Unit - 2

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Spectroscopic : Techaniques and Application

* Introduction of ultra voilet and visible spectroscopy:

The uv and visible spectra involves the promotion of e⊖'s from the ground state to the higher energy state. therefore, this spectra of organic compounds are associated with transition b/w electronic energy levels. & the transition are generally b/w a bonding or lone pair orbitals and an unfilled non-bonding or antibonding orbitals.

The wavelength of the absorption is then a measure of the seperation of energy levels of the mo orbitals concerned. the highest energy seperation is found when e⊖ in σ bond are excited, giving rise to absorption in the ~~farther~~ 12 - 200nm range. above 200nm, However excitation of e⊖ particulary in π conjugative systems, give rise to readely measure and informative spectra.

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The strength of electronic spectroscopics lies in its ability to measure the extent of multiple bond or aromatic conjugation with in the molecules.

Note: Visible and UV range covers the wavelength range from 200 to 800nm

* The absorption Laws:

*

There are two types of law the absorption of light by the molecules. These are

(a) Lambert Law:

State that when a beam of light passing through a homogenious absorbing medium, the fraction of the incident light absorbed is independent of the intensity of the source.

(b) Beer's Law:

States that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the absorption is proportional to the no. of absorbing molecules.

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* The mathematical form of above two laws is

$$\log_{10} \frac{I_0}{I} = \varepsilon l c$$

Here I_0 and I are incident and transmitted light respectively, l is the path length of the absorbing solution in cm, and c is the conc. in mol L^{-1}.

$\log_{10} \frac{I_0}{I} = \varepsilon l c$ is called the absorbance or optical density, ε is known as molar extention coefficient.

* Types of Electronic Transition :

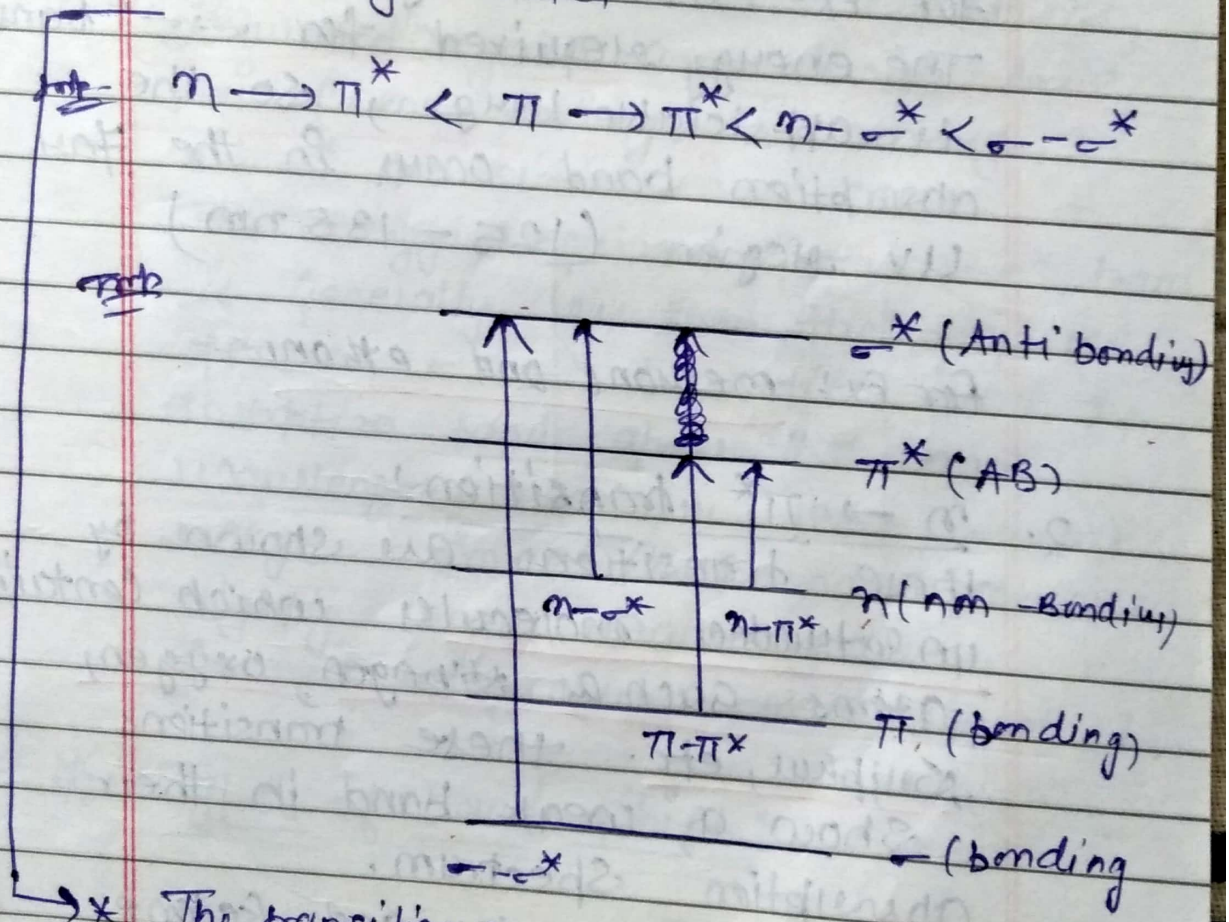
(1) Electronic transition for organic molecules involve absorption of UV and visible radiations by $e^{\ominus}$ in σ, n or π orbitals and result in their promotion to some higher energy anti bonding orbitals (Excited

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The transitions are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transition are allowed.

The energy level for a molecule is shown in figure. From the figure, it is evident that energy values for different transitions are in the following order

$$n \longrightarrow \pi^* < \pi \longrightarrow \pi^* < n - \sigma^* < \sigma - \sigma^*$$



The transition are $\sigma - \sigma^*$, $n - \sigma^*$, $\pi - \pi^*$. When selection rules are applied, $n - \pi^*$ transition are forbidden, while only $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ transitions are allowed

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The main features of all the above mentioned below

1 $\sigma \rightarrow \sigma^*$ transition:

These trans. all occur in only those comp. in which all the $e^{\ominus}$s are involved in single bond no lone pair of electrons are available.

for Ex- Saturated hydrocarbons.

The energy required for $\sigma \rightarrow \sigma^*$ trans. is appreciable-Large, so the absorption band occurs in the far UV region (125 – 135 nm)

for Ex: methane and ethane

2. $n \rightarrow \pi^*$ transition:

these transitions are shown by unsaturated molecules which contain atoms such as Nitrogen, oxygen, Sulphur, etc. these transitions show a weak band in their absorption spectrum.

for Ex: aldehydes and ketone

3. $\pi \rightarrow \pi^*$ transitions:

~~These transitions~~

this transition involves a excitation of an $e^{\ominus}$ from a bonding π orbital

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to an antibonding π^* orbital.
molecules which have a π electron system show $\pi \rightarrow \pi^*$ transitions. These transition occur in the near UV and visible region

4. $n \rightarrow \sigma^*$ transition:
In addition to $\sigma - \sigma^*$ transitions, Saturated Organic comp. with lone pair (non-bonding) & undergo $n - \sigma^*$ transition.
The energy required for $n - \sigma^*$ tran. is Generally less then that required for a $\sigma - \sigma^*$ transitions and the absorption band apear that longer wavelength near UV (180 - 200 nm) range. Some Compound absorbs at slightly longer wavelengths.
for ex methyl chloride, methyl alcohol etc

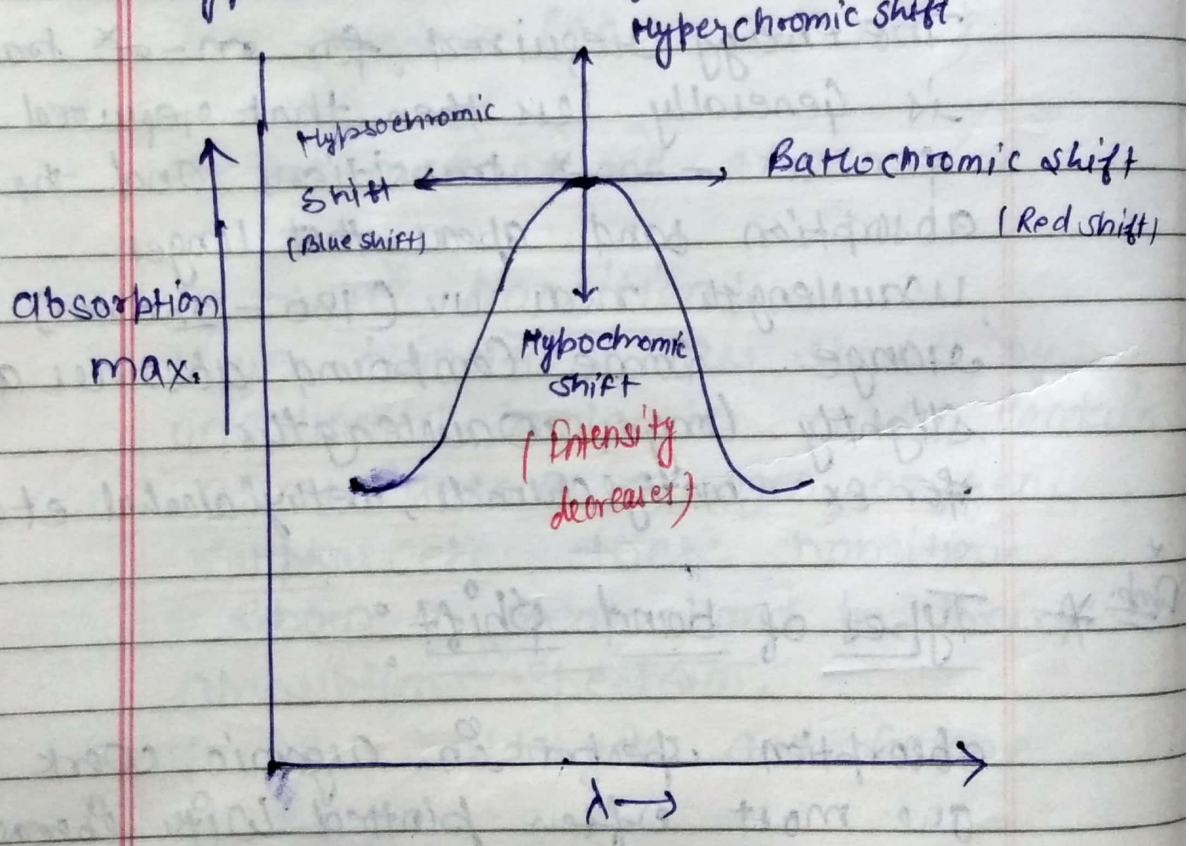
Imp. * Types of band shift:

absorption spectra in organic work are most often plotted with increasing ε (absorption maximum), on the ordinate and with wavelength (λ) on the abscissa increasing from left to right.

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When a change in solvent or a change in a substituent causes λ_{max}. for a band shift, we can state whether the shift occurs to longer wavelength or to shorter wavelength. the change in shifts are

1. Bathochromic shift (Red shift)
2. Hypsochromic shift (Blue shift)
3. Hypochromic shift.
4. Hyperchromic shift.



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1. Bathochromic (Red shift)

it is an effect by virtue of which the absorption max. is shifted towards longer wavelength - due to the presence of an auxochrome such an absorption shift towards longer wavelength is called red shift or Bathochromic shift

2. Hypsochromic (Blue shift)

It is an effect by virtue of which the absorption max. is shifted towards shorter wavelength this is called blue shift or Hypsochromic shift

3. Hypochromic shift :

It is an effect due to which the intensity of absorption max. is decreased this distortion cause by the methyl group is in methyl by phenyl.

4. Hyperchromic shift :

It is defined as an effect due to which the intensity of absorption max. increases. the introduction of an auxochrome usually

yellow
Nitrocompound NO_2 → auxochrome

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increases intensity of absorption.

* Chromophore and auxochrome:

- Chromophore: A chromophore is any system is responsible for imparting Colour to the Compound.
For Ex- In Nitrocompounds the yellow Colour is due to NO_2 group, clearly are Nitrocompound are the chromophore which observe the yellow colour.
There are two types of chromophore

- firstly those which Contain π electrons and undergo $\pi \rightarrow \pi^*$ transition.
for Ex: ethylene, acetelene

- Secondly those which Contains both π and n electrons and undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions
For Ex: Carbonyl, Nitryls.

- auxochrome:
An auxochrome can be defined as any group which does not itself act as Chromophore but whose presence brings shifts towards the longer wavelength of the spectrum.

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It is the colour enhansing group, It has an ability to extend the Conjugation of chromophore. by sharing of non-bonding electron. for Ex, —OH, —OR, —NH_2

* Applications of ultra violet & visible spectroscopy:-

1) uv spectroscopy is very useful to measure the no. of conjugate double bonds and aromatic conjugation b/w various molecules. It is very useful to distinguish b/w conjugate and non-conjugate system.

2) Detection of impurities
for Ex. benzene is the common impurity in cyclo Hexane and It presence can be easily dected by the absorption at 255 nm.

3. Determination of Unknown Conc^n.-
Since absorbance is given by

$$A = \varepsilon C x$$

for a solution of some compound in the same sample cell ε and x are constant

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Absorbance of standard solution (A_s) and unknown solution (A_u) is measure with the help of spectrophotometer. Knowing the value of Conc^n of Standard solution (C_s), Conc^n of unknown solution (V_s) can be determine

Since,

$$\frac{A_s}{C_s} = \frac{A_u}{C_u} \Rightarrow C_u = \frac{A_u}{A_s} \times C_s.$$

4. Determination of molecular wt. -
m.wt determination is possible Provided suitable derivatives could be prepared which absorbs in the UV visible Range.
for Ex- m.wt of amine can be determined by first converting it into amine Picrate.
unknown wt of it is dissolved per litre of solution and its absorbance is determined at λmax.

Since, $A = \varepsilon c x$
Hence c can be determined, which is in mole per litre units,
Since wt of amine Picrate dissolved in per litre of solution is known,

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so molecular wt of amine picrate and hence of amine can be determined

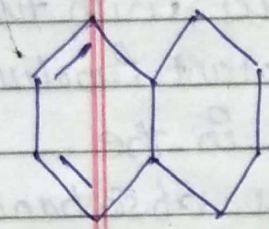
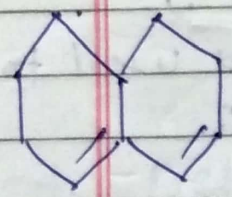
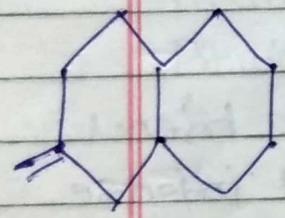
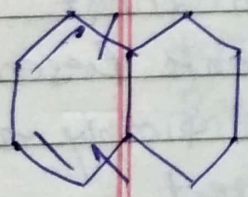
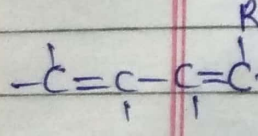
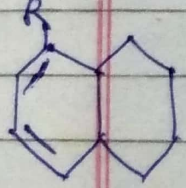
* Study of kinetics of chemical Rxn :-
It is done by measuring the change in Concn of Reactant of Product with time Provided one of the reactant Product exibit suitable absorption in the ultraviolet visible region. as absorbance is directly Proportional to Concn., UV spectrophotometry can be used to follow the corse of the Rxn.

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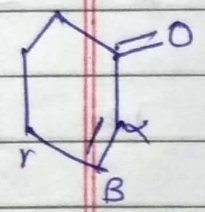
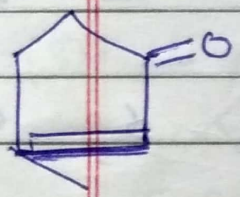
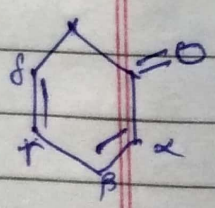
* Woodward FIESER Rule :-

~~Woodward~~ for dienes and trienes the position of the most intense band can be correlated in most instances with the substuents presence. To use the rules, it is simply a ~~method~~ matter of choosing the correct λmax value and adding the contribution is made by each substuents

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Chemical Structure	Name	λ_{max}
$-\overset{|}{C}=C-\overset{|}{C}=C-$	Acyclic or Conjugate diene	217 nm.
	homoannular diene	253 nm
	Heteroannular diene	215 nm.
	Exocyclic double bond	5nm.
	Ring Residue (for one)	5nm.
$-R$	Alkyl Residue	5nm.
	Alkyl Residue	5nm
	Alkyl Residue	5nm.

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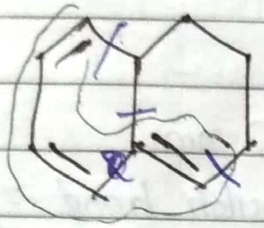
$-C=C-$	additional conjugation	30 nm.
$-OR$	alkoxy	6nm
$-SR$	Thioether	30nm
$-Cl, Br$	chloro, Bromo	5nm
$-\overset{\beta}{C}=\overset{\alpha}{C}-CO$	Acyclic ketone	~~250 nm~~. 215 nm.
	6 ring cyclic	215 nm
	5 ring cyclic	202 nm
$-\overset{}{C}=\overset{}{C}-CHO$	Aldehyde	207 nm.
$-\overset{\delta}{C}=\overset{\gamma}{C}-\overset{\beta}{C}=\overset{\alpha}{C}-CO$	if additional conjugation is given then add value to basic value	30 nm.
	second double bond is homoannular with the first then add given value to basic value	39 nm.

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Substituents	Position	Position		
	∝(nm)	β(nm)	γ(nm)	δ(nm)
-R	10	12	17	17
-OR	35	30	17	31
-OH	35	30	30	50
-SR	-	80	-	-
-Cl	15	12	12	12
-Br	25	30	25	25
-OCOR (acyloxy)	6	6	6	6
$-NH_2$	-	95	-	-

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Q. Calculate the λ_{max} for following Compounds.

(1) 

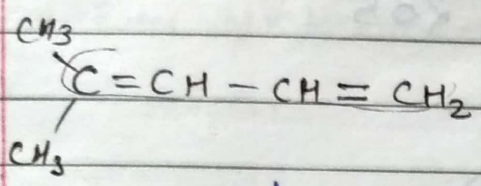
$\lambda_{basic} = 253$

1 exocyclic double = 5nm

3 Ring Residue

$= 3 \times 5 = 15$

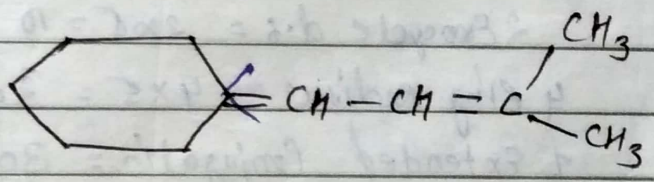
$\lambda_{max} = 273\ nm.$

(2) 

$\lambda_{basic} = 217$

2 Alkyl Residue $= 2 \times 5 = 10$

$\lambda_{max} = 227.$

(3) 

$\lambda_{basic} = 217$

2 Alkyl Residue $= 2 \times 5 = 10$

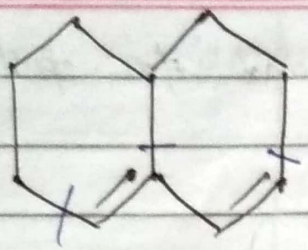
1 exocyclic double bond $= 5nm$

2 Ring Residue $= 10\ nm$

$\lambda_{max} = 242$

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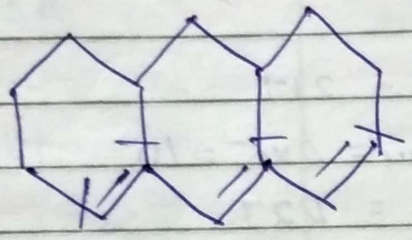
4.



λ_{basic} = 215 nm
1 exocyclic double bond = 5nm
3 Ring Redisue = 3×5 = 15nm.

λ_{max} = 235

5.

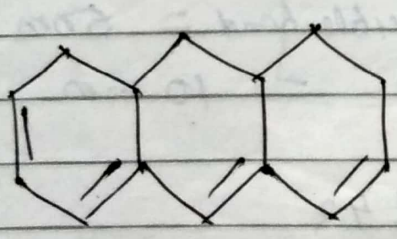


(Ring redunt)

λ_{basic} = 215nm
2 Exocycle d.b = 2×5 = 10 nm
4 Ring Redisue = 4×5 = 20 nm
1 Extended Conjugation = 30 nm

λ_{max} = 275nm

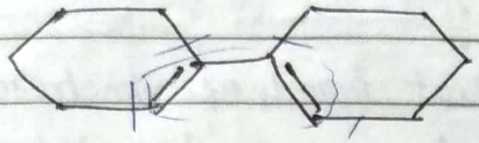
6.



λ_{basic} = 253 nm.
2 Extended Conjugation = 30×2 = 60 nm
4 Ring Residue = 4×5 = 20nm
2 Exocyclic d.b = 5×2 = 10
λ_{max} = 343 nm.

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7.



∴ $\lambda_{basic} = 215$ nm.

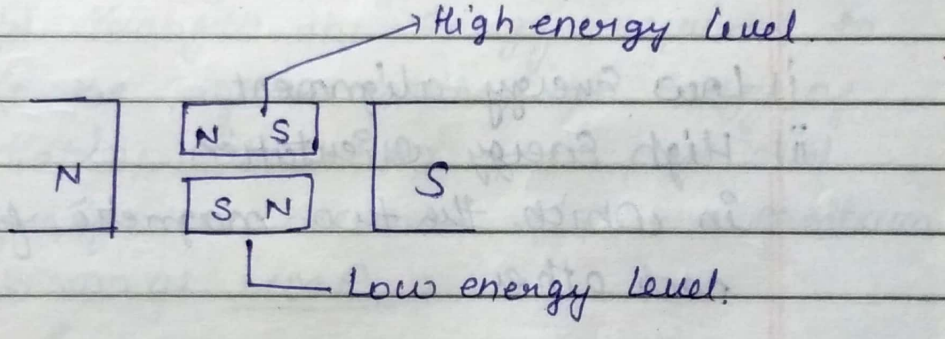
∵ Ring Residue = $4 \times 5 = 20$

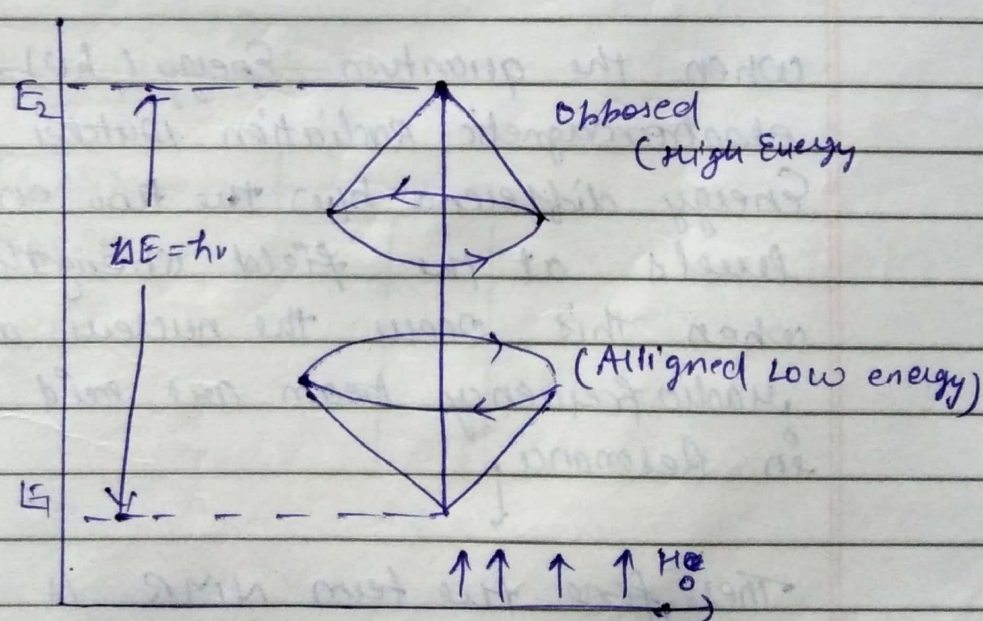
$\lambda_{max} = 285$.

20 marks

* **Nuclear Magnetic Resonance (NMR):**

(Proton NMR)





Energy level of a proton

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* Introduction :-

NMR is that branch of spectroscopy in which radiofrequency waves induced transition b/w magnetic Energy level of Nuclei of a molecule, which are created by keeping the nuclei in a magnetic field.

When a Proton is Placed in a magnetic field, it allines itself in one of the following two ways w.r.t applied field.

i) Low Energy alignment
ii) High Energy orientation
in which the two magnetic field oppose each other.

When the quantum Energy ($h\nu$) of electromagnetic Radiation matches up the Energy difference b/w the two energy levels at the field strength B_0. When this occurs the nucleus and radiofrequency beam are said to be in Resonance.

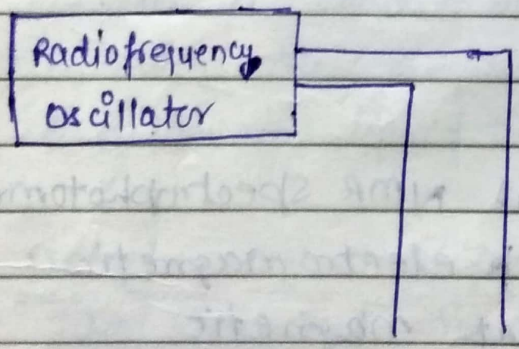
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Therefore the term NMR is used

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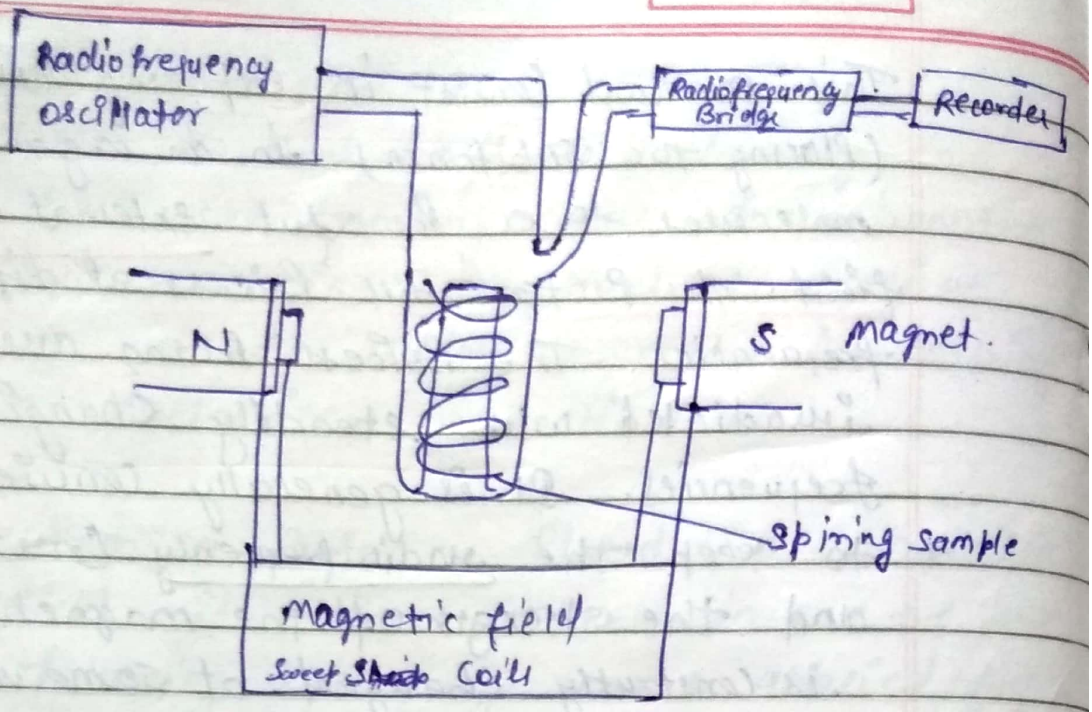
This method consist in exposing the protons (Placing the substance) in an organic molecules to a powerful external magnetic field. the Proton will Precess at different frequencies. The Precess Proton are now irradiated with steadily changing frequencies. It is generally convienent to keep the radio frequency Constant and the strength of the magnetic field is constantly changed. at some value of field strength the Energy required to flip the protons matches the Energy of radiations, absorption takes place and a signal is observed. Such a spectrum is known as NMR.

* Instrumentation:



Radiowave

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Basic Arrangement for NMR Spectrophotometer

(a) NMR spectrophotometer consist of a magnetic, a radiofrequency source, a detector and amplifier, a brief description of the spectrophotometer is Given below

(i) Magnetic:
In Commercial NMR Spectrophotometer are either electromagnetic or paumanent magnetic. electromagnetic are used with their help the strength of M.F can be easily change as per our experimental Requirement

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These

(2) Magnetic field sweep coil:
these consist of a pair of coils which are located Parallel to the magnetic face a direct current is varied b/w these coils show that effective field can easily be changed

(3) Radio frequency source:
A Plan Polarised Radiation is obtain by transmitting a signal: from Radio frequency source into a pair of coils. the frequency must be constant for high resolution

4. Spinning Sample holder:
It holds the sample tube in a fixed position it consist of a sample cell in which the sample is kept in either in liquid and solid state

5) Detector and amplifier:
The Electrical signal generated by the coil is amplified. These amplified signal are detected and fed to a cathod ray Oscillograph or to a strip chart recorder.

V. Imp / 10 marks

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No. of Signals:

The proton with the same environment in a molecule absorbs at the same applied field strength and are known as equivalent protons.

The protons with different field strength absorbs at diff. applied field strength.

A set of protons with the same environment are said to be equivalent and vice versa. The no. of signals in an NMR spectrum tells us, there for how many sets of equivalent protons. i.e how many kinds of proton are present in a molecule. each equivalent proton gives one NMR signal, while non equivalent protons give different signals in NMR spectrum

For Ex- $\underset{a}{CH_3} - \underset{b}{CH_2} - Cl$

2 NMR signal

$\underset{a}{CH_3} - \underset{b}{CH_2} - \underset{a}{CH_3}$

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- $CH_3(a)-CH_2(b)-CH_2(c)-Cl$

3 NMR Signal

- $CH_3(a)-CH(b)(Cl)-CH_3(a)$

2 NMR Signal

- $CH_3(a)-C(=O)-O-CH_2(b)-CH_3(c)$

$CH_2-C(=O)-O-CH_2-CH_3$

3 NMR Signals.

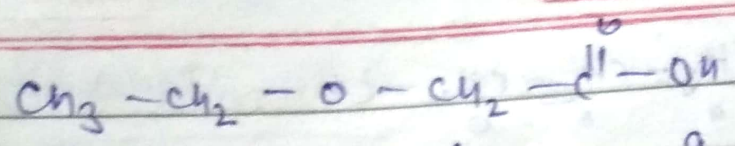
- $CH_2(a)-CH_3(b)$ on benzene ring, c

3 NMR Signal

CH_3, CH_3, CH_3 on benzene ring

- 2 NMR Signals

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Q. = CH3 give the no. of signals in the following organic molecules

i) $CH_3 - CH_2 - Cl$ — 2 NMR

ii) C_6H_6 — 1 NMR

iii) $C_6H_5 - CH_2$ — 2 NMR

$C_6H_5 - CH_3$

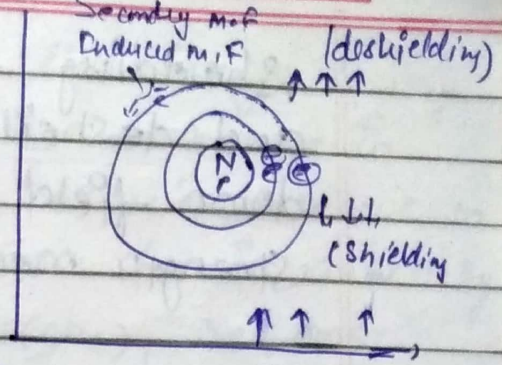
iv) $CH_3 - O - CH_3$ — 1 NMR

v) $CH_3 - CH_2 - OH$ — 3 NMR

Position of NMR Signal due to shielding

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* Chemical shift :



when a molecule (substance) is placed in a magnetic field, its electrons are caused to circulate and thus, they produced secondry M.F (induced M.F). Rotation of electrons about the protons itself generate a field in such a way that at the proton, it opposes the applied field. therefore the ~~field~~ field felt by the proton diminished and the proton is said to be shielded. Rotation of πs (Spacially π electrons) about the near by Nuclei Generates a field that can either oppose or rein force. the applied field at the protons, If the induced field opposes the applied field then the protons is said to be shielding if the induced field rein forces the applied field then the proton feels a higher field strength and such proton is said to be de shielded

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Shielding shift the absorption upfield and deshielding shifts the absorption down field to get an effective field strength necessary for absorption.

Such shifts (compared with a standard reference) in the positions of NMR absorption which arrives due to the shielding or deshielding of protons by the electrons are called chemical shift.

The chemical shift is affected by following factors.

i) Inductive effect
ii) Vander walls deshielding
iii) Space or anisotropic effect
iv) Hydrogen bonding.

To carry out NMR studies, the compound under investigation, which is either a pure liquid or a solution in a non-protonic solvent, is mixed with a small amount of tetra methyle silane (TMS) and the spectrum is recorded.

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since. the variation in field strength is very slight, so, it is not measure in actual magnetic unit, but with reference to the resonance conditions for an arbitrary standard TMS; $Si(CH_3)_4$ i.e TMS
This compound have been chosen as standard because

i) It has twelve equivalent protons Hence has a single peak.
ii) It is miscible with almost all organic substances
iii) It is highly volatile, so it can be readily removed from the system
iv) It does not take part in inter molecular association with the sample.

The spectrum shows an absorption for TMS at a magnetic flux density, B(standard) equal for a particular proton in the compound say B(sample). Therefore the chemical shift is given by δ

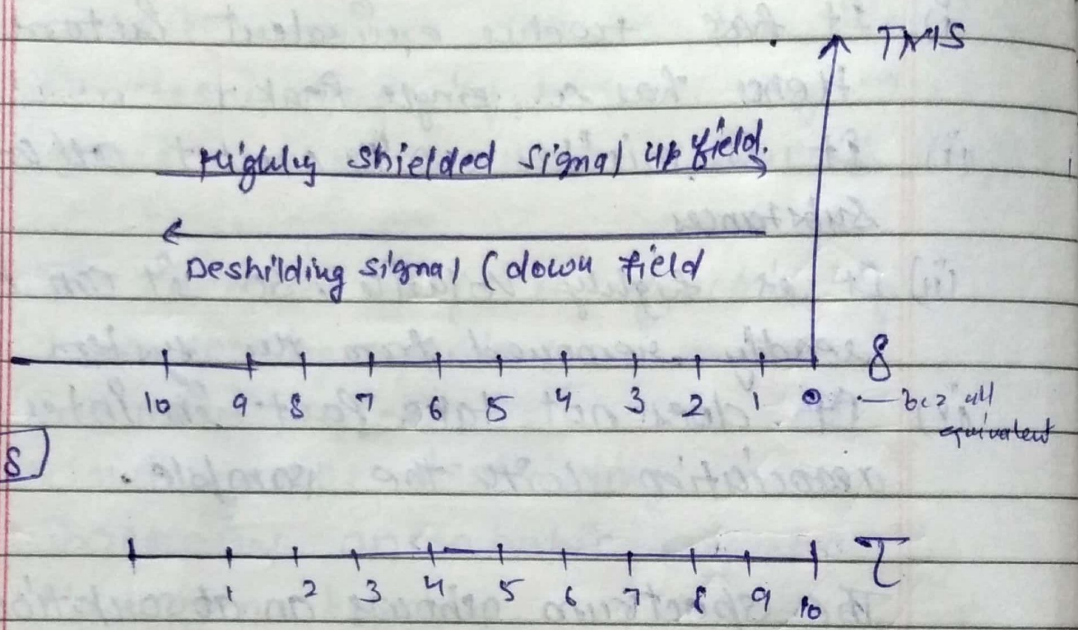
$$\delta = \frac{\Delta B}{B_0} \times 10^6$$

ΔB = $B_{standard} - B_{(sample)}$
B_0 = magnetic flux density.

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In other words the diff. in the absorption position of the protons w.r.t TMS signal is called chemical shift (δ value).

The assigning value (δ value) for TMS is equal to zero.



In terms of frequency units δ takes the form.

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\nu_{reference}} \times 10^6 \text{ ppm}$$

the chemical shift is dimension less and is expressed in ppm on account of the factor 10^6 in the above eq^n.

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* Interpretation of NMR spectrum:

1) The no. of signals in NMR spectrum tells us how many different environments are present in a molecule.

2) The area under each NMR signal is proportional to the no. of H atoms in that environment. So the relative areas of diff. peaks correspond to no. of protons present in diff environments

3. The multiplicity or no. of lines in NMR signal for a group of protons in forms us about the atoms present in the neighbouring groups. If there are n neighbouring protons then multiplicity of the signal n+1. So, the multiplicity of the signal from a group of protons is obtained by adding one to the no. of neighbouring protons (n)

4. In case a group of protons have different chemical environments on either side then, multiplets consisting of (n+1)(n'+1) lines is observed.

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where n and n' are the no. of protons on one and the other side of particular group understudy.

5. The relative intensities of different signal can be obtain with the help of Pascal triangle shown below

Neighbouring Protons (n)	No. of signals (n+1)	Relative intensities of signals
0	1	1
1	2	1 1
2	3	1 2 1
3	4	1 3 3 1
4	5	1 4 6 4 1
5	6	1 5 10 10 5 1
6	7	1 6 15 20 15 6 1

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6. Speliting of Signals:

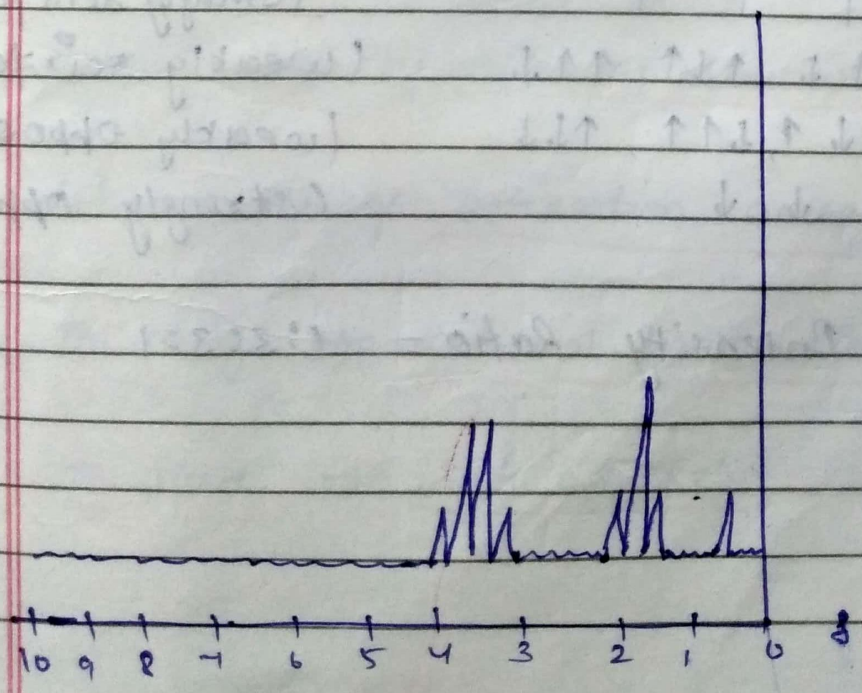
IN an NMR spectrum each signal represents one kind or one set of protons in a molecules. Signal spliting is a phenominan that arises from magnetic influences of hydrogens on atoms adjacent to those bearing the H atom. Causing the signal to be considered. It is found that in cutain molecules, a ~~sig~~ Singele peak (singlet) is not observed, but instead a multiplet (Groups of Peaks) is observed.

Consider a Simple molecules :

$CH_3 - CH_2 - F$

$(-CH_2)$: $(-CH_3)$

$n+1 = 3$ $n+1 = 4$



* Spin-Spin Coupling :

In NMR Spectrum the sight we expect from each set of equivalent protons is appearing not as a single peak but as a group of peaks. Spleting reflects the environment of the absorbing protons, Not wrt electrons, but w.r.t other near by Protons.

Ex $CH_3 - CH_2 - Br$

- Coupling of CH_2 Protons :

i)	↑ ↑	(Reinforce)	Intensity Ratio 1:2:1
ii)	↑ ↓ , ↓ ↑	(unaffected)	
iii)	↓ ↓	(oppose)	

- Coupling of CH_3 Protons :

i)	↑ ↑ ↑	(strongly reinforce)
(ii)	↓↑↓ ↑↓↑ ↑↑↓	(weakly reinforce)
(iii)	↓ ↓ ↑, ↓↑↑, ↑↓↓	(weakly oppose)
iv)	↓ ↓ ↓	(strongly oppose)

Intensity Ratio = 1:3:3:1

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S.N

* Coupling Constant:

The distance b/w the peaks in a multiplet is refered to as coupling constant. it is denoted by symbol J. and is expressed in the units cps (cycle per second) or Hertz (Hz).

This constant is measure of the magnitude of spleting effect. unlike the chemical shift, the values are independent of the applied m.f But depend markedly on the molecular structure.

* Application of NMR spectroscopy:

1. NMR spectrum can tell us how many protons are present in a molecules
2. determination of molecular structure.
3. determination of activation energy
4. To study the ketoenol tautomerism
5. To study the rate of Rx^n

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6. Qualitive analysis
The NMR spectrum helps to establish the presence or absence of functional group or other characteristics structural features of a given substance from their characteristic chemical shift. Appearance of a signal at δ 9.5, for Ex- is indicative of CHO group in the sample

* Advantages of NMR spectroscopy:
- It is totly non destective technique.
- Compared to IR spectroscopy, It is much easier to study solid samples by this Technique as a wide variety of solvents is available
- The NMR spectrometer used now a days are so improved that the spectra can be Recorded at fast or even faster then IR spectra
- It is possible to help computer calculation of NMR spectra.

Q. how many NMR signal do you expect from each of the following compounds

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1. CH_3-CH_2-OH — 3 NMR Signal

2. CH_3-O-CH_3 — 1 NMR Signal

3. $CH_3-CO-CH_3$ — 1 NMR

4. CH_3-CH_2-COOH — 3 NMR

5. C_6H_6 — 1 NMR

Q. How ethanol and diethyl ether will be distinguished with the help of 1H NMR Spectroscopy Give the spleting Pattern as well.

CH_3-CH_2-OH — 3 — 1 :

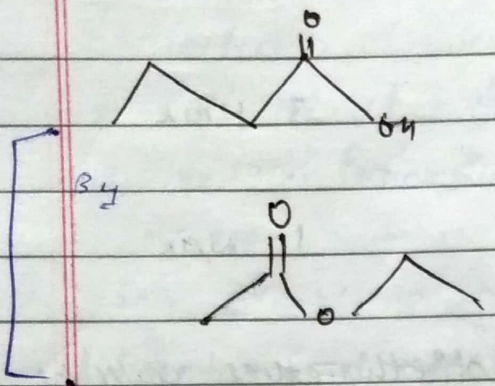
$(C_2H_5)_2O$ — 2

CH_3-O-CH_3 — 1 Singlet Peak

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Ans

Q. Explain how you would distinguished the three isomers below using ^1H NMR spectroscopy. Give specific examples of peaks, chemical shift and spleting pattern that would illustrate the differences



$CH_3 - CH_2 - CH_2 - COOH$

4 NMR

$CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - O - CH_3$ = 3 NMR

$CH_3 - CH_2 - CO_2$ $\quad CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_3$ 1.3 PPm → triplet

3 NMR 2.0 PPm Singlet 4.1 PPm quartet

	δ value
$R-CH_3$	0.7 – 1.6
$O-CH_3$	3.32 – 4.3
$R-CH_3-C=O$	2.02 – 2.9

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* IR Spectroscopy : (Vibrational Spectroscopy).
Atoms in a molecules are continuously vibrating the vibrational changes depends upon two
1. mass of atoms
2. these spatial arrangement in a molecules
3. electromagnetic radiation of IR region get absorbed by organic molecules.
The extent of absorption depends on wavelength or frequency of IR radiation and structure of the molecules.
absorption of radiation causes, stretching and bending modes of vibration of bonds. It gives rise to close packed absorption bend called IR absorption spectra. The plot of percentage transmission of IR Radiation vs wavelength called IR spectrum.

It is known as vibrational spectroscopy also., because it involves transition b/w vibrational energy level or more luckily in vibration and rotational level. IR Radiation do not have sufficient energy to cause excitation of electrons.

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each organic compound has its absorption band depending upon
i) nature of functional group
ii) nature of bonds present in them.

- IR spectra is divided in 3 regions

i) functional group Region
ii) b/w (4000 cm^{-1} to 1300 cm^{-1}).
Because characteristic streching frequencies for functional gp as C=O, OH, -NH, occur in this region

a) finger print region:
It is middle frequency region b/w 1300 cm^{-1} – 900 cm^{-1}.
This region is
a) rich in absorption caused by bending vibration.
b) rich in many absorption resulting in streching vibration
C–C, C–O, and C–N bond
c) rich in absorption bend because the no. of bending vibration is usually more then streching vibration.
Thus, each organic compound has its own unique absorption in the region, therefore called fingerprint region

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3) Aromatic region :
(900 cm^{-1} to 650 cm^{-1}).
The absence of absorption in this region indicates absence of aromatic compounds.

* Molecular vibrations :
There are two types of molecular vibrations
(1) Streching
(2) bending.

In streching vibration the distance b/w two atoms decrease or increase but atom remain in the same bond axis.

In bending Vibration the Position of atoms changes relative to the original bond axis

Or

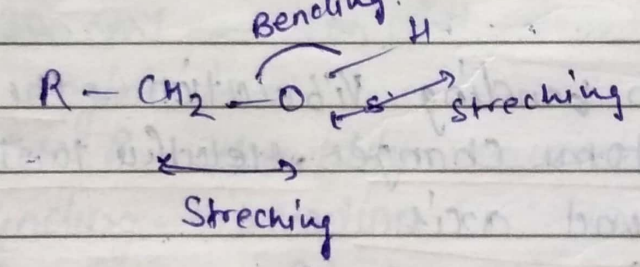
Vibrations can either involve a change in bond length (streching) or bond angle (bending)

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The bending vibration require less energy and occur at longer wavelength (or low frequency) than streching vibration.

The streching vibration are found to occur in order of bonds as
($\nu_{C-C} < \nu_{C=C} < \nu_{C\equiv C}$)

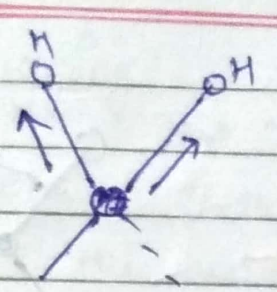
$R-CH_2-OH$ would have bent corresponding to CO streching vibration (1300 to 1000 cm^{-1}, OH streching vibration (3600 cm^{-1} to 3000 cm^{-1}) and COH bending vibration (1500 cm^{-1} to 1200 cm^{-1}) are $R-CH_2OH$



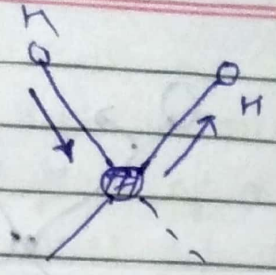
* Streching of bonds:

1. When Streching and Comporesion occur in Symmetrical manner then it is called symmetrical streching

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Symmetrical Streching



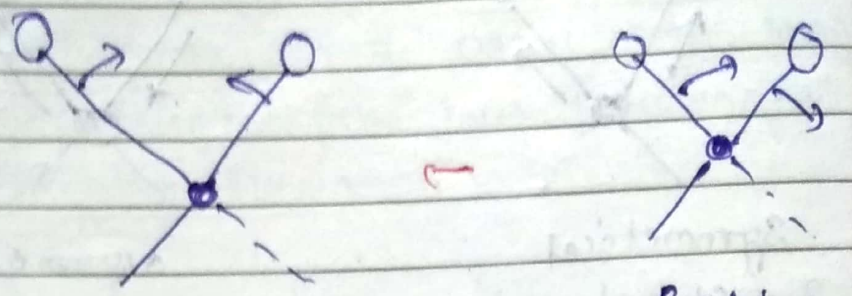
asymmetric streching

(2) When one bond is streching and other bond is compressive it is called asymmeteric streching.
i.e one atom approaches central atom while other moves away.

* Bending of Bonds:

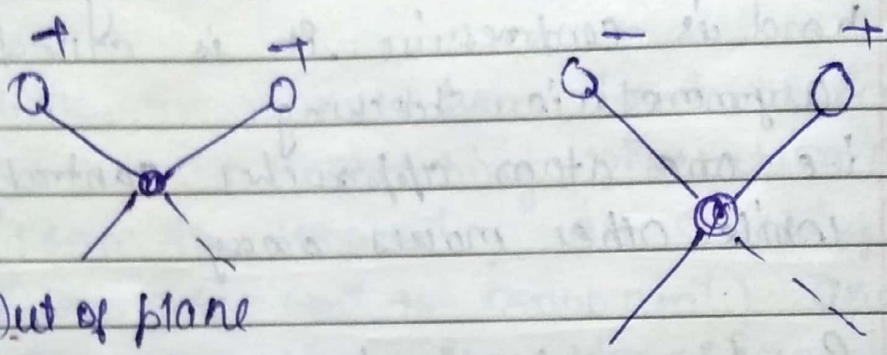
1. Rocking:
When two atoms joining a central atom, move back and forth in the plane of molecules, resulting deformation called rocking (moment of atoms takes place in same direction)

2. Scissoring:
When two atoms joining a central atom, move towards and away from each other then deformation produced is called scissoring,



Scissoring

Rocking



Out of plane wagging

Out of plane twisting.

Bond angle changing in this case (atoms approaching each other w.r.t central atom)

(iii) twisting :

The structure unit rotate about the bond which joins it to the rest of the molecules.

i.e one atom moves up and the plane and other moves down the plane w.r.t central atom

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(4) Wagging:
The structural unit moves back and forth out of plane of molecule, i.e the two atoms moves up and below the plane w.r.t central atom.

numerical

* Degree of freedom:
or
No. of fundamental vibrational.

The no. of fundamental vibrations depends upon the structure of the molecules.

- A Poly atomic non linear molecules having n atoms has a total of 3n degree of freedom:

Total degree of freedom(3n) =

$$= \left[\begin{matrix}\text{translational} \\ \text{degree of freedom}\end{matrix}\right] + \left[\begin{matrix}\text{Rotational} \\ \text{degree of freedom}\end{matrix}\right] + \left[\begin{matrix}\text{vibrational} \\ \text{degree of freedom}\end{matrix}\right]$$

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Translational degree of freedom

= 3

Rotational degree of freedom = 3

Hence vibrational degree of freedom = 3n-6

there are 3n-6 energy level Patterns, each with e its own spacing and same 3n-6 absorption bands

Ex CH_4 ⇒ 3n-6
3(5)-6 = 15-6 =

CH_4 is non linear Compound
vibrational ~~total~~ degree of freedom
n = 5
3x5-6 = 15-6 = 9 Ans

C_6H_6
⇒ n = 12
36-6 = 30

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* for ~~linear~~ linear molecules,
If n be the no. of atoms,

total degree of freedm = 3n

Translational dof = 3

Rotational dof = 2

Vibrational dof = 3n - 5

Eg CO_2 ⇒ 9 - 5 = 4 O=C=O

C_2H_2 - 12 - 5 = 7 C≡C

* Vibration spectra of a diatomic molecules :

A diatomic molecules undergoes vibrational motion same as vibration of Simple Haumonic oscillation acc. to Hooks law

$$F \propto -x$$

$$F = -Kx \quad \text{—(1)}$$

where F is restoring force, which is proportional to the displacement (x), K is force constant.

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Frequency (ν) for simple Harmonic motion is given by

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

μ → reduced mass

Vibrational energy is also quantised like other molecular energies. Energy associated.

Since in spectroscopy, wave number $\bar{\nu}$ is used, Hence dividing the equation with velocity (c) as the

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

Vibrational energy is also quantised like other molecular energies. Energy associated with any vibration state is given by.

$$E = h\nu_0\left(v + \frac{1}{2}\right) \text{ Joules} \quad \text{--- (4)}$$

where v is vibrational quantum no. and ν_0 is fundamental vibrational frequency.

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If there is a transition from lower frequency vibrational level to higher frequency vibrational level then

$$\Delta E_{(vib)} = E' - E$$

$$E' = \left(v' + \frac{1}{2}\right) h\nu - \left(v + \frac{1}{2}\right) h\nu$$

$$= (v' - v) h\nu = \Delta v\, h\nu \quad -(5)$$

for transition b/w adjecent vibrational Energy levels by applying selection Rule

$$\Delta v = \pm 1$$

ΔE above eq^n will be

$$\Delta E = h\nu$$

from eq^n (4) and (5)

$$\boxed{h\nu_0 = h\nu} = \boxed{\nu_0 = \nu} \quad -(6)$$

i.e the frequency of the absorbed I.R radiation (ν) should be the same as the fundamental frequency (ν_0) of the molecules.

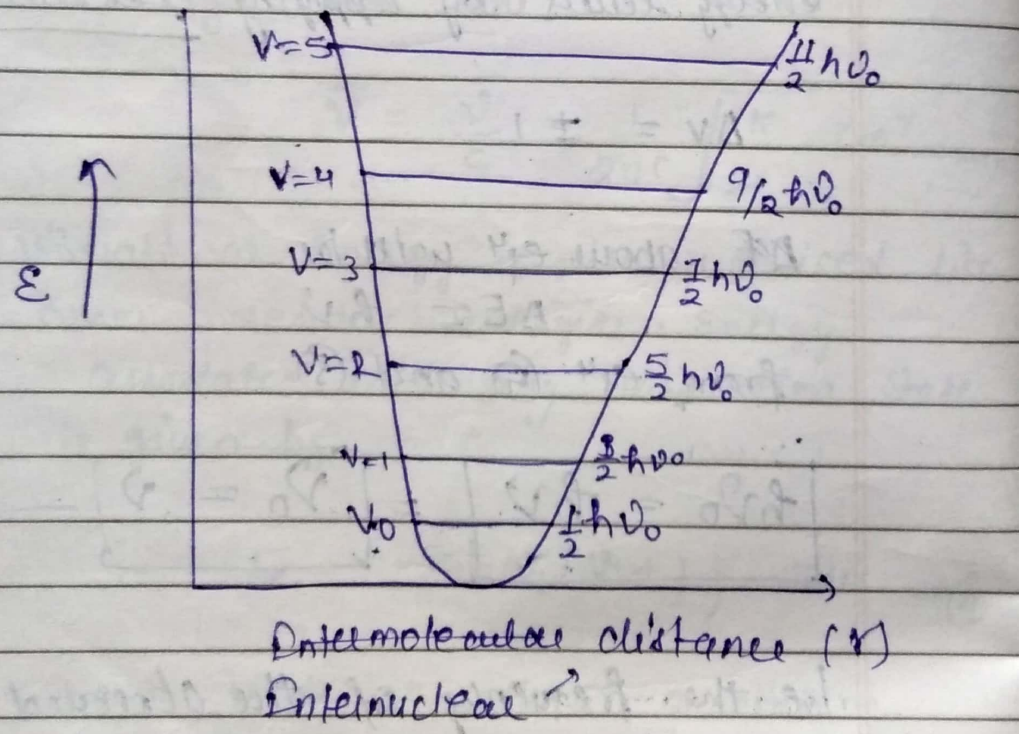
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* Selection Rule for a Harmonic viberation transition: acc. to Shrodinger eq^{n}

$\Delta V = \pm 1$

i.e the increase or decrease in the vibeath quantum no is by one unit only.

Therefore, the energy difference b/w two vibrational levels involved in a transition would always be equal to spacings ($h\nu_0$). Consiquently all the lines in the spectrum fall in the same place

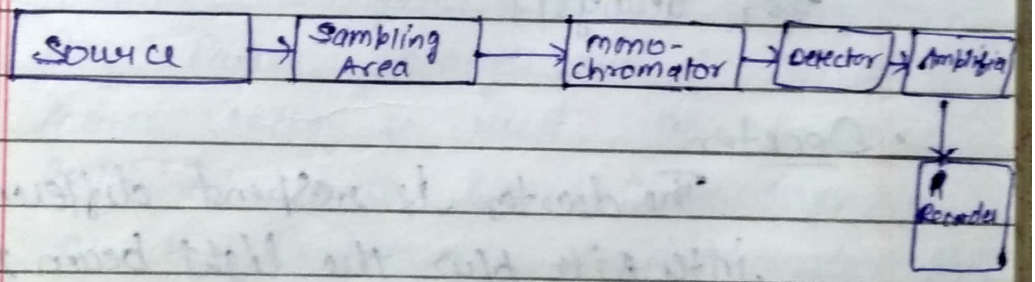


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* Condition for Infra Red absorption:

1. Freq. of the vibration must satisfy the relation $E = h\nu$.
2. Natural freq. of vibration of molecules must be equal to the freq. of incident radiation.
3. Changes in vibration must stimulate changes in dipole moment of molecules.
4. The intensity of absorption must be proportional to square of the rate of change of dipole.

* Instrumentation:



- **Source:**
  Silicon carbide rod heated to emmit radiation (Globar).

- **Monochromator:**
  Prism of NaCl or diffraction grating.

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* Sample holder: KBr, CsBr or AgBr ~~Sampling~~

Sampling:

- Gaseous Substance are directly Placed in gas cells
- Liquid substances

A drop of liquid is Squeezed b/w two flat plate of NaCl to form a thin film of Liquid for test

- Solid substance:

mixed with KBr and almost transparent plate is prepared for analysis

* Decetor:

The decetor is respond difference in intensity b/w the light beam from reference and Sample cells.

Recorder:

It is automatically records the IR spectrum of the given compound on the chart with recorder pen

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Locotime

* FTIR:

Fourier transform Infra Red Spectroscopy:

The dispersive IR spectrometer are poor in sensitive, speed and accuracy, therefore cannot be teiken as fast process of anaylsis.

In FTIR the light from a source through a scanning ~~an~~ Michelson interferometer and fourier transformation gives a plot of intensity vs frequency. It takes only few milli seconds and produces more intense signal. In fact, entire radiation Range Passes through the source all of source energy is used. It can be combined with liquid chemotography or High Reiformance liquid chomatography (HPLC) to get complete anaylsis.

* Application of IR spectra:

22/2/19

1. Qualitative analysics: It is done by compaving the spectrum of unknown sample with standard sample compound

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2. Quantitative Analysis:
Conc^n of a particular functional gp is determined since each functional group has its characteristic frequency.

3. estimating impurity:
Presence of impurity in compound causes broadening of energy bands and appearence of extra bands.
Therefore can be easily dected by compairsion with IR spectra of standard pure compound. Small amount of ketone can be detected in a hydrocarbon, since hydrocarbon shows no absorption near 1720 cm^{-1} which is characteristic frequency of ketone

4. Presence of water in sample:
It is detected by band at 3600 cm^{-1} and weak band at 1650 cm^{-1} showing water of crystalisation

5. Study of Chemical Rx^n:
Rx^{n}s involving change in functional group can be study it by analysing IR Spectrum obtained during Rx^n.

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6. Study of Coordination Compound:
The IR Spectra of some EDTA Complexes indicate that it behaves as tetra, Penta or hexa deutate Ligands in various Complexes.
Detected by absorption band in Carbonyl region Corresponding to free and Complex Carbonyl Compound.

7. Used to estimate bond Strength and force Constant:
Measures force required to deformed a bond
Ex: force Constant for HF is 9.7×10^5 dyne cm^{-1} and HCl (4.84×10^5 dyne cm^{-1}), which shows that HCl bond is weaker then HF

Greater the force Constant Stronger the bond.

Q. HCl gives absorption band at 2890 cm^{-1} Calculate the force constant.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Degree of the Instrument Applied

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$$K = 4\pi^2 c^2 \mu (\bar{\nu})^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} =$$

$$m_H = \frac{1.008}{N_A} \qquad m_{Cl} = \frac{35.46}{N_A}$$

$$\mu = \frac{1.008 \times 35.46}{1.008 + 35.46} \times \frac{1}{6.023 \times 10^{23}}$$

$$= 4\pi^2 \mu (2890)^2 c^2$$

$$= 4\pi^2 \times (3 \times 10^{10})^2 (1.67 \times 10^{-24}) \cdot (2890)^2$$

$$= 4.84 \times 10^5 \text{ dyne/cm}$$

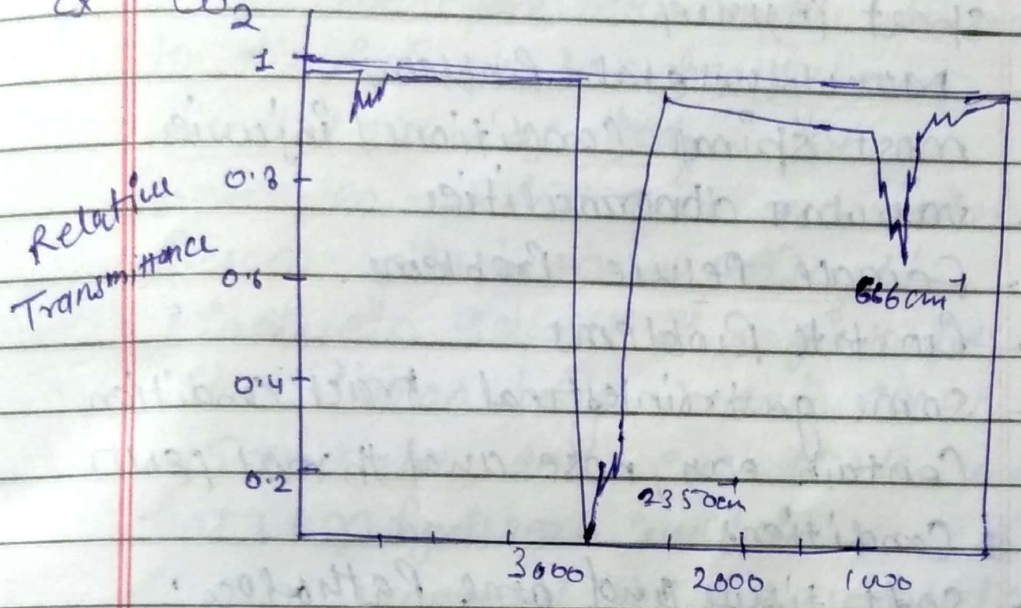
Q. Distance b/w Intra and Inter molecular Hydrogen bonding:

IR spectra of the compound is recorded at diff. concentration. with increase in concentration the absorption bend, due to intermolecular hydrogen bonding increases while that due to intra molecular H Bonding remain unchanged

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(2) Structure elucidation:
Bond length, Bond strength, dipole moment molecular symmetry can be determined

Ex CO_2



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* MRI (Magnetic Resonance Imaging):

What can be diagnosed by an MRI scan
- most ailments of the brain, including tumours
- Sport injuries
- Musculoskeletal problems
- most spinal conditions / injuries
- vascular abnormalities
- Female Pelvic Problems
- Prostate Problems
- some gastrointestinal tract condition
- Certain ear, nose and throat (ENT) conditions
- soft tissue and bone Pathology.

Who can't have an MRI Scan
- A cardiac Pacemaker
- certain clips in your head from brain operations
- A cochlear implant
- A metallic foreign body in your eye
- Had surgery in the last 6 weeks
- If you are pregnant

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* MRI employs Nuclear magnetic Resonance or Protons to Produce Proton density maps (or Images) of the human body.

Therefore MRI can be utilised to discriminate b/w healthy and diseased tissue of body. It is based on the fact that the Protons present with in water, i; fats etc resonate at a given frequency. Since human body contain about 75% water and each water molecule has two hydrogen nuclei,

so Image of the different Parts of the body can easily be taking. In a diseased condition of body Part the distribution of water, fats, lipids etc alter and hence by using MRI, one can detect the diseased Part of the body

Basic Procedure:

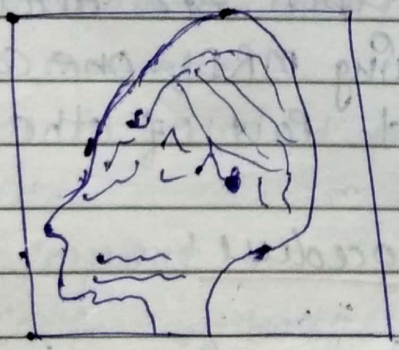
For geting an image in MRI, a very. Img magnetic field is applied across the body Part under consideration

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The protons in various regions of body come to resonance at different radio frequencies and the intensity of signal is proportional to the no. 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 Projection is combined by computer to get 3-D image of the body part.

MRI Requires very small time for Scanning a Particular Body Part



Cross section of a patient. Image (displaying soft tissue) obtained by MRI

Theory sence

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* Application :
1. for investagating the fn. of myocardium, Heart, etc.
2. To identify the regions exessive fat deposition in different body organs, Blood vessiols etc
3. For the analysis of blood by using (^{23}Na) MRI.
4. For estimation of flowine conc^n in different body parts by using (^{19}F) MRI.

* Fluorescence :
Certain substances (atoms or molecules) when exposed to light radiation of short wavelength (high frequency) emit light of different frequencies compared to those of incident radiation this process called fluorescence stop as soon as the incident radiation is cut off.
actually, decay period is very short namely 10^{-9} to 10^{-4} second.
The substance which exbits fluorescence is called fluorescent substance.

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For ex: CaF_2, Uranium, organic di (eosin), Organic dieste (eosin) fluorescent Chlorophyll, quinine sulphate solution, Vapour of sodium, iodine, mercury etc

When light is absorbed by fluorescent substance, the exited state of an atoms emits light radiation in several transitions of lower state. Consequently, The emitted light has different frequency for each transition. Therefore,

$$X + h\nu \longrightarrow X^* \quad \text{(Primary)}$$

$$X^* \longrightarrow X^{*'} + h\nu' \quad \text{(Secondary)}$$

$$X^{*'} \longrightarrow X + h\nu''$$

where X, $X^{*'}$ denotes the Energy state b/w X and X^*.

The emitted radiation frequencies ν' and ν'' are different from the Incident radiation frequency (ν).

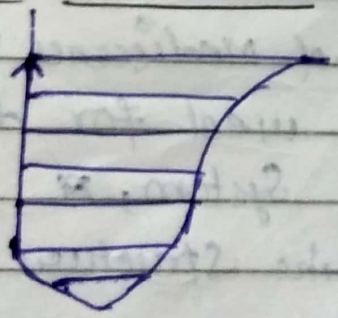
Fluorescence may be regarded as a Secondry and results from the primary process of

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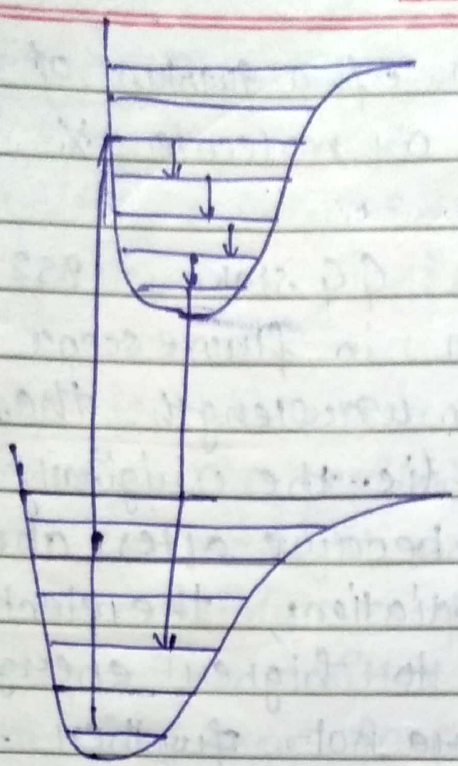
absorption of a quantum of light $h\nu$ by an atom or molecule X

Acc. to GG stoke 1852, the emitted radiation in fluorescence are of greater wavelength then the exiting radiation. (ie. the originally absorbed) this is because after absorbing the light radiations, the electrons are raised to higher energy level but are not further ejected completely. The electrons then return to the original level in steps. These jumps thus possess lesser energy then the original jump during initial excitation.

hence the emitted light has low frequency then the light absorbed.



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It is a powerful technique for studying molecular
in analytic Chemistry,
Cell Biology, , Cardiology,
Photo chemistry, and Environmental scieny

1. Biochemichy and Medicence:
   1. Fluoresente is used for drug interaction with biological System, PNEST research, Proteine Structure and flooddy
   2. Protine - antibody interaction,
   3. donor acceptor distances
   4. Enzyme Confirmation in proteines and membrane.

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5. dynamics and structure of nucleic acid
6. ~~Auto~~ Photochemistry of vision
7. mechanisms of Photosynthesis

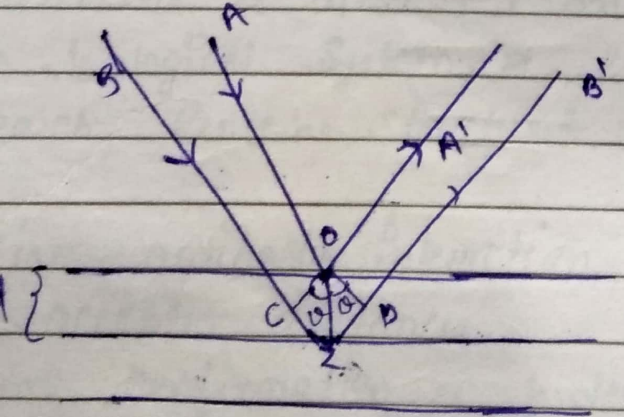
* Petrolium research:
1. Fluorescents is used for Chevichrasion of Crude oil
* Environmental research:
fluoresene is used for detection and identification of pollutents.
* anayletical Chemistry:
Fluorescents is used for identification and detection of Complex mixtures of fluorescent Substances

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* X-Ray :
Bragg's Law :

Bragg's Pointed out that the scattering of X-Ray would be considered as reflection of successive planes of atoms in the crystal. the rays reflected from the different plane will be in same phase if there Path difference is an integral multiple of wavelength of X-Ray.

Let the x-Ray beam fall on Crystall surface at an angle θ. Sum of the rays will reflect from upper plane at the same angle θ while sum other will absorve and reflect from Successive layers which is shown below.



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Let AOB Beam light incident on first plane and reflect in the dir of OA' at an angle θ.

Similarly the Beam of BZ incident on second plane of crystall at same angle θ and reflect in the direction of ZB'.

The dist. b/w two Planes of crystal is d (interplanes distance).

acc. to Bragg's Principle Pd there path is

the Path difference

$$BZB' - AOA' = n\lambda$$

Or $CZ + ZD = n\lambda$

or Consider a triangle

ΔDOZ and ΔCOZ

angle O is common, distance OZ is common.

angle OCZ and $\angle ODZ = 90°$

therefore $\Delta DOZ \cong \Delta COZ$

this means both triangles are Congreunt.

$$CZ = ZD$$

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Q4

$$2ZD = n\lambda$$

$\sin\theta =$

In ΔDOZ,

$$\sin\theta = \frac{ZD}{OZ}$$

or $$ZD = OZ \sin\theta$$

or

$$ZD = d \sin\theta \quad (OZ = d)$$

Hence

$$\boxed{n\lambda = 2d \sin\theta}$$ Bragg's eq^n.

As we know that Interplanar spacing in terms of unit cell parameter is given as

Formula:

$$d_{hkl} = \frac{1}{\sqrt{h^2 + k^2 + l^2}}$$

Here a = length of the cube edge (lattice parameters)

For cubic symmetry

$$\boxed{a = b = c}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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$$\sin\theta = \frac{n\lambda}{2a}\sqrt{h^2+k^2+l^2}$$

Q.1 X-Ray of wave length 1.54 A° is falling at an angle of 14°12' on a crystal to show 1st order diffraction. Calculate the seperation b/w two parallel plates of the crystal.

Sol^n

$$n\lambda = 2d\sin\theta$$

$$d = \frac{n\lambda}{2\sin\theta}$$

$$d = \frac{1\times 1.54\times 10^{-10}}{2\times}$$

$$d = \frac{1.54\times 10^{-10}}{2}$$

$14^\circ 12'$

$= 14.\frac{12'}{60} = 14.02$

$\sin 14.02 =$

$= \frac{0.77\times 10^{-10}}{0.245} = 3.142\times 10^{-10}$

$= 3.156\ A^\circ$

Q.2 State and derive bragg's law. X-rays ~~beam~~ beam of 0.824 A° wavelength is incident on a crystal a glancing angle of 8°35' when 1ST order diffraction occur

(ii) determine the glancing angle for 3rd order diffraction and interplanal of the crystal

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Ans $\lambda = 0.824\ \text{Å} = 0.824 \times 10^{-10}$

angle (θ) $8° 35' = 8.58°$

(i) $n = 1$

d

$n\lambda = 2d \sin\theta$

$d = \frac{n\lambda}{2\sin\theta}$

$= \frac{1 \times 0.824 \times 10^{-10}}{2 \times \sin(8.58°)}$

$= \frac{0.412 \times 10^{-10}}{\sin\theta(8.58°)}$

$= \frac{0.412 \times 10^{-10}}{0.1491} = 2.76\ \text{Å}$

(ii) when $d = 2.76\ \text{Å}$

$n = 3$

$\lambda = 0.824 \times 10^{-10}$

$\theta = ?$

$\sin\theta = \frac{n\lambda}{2d}$

$= \frac{3 \times 0.824 \times 10^{-10}}{2 \times 2.76}$

$= \frac{2.472}{5.52} \times 10^{-10}$

$\sin\theta = 0.447 \times 10^{-10}$

$\theta = 26.55°$

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Q. what is bragg's law? derive bragg's law eq 4
by crystals. at what glancing angle would the 1st order diffraction occur, when copper radiation ($\lambda = 1.54\ A^\circ$) interact with the 1st order lattice planes with interplanner spacing of $1.54\ A^\circ$

Ans
$$\lambda = 1.54 \times 10^{-10}$$
$$d = 1.54 \times 10^{-10}$$

$$n\lambda = 2d \sin\theta$$
$$\sin\theta = \frac{2}{2}\frac{n\lambda}{d}$$
$$= \frac{1 \times 1.54 \times 10^{-10}}{2 \times 1.54 \times 10^{-10}}$$
$$\sin\theta = \frac{1}{2}$$
$$\theta = 30^\circ$$ Ans

Q at what glancing angle would the 1st order diffraction from (110) plane of KCl be observed, using x-rays of wavelength 154 pm. The dim. of unit cell is 315 pm.

$$\lambda = 154 \times 10^{-12}\ m$$
$$\sin\theta = \frac{n\lambda}{2d}$$
$$\sin\theta = \frac{1 \times 154 \times 10^{-12}}{2 \times \sqrt{2}}$$
$$\sin\theta = \frac{77 \times 10^{-12}}{}$$

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$$\sin\theta = \frac{1.54 \times 10^{-12}}{2 \times \frac{a}{\sqrt{h^2+k^2+l^2}}}$$

$$= \frac{1.54 \times 10^{-12}}{2 \times \frac{3.15 \times 10^{-12}}{\sqrt{1+1}}}$$

$$= \frac{1.54 \times 10^{-2}}{\sqrt{2} \times 3.15 \times 10^{-12}}$$

$$= \frac{1.54}{\sqrt{2} \times 3.15}$$

$$\sin\theta = 0.345$$

$$\theta = \sin^{-1}(0.345)$$

$$\theta =$$

Qu: Calculate the angle at which 1st order diffraction will occur in an x-ray diffracted while x-ray of wavelength 1.54 Å are diffracted by the atom of a crystal Given that the interplanar dist is 4.04 Å

Sol: $n\lambda = 2d\sin\theta$

$$\sin\theta = \frac{n\lambda}{2d} = \frac{1 \times 1.54 \times 10^{-10}}{2 \times 4.04 \text{ Å}}$$

$$\sin\theta = \frac{1.54}{8.08} = 0.$$

$$\theta = \sin^{-1}(0.190)$$

$$= 10.98^\circ$$

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* Raman Spectroscopy :-

Introduction :

Raman scattering was discovered in 1928 by C.V Raman. who won the nobal prize.

Raman spectroscopy is one of the vibrational spectroscopic technique used to provide information on molecular vibrations and crystal structures. this technique uses a Laser light.

Laser light shows to irradiate a sample, and generate an amount of Raman scattered light, which is detected as a raman spectrum

Raman spectroscopy is much like IR spectroscopy. However, whereas IR vents arrive from a change in the dipole moment of a molecule due to an interaction of light with the molecules, Raman vents arise from a change in the polarisability of the molecules due to some interaction

when light is scattered by matter, almost all of the scattering is an elastic process, which is called ~~retay~~ sea rayleigh scattering,

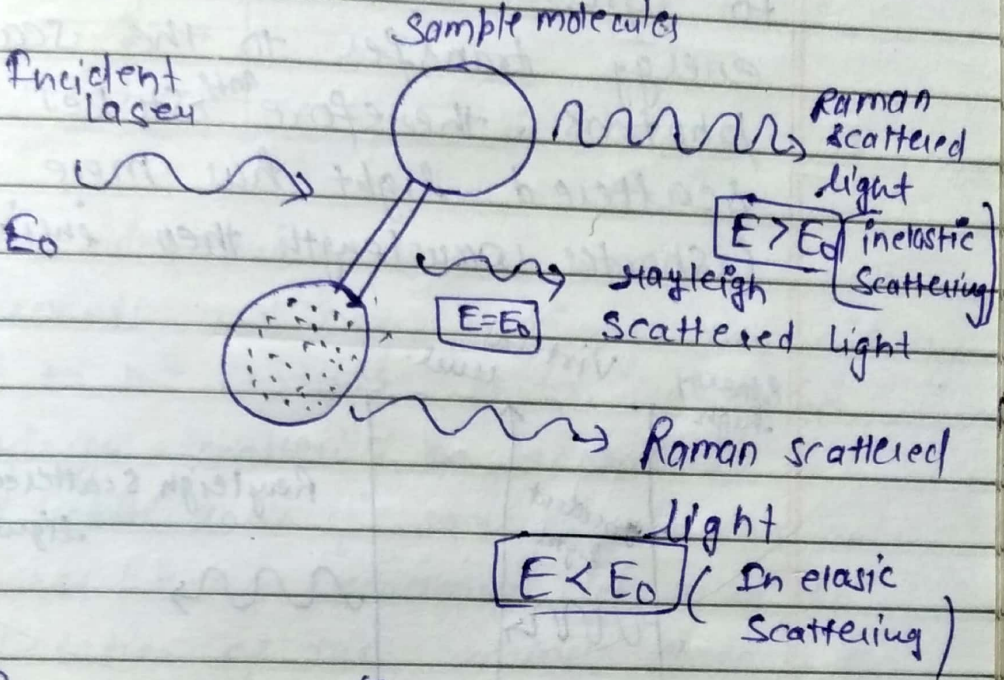
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and there is no change in energy. however, a very small percentage of scattering is an inelastic process. i.e the scattered light has different energies from incident light. this inelastic scattering of light was first observed experimently by Chandra shakar vankat Raman (CVRaman) in 1928, which is why this inelastic scattering is called Raman scattering.

In other words, Inelastic scattering ~~mean~~ beams that the frequency of photon in monochromatic light changes upon interaction with a sample. photons of the ~~tay~~ laser light and absorbe by the sample and then re-emitted.
frequency of re-emitted photons is shifted up or down in comparision with original monochromatic frequeny, which is called the raman effect. this raman shif occurs because photons (particles of light)

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Exchange part of their Energy with molecular vibrations in the material. this shift provides information about vibrational, rotational and other low frequency transitions in molecules.



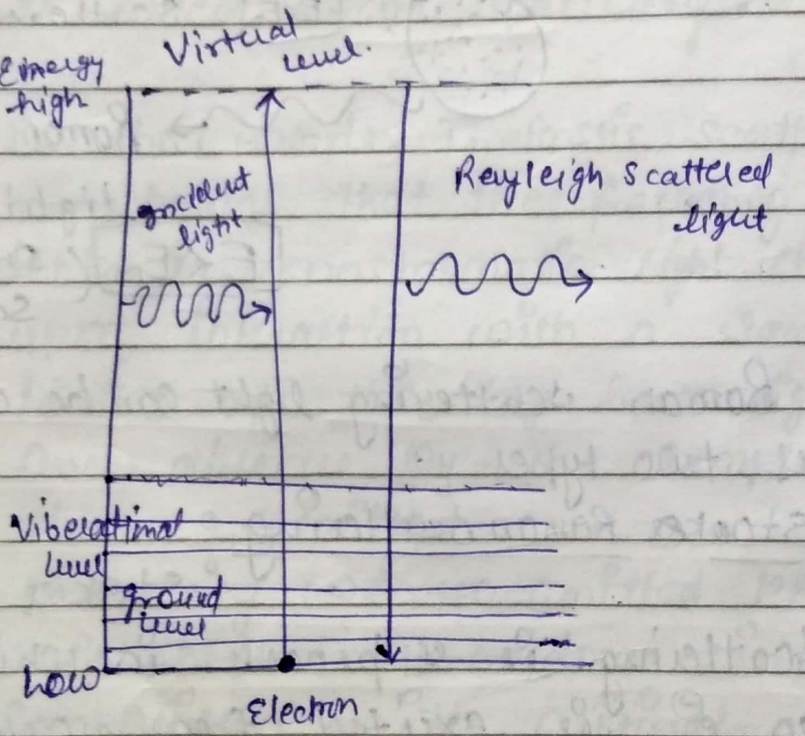
Spectrum: Raman scattering light can be classified as two types.

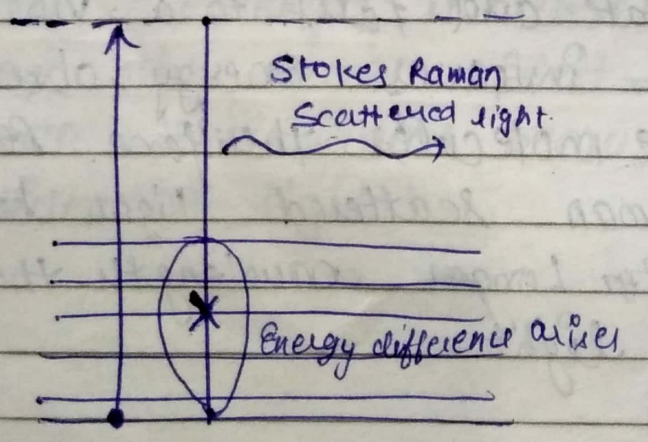
Q. Stokes Raman scattering :- Stokes Raman Scattering is a process in which an $e^{\ominus}$ is excited from ground state and falls to a vibrational level It involves energy absorption by the molecules therefore Stokes Raman Scattered light has less energy (or Longer wavelength) then incident light

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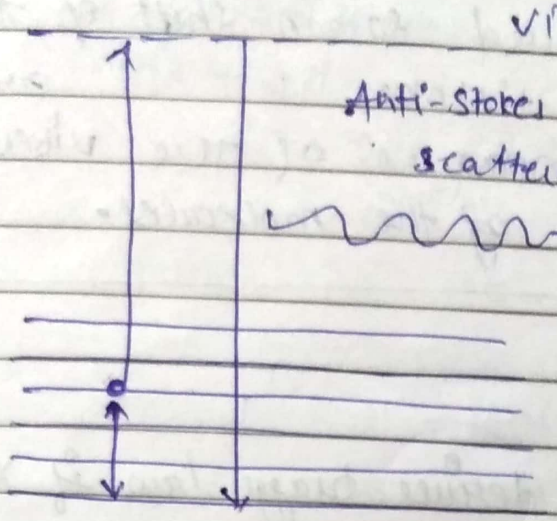
(b) anti-stokes Raman scattering

anti stokes Raman scattering is a process in which an electron is excited from the vibrational level to ground level. It involves an energy transfer to the scattered photons. therefore anti-stokes Raman scattered light has more energy (shorter wavelength then incident light).





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- Raman Scattering is an extremely weak process and only Every one in Every 10^6 to 10^8 photon's photon scattered rayleigh scattering is a dominant.
the ~~relati~~ ratio of stokes raman and anti stokes raman scattering depends on the population of the various state of the molecules. at room temperature the no. of molecules in an excited vibration level is smaller then that of in the ground level; Therefore generally the intensity of stokes Raman light is higher then anti Stokes Raman light.

In standard raman measurement rayleigh scattered light is rejected using a filter and only the stokes raman scattering scattering light is recorded for simplicity.

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The observed raman shift of the stokes and antistokes are the direct measure of the vibrational Energies of the molecules.

X-Ray:

Q.2 State and derive Braggs law if X-Ray of 120 pm is incident at an angle of 15° for second order reflection then the calculate the dist b/w the planes

$$n\lambda = 2d \sin\theta$$

$$d = \frac{n\lambda}{2\sin\theta} = \frac{2 \times 120 \times 10^{-12}}{2 \times \sin(15^\circ)}$$

$$= \frac{120 \times 10^{-12}}{0.2588} = 463.67 \text{ pm}$$

Q 1st order X-Ray ($\lambda = 154$ pm) reflection max. from a set of (2,0,0) planes of a body centered cubic lattice was observed at θ 16° 6'. Calculate the length of edge of units.

$h = 2, 0, 0$

$$d = \frac{\theta}{\sqrt{1}}$$

technique

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$n\lambda = 2d\sin\theta$

$n\lambda = 2d$

$d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 154 \times 10^{-12}}{2 \times 0.277}$

$= \frac{154}{0.277}$

$= \frac{154 \times 10^{-12}}{0.554} = 280\,pm$

$= 277.67\,pm$

$2d$

$\frac{a}{\sqrt{h^2+k^2+l^2}} = 280$

$\frac{a}{2} = 280$

$a = 560\,pm$

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* Surface characteristic ~~technic~~ technique:

Surface characteristic of a materials means the property associated with its surface. Typically measurement of surface area, surface roughness Pore size and surface characteristic.

Information on surface characteristics is very important for a possible application of surfaces as semiconductors, heterogenious catalyst and also in biological research.

These techniques could be classified in two categories

1. Classical methods
2. Instrumental methods

1. classical methods:

i) Langmuir ~~method~~ model:

In an adsorption system where langmuir model is follows, the maximum amount of adsorbate per gm of adsorbent for the formation of monolayer, X_m (mg/g) value is determined

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Surface area of adsorbent could be calculated using following equation

Surface area of the adsorbent $(m^2/g) =$

$$= \frac{Xm\ (mg/g) \times N \times S\ (m^2/molecules)}{M.}$$

Here X_m = maximum amount of adsorbate adsorbed per gm of adsorbate for monolayer formation

M = molecular wt. of adsorbate (mg/molecule)
N = Avagadro's number
S = Contact surface area by each molecules (m^2)

(iii) BET equation:

BET (Brunauer, emmette and teller) equation is used to give specific surface area from the adsorption data. BET equation is as follows

$$\frac{z}{(1-z)} \cdot \frac{1}{V} = \frac{(c-1)z}{c\,V_{mono.}} + \frac{1}{c\,V_{mono.}}$$

Where V = volume of gas adsorbed at pressure P.

V_m = amount of gas corresponding to one monolayer

z = Pressure of gas and pressure at saturation. (P/P°)

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c = constant.

* Spectroscopic methods :-
These methods may used of the Principle that when a beam of electron or high energy radiation (usually X-Rays) are bombarded at the surface, the surface electr from the upper layer are ejected. these electrons are called secondy electrons.

In spectroscopic methods, Surfaces are analysed by capturing secondy electrons of different energies, which are characteristics of their environment. Based on spectroscopic theory some of the techniques are disscused below.

(i) X-Ray photoelectron Spectroscopy (XPS) :-
X-Ray photoelectron spectroscopy (XPS) was developed in mid 1960. by K. Siegbahn and his colligue, later K. Siegbahn was awarded by Nobel Prize for Physics.
for the work on XPS.

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This technique provided a wide range of regarding atomic composition, oxidation state and chemical structure. Because its versitility it is also called electron spectroscopy for chemical Analysis (ESCA). Basic principle of this technique is based on phenominan called photoelectric effect by Albert einstien in 1905.

when photon have known energy (usually x-Ray) knock the surface, an electron from K-shell is knocked down, kinetic energy of this electron is measured in the spectroscopy. the spectrum is given as the binding energy as function of electrons counting rate. The binding energy of an atom can be calculated from the following equation.

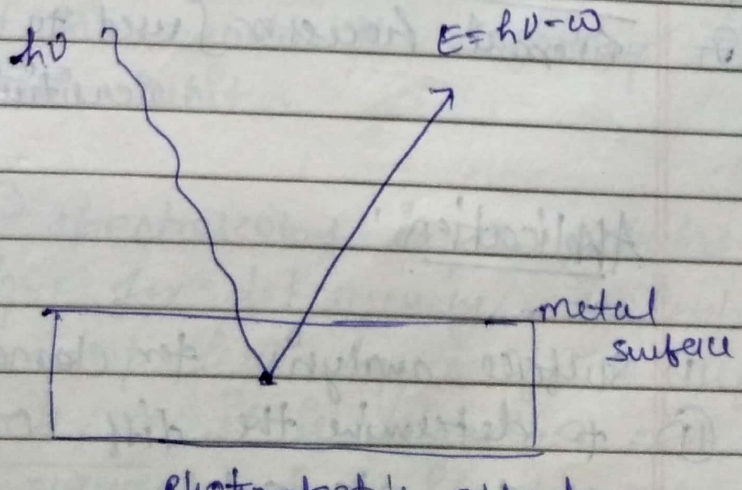


Photo-electric effect

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Binding Energy (E_b) = $h\upsilon - KE - W$

$h\upsilon$ = Incident Energy

KE = Kinetic Energy of the ejected e^-

W = work function.

In the XPS Spectrum, the innermost orbital appears at higher binding energy than the outer orbital.

- Basic components of XPS instrumentation

i) Source: X-Ray tube with both Al or mg target suitable filter

ii) Sample holder: Sample like of a piece of metal are mounted close to the surface.

iii) analisizer: hemispheric analisizer

iv) detector :
v) Signal Processor } Solid state detector are used to attained Require sensitivities.

Application:

(I) Surface analysis for elemental composition

(II) to determine the diff. oxidation state of the element.

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(iii) for structural analysis of molecules
(iv) It is also useful for qualative analysis of the surface.

*

* Auger Electron spectroscopy : (AES) :-
In AES the source is electron beam unlike x-ray in XPS. electrons of energy 3-20 kev are incident upon a conducting semple, these electrons cause core electrons from the atom contained in the semple to be knocked out, giving a photoelectron and atoms with a core hole some energy is released in the transition, this released energy ejects another electron from the next higher level which is called Auger e⁻.

The kinetic energy of Auger electron is the difference b/w the energy released in Relaxation of excited ion and Energy Required to remove the secondry e⁻ from the orbit.

Auger e⁻ spectroscopy is a popular technique for determining the composition of the top few layers of the surface. except H, He. It is sensitive for all other elements. But it is more sensitive to liter elements than

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Heavy elements.

Since Auger electrons are very weak, only electron from the surface of a few atomic layer can reach the detector.

Instrumentation:

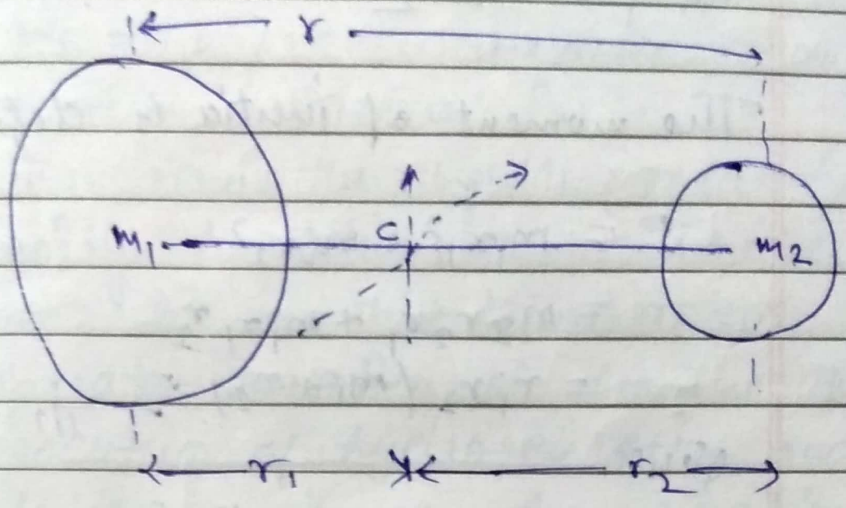
It is somewhat similar to XPS except for the electron source. A common electron gun is the source of e. Its basic mechanism involves the application of about 5 kev applied to cylinder which produces electron. The produced electrons are converged to a spot by positive potential. This spot is used to scan the surface.

Application:

(i) Qualitative analysis of solid surfaces
(ii) depth profiling of solids.

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* Rotational Spectra of di-atomics:



Sol: A rigid di-atomic with masses m_1 and m_2 joined by a thin rod of length (r) ($r = r_1 + r_2$)

Center of mass is at C.

The two independent of this molecules w.r.t the two axis which pass through C. and are perpendicular to the bond length r. The rotation w.r.t the bond axis is possible only for classical objects with large masses. for quantum objects the rotation with r.t the molecular axis does not correspond to the any change in the molecules as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments of both segments of the

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For the segments of the molecular axis

$m_1 r_1 = m_2 r_2$ — (i)

The moment of inertia is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{(ii)}$$
$$= m_2 r_2 r_1 + m_1 r_1 r_2$$
$$= r_1 r_2 (m_1 + m_2) \quad \text{(iii)}$$

Since

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_1),$$
$$(m_1 + m_2) r_1 = m_2 r$$

Therefore

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad \text{(iv)}$$

Substracting the above eq^n in (iii) we get

$$I = \frac{m_1 m_2 r^2}{m_1 + m_2} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

where μ the reduced mass is given by (v)

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of diatomic is equivalent to a rotation of a mass μ at a

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distance of r from the origin. the K.E of this rotational motion is K.E.
$KE = l^2/2I$ where l is the angular momentum. $l = I\omega$
where ω is the angular (rotational) velocity in radians/sec. The operator for l^2 is the same as the operator ~~equation~~ l^2 for the angular momentum of hydrogen atom and the solution of the operator equation $l^2 Y_{lm} = l(l+1) Y_{lm}$, where are the spherical harmonics which have been studied.

The quantized rotational energy levels for the diatomic molecules are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

The energy difference b/w two rotational levels is usually expressed in cm^{-1}. The wave no. corresponding to a given ΔE is given by

$$\nu = \Delta E / hc \ , cm^{-1}$$

The energy level in cm^{-1} are therefore

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$$E_J = B(J(J+1))$$

where $B = \frac{h}{8\pi^2 I_c}$

The rotational Energy level of a diatomic molecules are shown

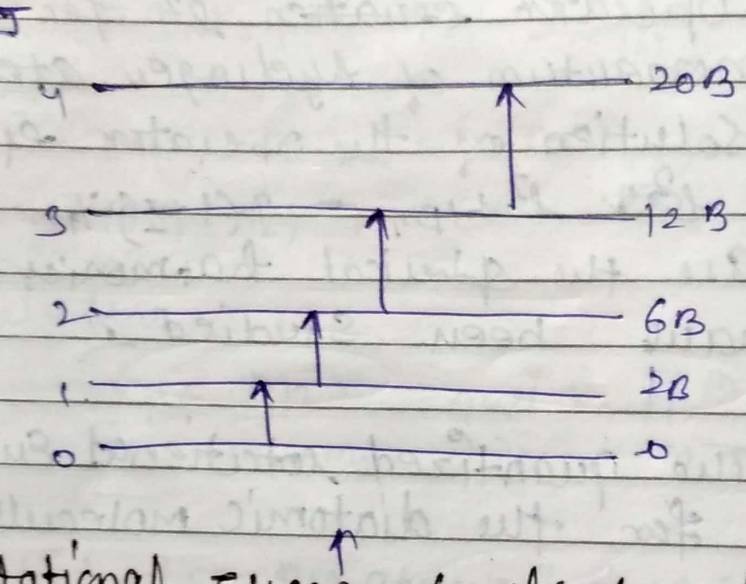


Fig- Rotational energy levels of a rigid diatomic molecules and the allowed transitions.

The selection rule for a rotational transition is

$$\Delta J = \pm 1$$

In addition to this requirement the molecules has to possess a dipole moment. As a dipolar molecules.

molecular attraction

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rotates, the rotating dipole constitutes the transition dipole operator. Molecules such as HCl and CO will show rotational spectra, while H_2, Cl_2, CO_2 will not. The rotational spectrum will appear as follows

