $n_f = 5$.

} I.R

Energy levels of H-atom:-

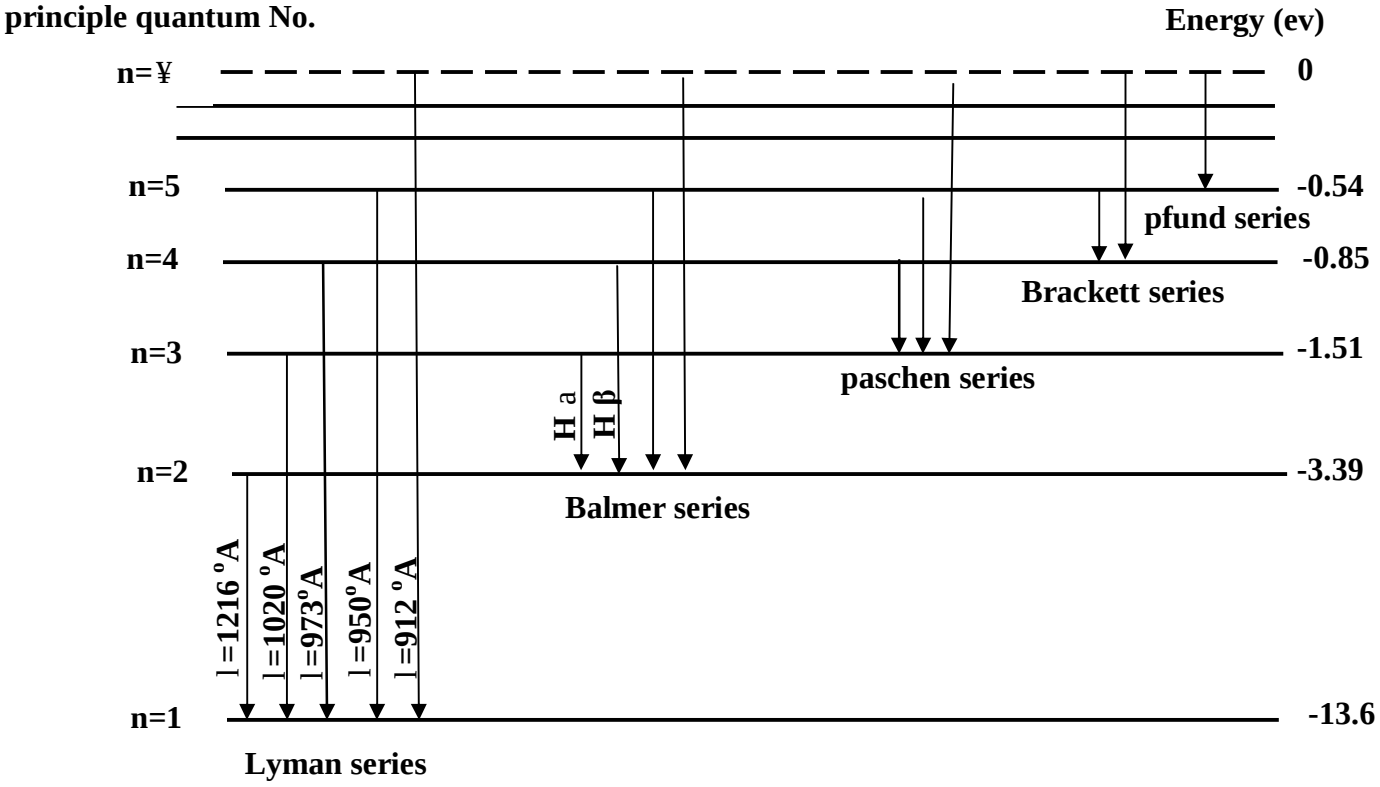
Bohars second postulation that there are only certain discrete energy levels in the hydrogen atom is especially important because it has been found to have wide application throughout atomic physics.

Energy levels are most expressed in electron –volt (ev) , if E_n is in jouls it may be converted in to electron volts by dividing by the $1.6x10^{-19}$ j/ev .

$$E(ev) = \frac{E_n}{e} = -\frac{1}{e}\,\frac{me^4Z^2}{8\in_\circ^2 h^2}\cdot\frac{1}{n^2}$$

up on substituting the values of the constant in this equation and letting Z=1, we find that the energy levels of H-atom are given by $E(ev) = -\frac{13.6}{n^2}$

If the Hydrogen is illuminated it may absorb energy from a photon , and the electron is excited and then the transition may be construct may series of spectrum as shown in next fig.



H.W:- Determine the spectrum region of Hydrogen series Lyman, Balmer , Paschen , Brackett , and pfund .

The broadening of spectrum line:-

Many parameters affected on broadening of spectrum lines such as

1- **The aperture of spectrum instrument:-**

The emission or absorption of spectrum appear broadening bonds due to aperture of instrument which permit to range of frequencies fall on detector instead of single frequency , and this leads to un sharpness spectrum.

2-The Herisenberg uncertainty:-

The Herisenberg uncertainty refer to when the system found in a certain level for a certain time (Δt) the uncertainty in the energy equal to (ΔE) then

$$\mathbf{DE\ x\ Dt\ @\ h\ @\ 6.6x10^{-34}\ J.s}$$

When the lower level $\Delta t = \infty$ then $\Delta E = 0$

but for electron (e) $\Delta t = 10^{-8}$ sec $\Longrightarrow \Delta E = \frac{6.6x10^{-34}}{10^{-8}}$

$\therefore \Delta E = 10^{-26}$ J

3-Collision broadening:-

The motion of atoms and molecular in liquid and gas phase can be continuous and this lead to collision between them and as a result to this collisions the energy of outer electrons is perturbing and then the line spectrum is not sharp.

4-Doppler effect:-

The motion of atoms in liquid and gas phase lead to Doppler effect appear because the velocity of molecule (v) as a ratio to the measurement speed (-v,+v) and this leads to the frequency of radiation is change and this change depend on the direction of molecule motion. This effect is very clearly in light atom such as H_2 at 300^oK.

Notes:-

1-**The collision broadening is important in liquids where the Doppler broadening is important in gases.**

2- **The Intensity of spectrum depend on:-**

- The probability of transmission.
- The No. of atom and molecules in the levels which transfer take place in it (population).
- The amount of material which the spectrum is measured.
- The length of bath.