KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

LECTURE PLAN
DEPARTMENT OF PHYSICS

STAFF NAME	: Dr. S. KARUPPUSAMY	
SUBJECT NAME	: PHYSICS	SUB.CODE:17PHP204
SEMESTER: II		CLASS: I M.Sc., (PHYSICS)

Sl.No.	Lecture Duration Period	Topics to be covered	Support Material/Page Nos.
		UNIT I	
1.	1	Introduction to spectroscopy	T1(1.1)
2.	1	Hydrogen spectra – Angular momentum	T1(1.20)
3.	1	Larmor precession – Spin-orbit interactions - Spectra of alkali metals	T1(1.34-1.40)
4.	1	Energy level and spectral transitions of Helium	T1(1.33)
5.	1	Normal Zeeman effect – Anomalous Zeeman effect – Paschen back effect	T1(1.48-1.50)
6.	1	Inference of nuclear spin, Hyperfine structure of spectral lines	T1(1.52)
7.	1	Stark effect – Characteristic X-ray spectra	T1(2.1-2.8)
8.	**1**	Microwave spectra: Classification of molecules – Interaction of radiation with rotating molecule	T1(2.1-2.7)
9.	1	Rotational spectra of rigid diatomic molecule – Isotopic effect – Non-rigid rotator	T1(2.8-2.18)
10.	1	Linear, symmetric and asymmetric top molecules	T1(2.18-2.20)
11.	1	Quadrapole hyperfine interaction – Microwave spectrometer	T1(2.21-2.23)
12.	1	Revision	
	Total No of Hours Planned For Unit I=12		
		UNIT II	
1.	1	IR spectroscopy: Practical aspects	T1(2.29-2.31)
2.	2	Theory of I.R rotation vibration spectra of gaseous diatomic molecules	T1(2.31-2.33)
3.	1	Applications of I.R spectroscopy	T1(2.78)
4.	1	Basic principles of F.T.I.R spectroscopy	T1(2.40-2.41)
5.	1	Raman spectroscopy	T1(2.83)
6.	1	Classical and Quantum theory of Raman effect	T1(2.85)
7.	1	Rotation vibration Raman spectra of diatomic and polyatomic molecules	T1(2.86)
8.	1	Applications	T1(2.92)

9.	1	Laser Raman spectroscopy	T1(2.98)
10.	1	Surface Enhanced Raman Scattering	T1(2.99)
11.	1	Revision	
	Total No of Hours Planned For Unit II =12		
UNIT III			
1.	1	Electronic spectra: Electronic excitation of diatomic species	T1(3.27)
2.	1	Vibrational analysis of diatomic molecules	T1(3.31)
3.	1	Deslandre's table	T1(3.32)
4.	1	Intensity distribution Frank Condon principle	T1(3.28)
5.	1	Rotational structure of electronic bands	T1(3.38)
6.	1	Resonance and Normal Fluorescence – Intensities of transitions	T1(3.44)
7.	1	Phosphorescence population of triplet state and intensity	T1(3.44)
8.	2	Experimental methods - Applications of Fluorescence and phosphorescence.	T1(3.45)
9.	1	Revision	
	Total No of Hours Planned For Unit III =10		
UNIT IV			
1.	1	NMR Spectroscopy: Quantum mechanical and Classical description	T1(2.235)
2.	1	The Bloch equation	T1(2,236)
3.	1	Relaxation process	T1(2.235)
4.	1	The experimental technique	T1(2.235-2.236)
5.	2	Principle and working of high resolution NMR Spectrometer	T1(2.237)
6.	1	Chemical shift – Applications of NMR	T1(2.237)
7.	1	NQR Spectroscopy: Fundamental requirements - General principle	T1(2.238)
8.	1	Experimental detection of NQR frequencies	T1(2.242)
9.	1	Interpretation and chemical explanation of NQR spectroscopy	T1(2.242)
10.	1	Applications of ESR	T1(2.242)
11.	1	Revision	
	Total No of Hours Planned For Unit IV =12		
UNIT V			
1.	1	ESR Spectroscopy: Basic principles of ESR	T1(2.245)
2.	1	Experiments	T1(2.245)
3.	1	ESR spectrometer reflection cavity and microwave bridge	T1(2.246)
4.	1	ESR spectrum hyperfine structure - Study of free radicals – Applications of ESR	T1(2.247)

5.	1	MOSSBAUER Spectroscopy: The Mossbauer effect	T1
6.	1	The recoilless emission and absorption of - Mossbauer spectrum	T1
7.	1	Experimental methods	T1
8.	1	Hyperfine interaction	T1
9.	1	Chemical Isomer Shift	T1
10.	1	Magnetic hyperfine and electric quadrupole interaction.	T1
11.	1	Revision	
12.	1	Old question paper revision	
13.	1	Old question paper revision	
14.	1	Old question paper revision	
	Total No of Hours Planned For Unit V =14		
Total Planned Hours		**60**	

Text Book : Spectroscopy by Gurudeep. R. Chatwal and Sham. K. Anand.

SYLLABUS

Atomic spectra: Hydrogen spectra – Angular momentum – Larmor precession – Spin-orbit interactions - Spectra of alkali metals – Energy level and spectral transitions of Helium - Normal Zeeman effect – Anomalous Zeeman effect – Paschen back effect – Inference of nuclear spin - Hyperfine structure of spectral lines – Stark effect – Characteristic X-ray spectra

Microwave spectra: Classification of molecules – Interaction of radiation with rotating molecule – Rotational spectra of rigid diatomic molecule – Isotopic effect – Non-rigid rotator – Linear, symmetric and asymmetric top molecules – Quadrapole hyperfine interaction – Microwave spectrometer

Hydrogen Spectrum Definition

A Hydrogen atom consists of only one proton and the electron that revolves in the electron cloud. The emission spectrum of Hydrogen is observed when the Hydrogen molecule breaks up into Hydrogen atoms and the electrons present in them are promoted to higher energy levels. The transition of electrons between the energy levels gives out a spectrum and hence the name. The Hydrogen spectrum is relatively simple and understandable easily as compared to other elements.

Hydrogen Spectrum Series

The complete spectrum of Hydrogen consists of separate series of distinct wavelengths concentrated in the ultra violet, visible and Infra-red regions of the electromagnetic spectrum. The six series found are named after their discoverers. In the order of increasing wavelength they are the Lyman series (ultra violet), Balmer series (visible), Paschen series, Brackett series, Pfund series, and Humphrey’s series (infra-red).Each of these series is called line spectrum because the images in spectrometer appears as a pattern of thin vertical lines.The Hydrogen emits a red- violet characteristic colour. This light when passed through a prism shows four separate lines in the visible range. These are Hα, Hβ, Hϒ, and Hδ. This is the spectrum of Balmer series for Hydrogen.

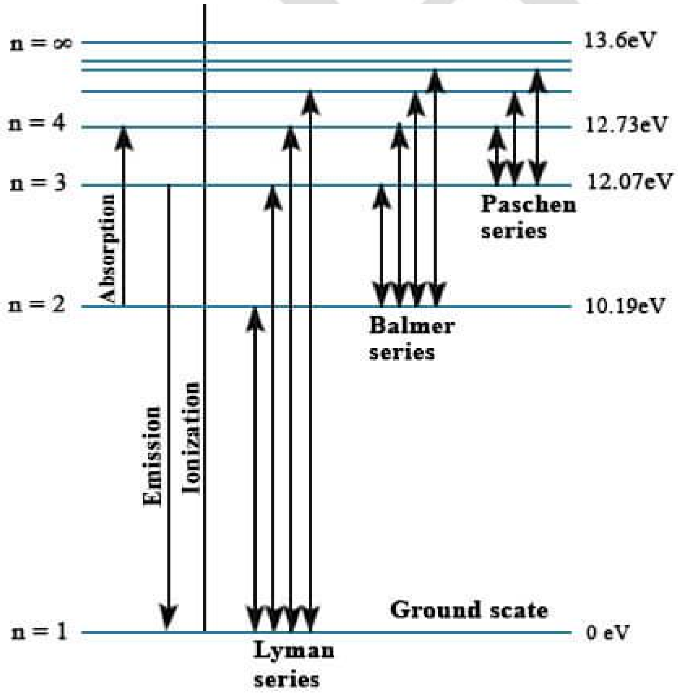
These individual lines become more closely spaced in a regular way as we get to see from longer to shorter wavelengths.

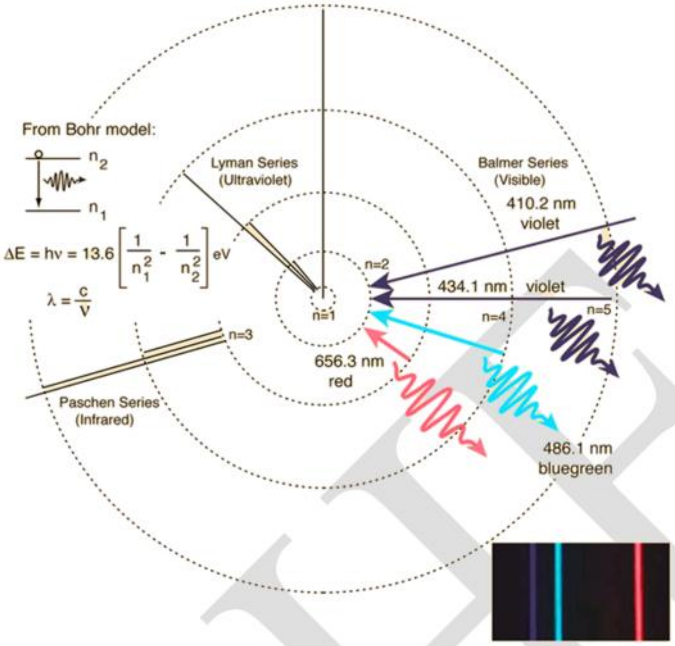
Mathematical representation,

$$\frac{1}{\lambda} = \nu = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where, λ is wavelength in meters, ν is the wave number, R_H is Rydberg constant (10967758 per meter) and n the series of integers.

Hydrogen Spectrum Diagram





This spectrum was produced by exciting a glass tube of hydrogen gas with about 5000 volts from a transformer. It was viewed through a diffraction grating with 600 lines/mm. The colors cannot be expected to be accurate because of differences in display devices.

Lyman Series of Hydrogen Spectrum

Bohr labelled each of the energy levels in Hydrogen atom with principle quantum number n. In any Hydrogen atom which is not in an excited level, the electron is in the energy level n = 1. This state of lowest energy for the atom is called the ground state.Bohr also showed that the series in high energy ultra violet region or the Lyman series arises from electronic transition from higher energy levels to the energy level **n = 1.** Each line in the Lyman series is due to electrons returning from a particular higher energy level to the level n = 1.

Balmer Series of Hydrogen Spectrum

Almost a century ago the wavelengths that were discovered in the element spectrum were found to get into a set of pattern called **spectral series**. The first any of such series was discovered by J JBalmer during the study of visible part of the Hydrogen spectrum.The line with the longest wavelength of 656.3 nm is designated to Hα and followed by next wavelength of 486.3 nm which was designated to Hβ. With the decrease in wavelength, the lines are found to be closer together and weaker in intensity till the series reaches a wavelength of 346.6 nm. Beyond this wavelength, there are no further separate lines but only a faint continuous spectrum.

Balmer series contains wavelength in the visible portion of the hydrogen spectrum. The spectral lines of Hydrogen in the ultra violet and infra-red regions fall into several other series. Balmer's formula for the wavelength of this series is as follows.

$$\frac{1}{\lambda} = \nu = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

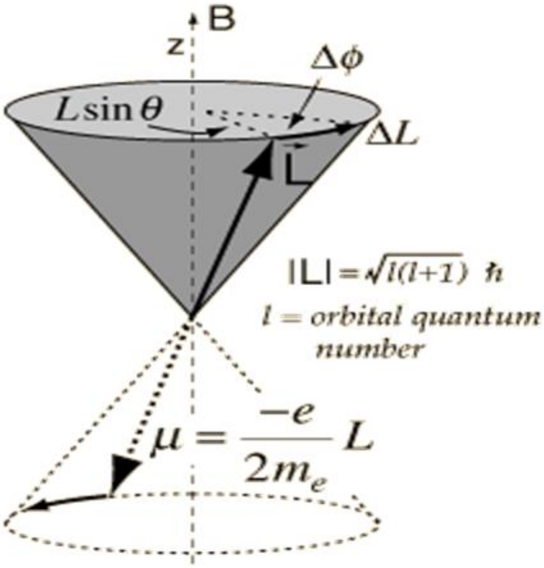
Where **R** is Rydberg constant with a value of 1.097 ×× 107 per meter and n = 3,4,5,… The Hα line corresponds to n = 3 and then Hβ line to n = 4 and so on. The series limit corresponds to n = ∞ so that this could occur at a wavelength of 4/R.

Larmor Precession

When a magnetic moment m is placed in a magnetic field B, it experiences a torque which can be expressed in the form of a vector product

$$\tau = \mu \;\; x \;\; B$$

For a static magnetic moment or a classical current loop, this torque tends to line up the magnetic moment with the magnetic field B, so this represents its lowest energy configuration. But if the magnetic moment arises from the motion of an electron in orbit around a nucleus, the magnetic moment is proportional to the angular momentum of the electron. The torque exerted then produces a change in angular momentum which is perpendicular to that angular momentum, causing the magnetic moment to precess around the direction of the magnetic field rather than settle down in the direction of the magnetic field. This is called Larmor precession.



When a torque is exerted perpendicular to the angular momentum L, it produces a change in angular momentum L which is perpendicular to L, causing it to precess about the z axis. Labeling the precession angle as , we can describe the effect of the torque as follows:

$$\tau = \frac{\Delta L}{\Delta t} = \frac{L\sin\theta\Delta\phi}{\Delta t} = |\mu B\sin\theta| = \frac{e}{2m_e} LB\sin\theta$$

The precession angular velocity (Larmor frequency) is

$$\omega_{Larmor} = \frac{d\phi}{dt} = \frac{e}{2m_e} B$$

These relationships for a finite current loop extend to the magnetic dipoles of electron orbits and to the intrinsic magnetic moment associated with electron spin. There is also a characteristic Larmor frequency for nuclear spins.

In the case of the electron spin precession, the angular frequency associated with the spin transition is usually written in the general form where is called the gyromagetic ratio (sometimes the magnetogyric ratio). This angular frequency is associated with the "spin flip" or spin transition, involving an energy change of 2mB. An example for magnetic field 1 Tesla follows.

$$\omega_{electron\,spin} = \frac{2\mu_e B}{\hbar} = \frac{2\cdot 2\cdot \frac{1}{2}(5.79x10^{-5}eV/T)(1T)}{6.58x10^{-16}eV\cdot s} = 1.7608x10^{11}s^{-1}$$

$$\nu = \frac{\omega}{2\pi} = 28.025\,GHz \quad \textit{Larmor frequency}$$

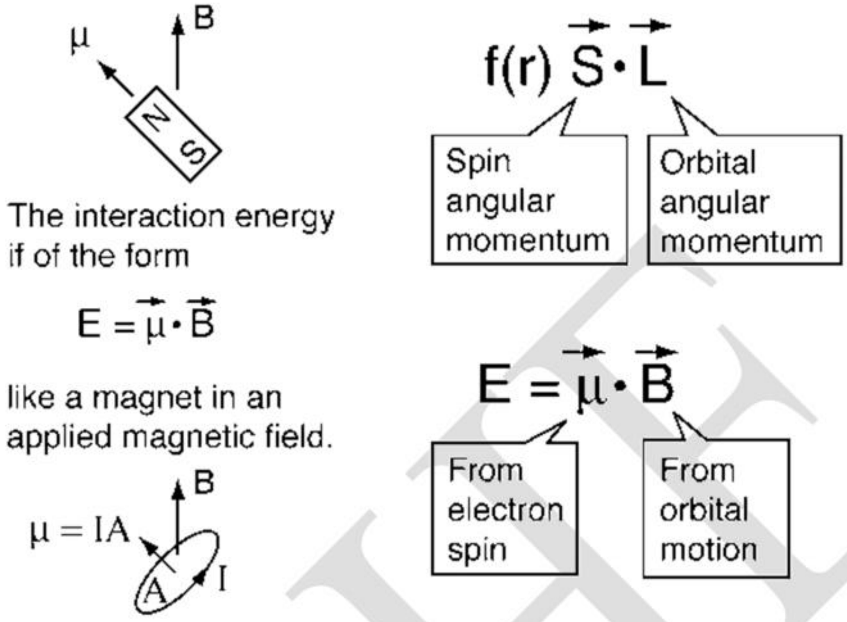
$$\omega_{proton\,spin} = \frac{2\mu_p B}{\hbar} = \frac{2(2.79)(3.15x10^{-8}eV/T)(1T)}{6.58x10^{-16}eV\cdot s} = 2.6753x10^{8}s^{-1}$$

$$\nu = \frac{\omega}{2\pi} = 42.5781\,MHz \quad \textit{Larmor frequency}$$

The characteristic frequencies associated with electron spin are employed in electron spin resonance (ESR) experiments, and those associated with the nuclear spin in nuclear magnetic resonance (NMR) experiments.

Spin-Orbit Interaction

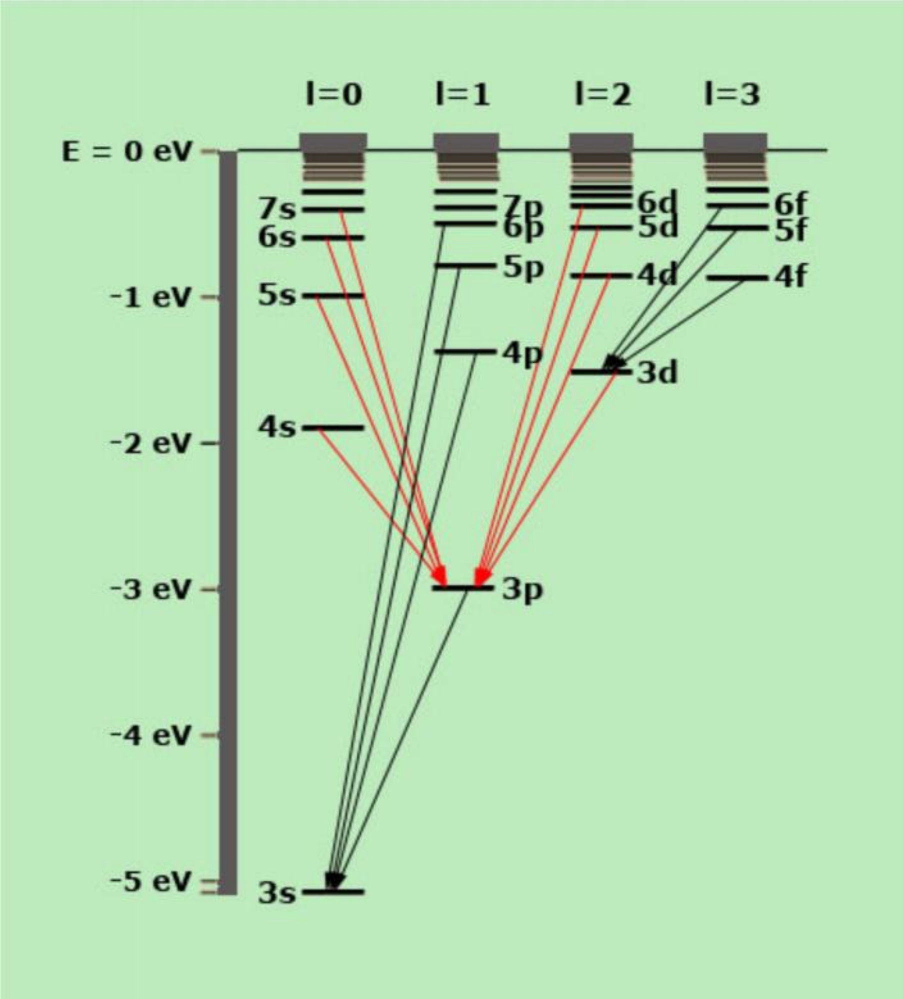
The energy levels of atomic electrons are affected by the interaction between the electron spin magnetic moment and the orbital angular momentum of the electron. It can be visualized as a magnetic field caused by the electron's orbital motion interacting with the spin magnetic moment. This effective magnetic field can be expressed in terms of the electron orbital angular momentum. The interaction energy is that of a magnetic dipole in a magnetic field and takes the form.



When atomic spectral lines are split by the application of an external magnetic field, it is called the Zeeman effect. The spin-orbit interaction is also a magnetic interaction, but with the magnetic field generated by the orbital motion of an electron within the atom itself. It has been described as an "internal Zeeman effect". The standard example is the hydrogen fine structure.

Spectra of alkali metals:

In the previous lecture we have learnt the quantum mechanical treatment of hydrogen atom. The similar picture is not able to explain the alkali atoms, the other elements in the first group of periodic table. Here, we will discuss the development of the theory to explain the alkali spectra. We will also elaborate the concept behind the modification of the potential required to explain the observation in alkali atoms. The absorption spectra of alkali vapors (Such as lithium, sodium) appear quite similar in many respects to the absorption spectrum of H atom. They are only displaced to a considerable extent, toward longer wavelengths. These spectra also consist of a series of lines with regularly decreasing separation and decreasing intensity.

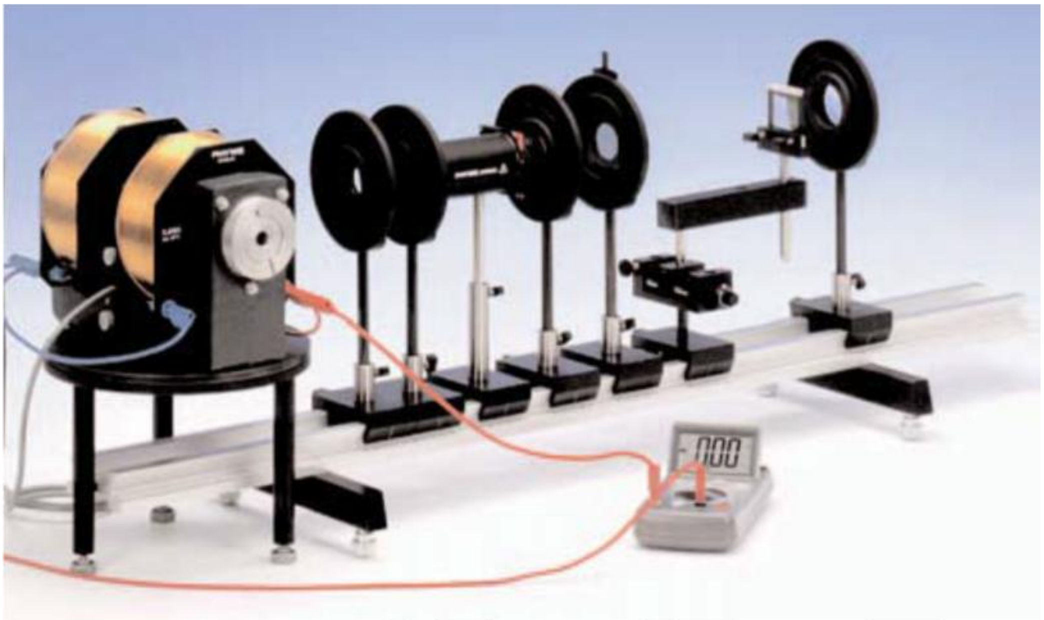


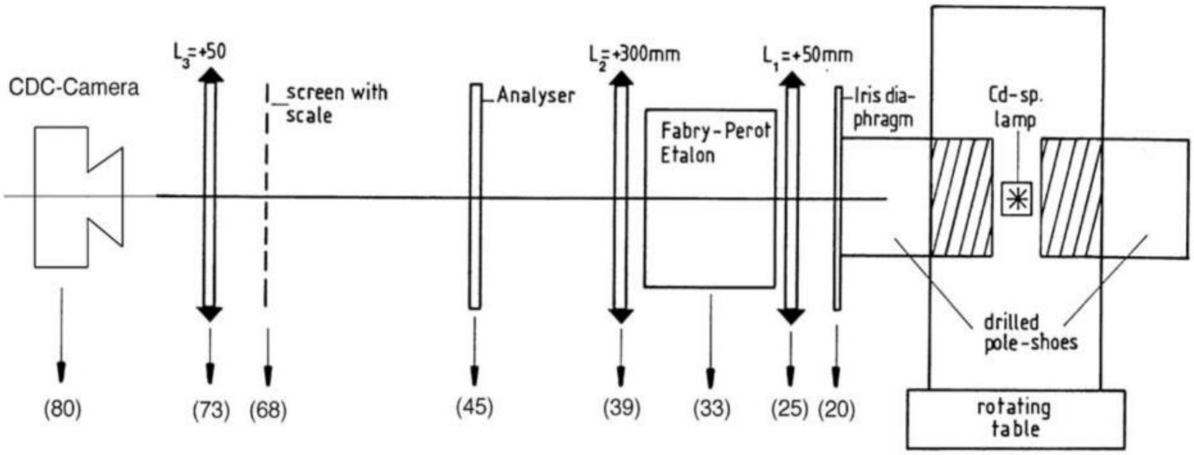
Zeeman effect:

The “Zeeman effect” is the energy shift of atomic states caused by magnetic field. This shift is due to the coupling of the electron orbital angular momentum to the external magnetic field. The normal Zeeman effect occurs when there is no spin magnetic moment – states with zero spin are necessary. In singulett systems the spins of the electrons cancel each other i.e. add up to zero. The energy shift of the atomic states in an outer magnetic field can be observed by the wavelength shift of the radiation emitted in atomic transitions between these states.

Normal Zeeman effect:

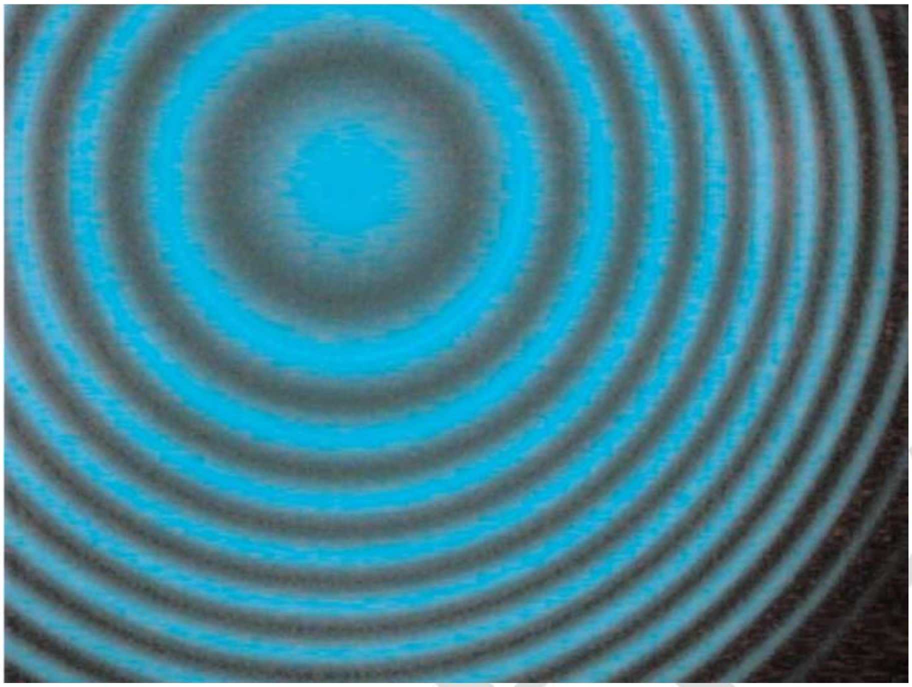
Transversal and longitudinal observation of the splitting of the red 643.847 nm Cd-line in the magnetic field showing the normal Zeeman effect. 1b. Anomalous Zeeman effect: Transversal and longitudinal observation of the splitting of the green 508.588 nm Cdline in the magnetic field showing the anomalous Zeeman effect. 2. Observation of the effect of polarization filter and polarization filter combined with l/4 plate for the splitted green and red lines in transversal and longitudinal direction. 3. Measurement of the frequency shift with help of the CCD camera and the supplied measurement software or with the screen with scale and the sliding device in the classical version for both of the above mentioned spectral lines.





Anomalous Zeeman effect:

The **anomalous Zeeman effect** is the more general case where the electron spins do not cancel each other and the energy of an atomic state in a magnetic field depends on both the magnetic moments of electron orbit and electron spin. The magnetic moment of the orbital angular momentum is as above and the magnetic moment of the spin.



Paschen back effect:

A theory of the molecular Zeeman effect in the Paschen-Back regime (PBR) was rest considered by Hill (1929), who described the splitting of molecular doublet levels for the intermediate case (a{b) using Hund's case (b) wavefunctions. However, he did not succeed in calculating the theoretical line strengths for this case. This was done much later by Schadee (1978), who repeated the analytical calculation by Hill using Hund's case (a) wave functions. He did not give details on line strength calculations, however, as the corresponding analytical expressions would have been too complicated. Both above approaches were limited to doublet states and to the Paschen-Back e®ect (PBE) on the ¯ne structure of molecular levels. Schadee's theory of the molecular PBE was successfully used to explain peculiar Stokes proles of molecular doublet transitions observed in sunspots: MgH (Berdyugina et al. 2000) and CN (Berdyugina, Solanki, & Frutiger 2001; Asensio Ramos, Trujillo Bueno, & Collados 2005).

1. Define Orbital angular momentum.
2. Discuss Normal and Anomalous Zeeman effect in details.
3. What is the basic principle of microwave spectra?
4. Explain the construction and working of Microwave spectrometer with suitable examples.
5. Define Spin angular momentum.
6. Discuss Paschan Bach effect in details.
7. Explain the following
    i) Hydrogen Spectra
    ii) Influence of Nuclear spin
8. Explain a Quadrapole hyperfine interaction in details.
9. Explain the following
    i) Anomalous Zeeman effect
    ii) Paschan Bach effect
10. Explain symmetric and asymmetric top molecules with help of microwave spectra.
11. Explain the spectra of Alkali metals
12. Give a note on hyperfine structure of spectral lines
13. Explain the concept of Non-rigid rotator and Isotope effect.
14. Calculate the internal magnetic field produced by the nucleus which causes the splitting of the 3p state of sodium atom.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641021
(For the candidates admitted from 2017 onwards)
DEPARTMENT OF PHYSICS
M. Sc. DEGREE EXAMINATION - APRIL 2018
Second Semester
PHYSICS
SPECTROSCOPY (17PHP204)
MULTIPLE CHOICE QUESTIONS

QUESTIONS	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
In normal atomic spectra ------ changes its orbit by absorbing radiation	Valence electrons	electron in the inner orbit	nucleus	proton	Valence electrons
Transition from a lower to upper level causes	emission of radiation	absorption of radiation	scattering of radiation	none of the above	absorption of radiation
An atom can absorb -----	any amount of energy	only energy equal to the diff	only energy less than the	only energy greater than the difference between two levels	only energy equal to the difference between two levels
The principal qantum of the ground electronic state is	0	1	-1	=+ or - 1	1
A photographic record of a spectrum is called	spectrogram	spectrograph	spectrometer	spectroscope	spectrograph
The spectral lines of hydrogen atom where the transitions end at n = 2 level, form	Lymann series	Bracket series	Pfund series	Balmer series	Balmer series
The study of both frequency and intensity of spectral lines is known as ----	spectroscopy	spectral study	spectrophotometry	spectrography	spectrophotometry
For an energy level of principal quantum number n, the azimuthal quantum number can bave	n+1 values	n-1 values	n values	n^2 values	n values
For principal quantum number n = 3, the values of azimuthal quantum number l are	1,2,3,4	-3,-2,0,1,2,3	0,1,2	1,3,5,7	0,1,2
Hamiltonian of a system represents	total energy of the system	only kinetic energy of the sy	only potential energy of t	none of the above	total energy of the system
For any real physical system represented by a Shrodinger wave equation, the eigen values	must be real and positive	can be complex but positive	can be real but negative	can be anything	must be real and positive
In the case of atomic spectra, the principal quantum numbers of two levels must be such that	they follow the selection rule d	they follow the selection rul	they follow the selection	dn may be any positive integer	dn may be any positive integer
The splitting of spectral lines in the case of alkali metals was explained by considering	orbital motion of the electron	spin of the electron	spin of the atom	spin of the nucleus	spin of the electron
For s orbital of electron the value of l is	0	1	2	3	0
Zeeman effect is splitting of spectral lines in the presence of	electric field	magnetic field	electric and magnetif fiel	none of the above	magnetic field
The decoupling of nuclear spin angular momentum vector I and the total angular momentum	Pachen Back effect	Back-Goudsmit effect	Stark effect	Anomalous Zeeman effect	Pachen Back effect
For normal Zeeman effect, there are ----- lines when observed parallel to the magnetic field	2	3	5	A large number of lines	2
The sodium D line is a member of -----	the principal siries	the diffuse series	the sharp series	the fundamental series	the principal siries
Anomalous Zeeman effect occurs in atoms whose S is	greater than 1/2	equal to zero	less than zero	greater than zero	greater than zero
In normal zeeman effect, pi lines are -----	polarized in the direction of the	polarized perpendicular to t	circularly polarized	non-polarized	polarized in the direction of the applied field
Which of the spectral series of hydrogen atom does not show fine structure?	Balmer series	Bracket series	Pfund series	Lymann series	Lymann series
Anomalous Zeeman effect occurs in the presense of a	strong magnetic field	electric field	weak magnetic field	both electric and magnetic field	weak magnetic field
Hyperfine structure in atomic spectra is observed due to	spin of the electron	spin of the nucleus	presence of isotope	temperature	spin of the nucleus
The intensity of a spectral line mainly depends on	number of electron in the atom	the atomic number of the el	the atomic mass of the el	the number of atoms in the initial energy level	the number of atoms in the initial energy level
Hyperfine structure of rotational lines are due to	nuclear quadrupole moment	rotaion of the molecule	rotation of the atom	dipole moment	nuclear quadrupole moment
The molecule with permanent electric or magnetic dipole moment absorb	infrared radiation	microwave radiation	UV radiation	radio waves	microwave radiation
Stark modulation spectrometer is used to study	IR spectrum	microwave spectrum	Raman spectrum	Fluorescence	microwave spectrum
In normal zeeman effect, there are ------ lines when observeed perpendicular to the magnetic	2	3	4	0	3
The decoupling of L and S vectors due to the application of very high magnetic field is caled	Pachen Back effect	Stern Gerlach effect	Stark effect	Back-Goudsmith effect	Pachen Back effect
The frequency of radiation absorbed due to rotational motion of molecules fall in the ---- regi	IR	UV	X-ray	Microwave	Microwave
The product eQq is known as	electric dipole moment	magnetic dipole moment	Quadrupole coupling con	total magnetic moment	Quadrupole coupling constant
The quantity eQ is known as the ----- of the nucleus	quadrupole moment	electric dipole moment	electric field strength	Magnetic field strength	quadrupole moment
The nuclear magneton (mu)N is ----- times the Bohr magneton (mu)B	1836	1/1836	2	none of the above	1/1836
The angular momentum associated with the orbital quantum number L is given by	L	L(L+1)	L(L+1)*h/(2pi)	[L(L+1)h/(2pi)}^1/2	[L(L+1)h/(2pi)}^1/2
The microwave region of the electromagnetic spectrum is between -----	1 mm and 300 mm	1mm and 30 mm	400 cm and 1200 cm	300 mm to 900 mm	1mm and 30 mm
The criterion for absorption of microwave is that the molecule should possess	either a permanent electric or	a permanent electric dipole	a permanent magnetic di	none of the above	either a permanent electric or magnetic dipole moment
For an asymmetric top molecule the moments of inertia are related as	Ia = Ib = Ic	Ia = Ib not equal to Ic	Ia not equal to Ib = Ic	Ia not equal to Ib not equal to Ib	Ia not equal to Ib not equal to Ib
In the case of a diatomic rigid rotator, the separation between nearby rotational lines is	B	3B	2B	4B	2B
If the first line in a microwave absorption spectrum of a diaomic (rigid) rotator is observed at	4B	6B	8B	10B	8B
In the case of a diatomic rigid rotator, the energy difference between ground level and first ro	2B	4B	6B	8B	6B
In the case of non-rigid diatomic rotator, the separation between adjacent spectral lines	increases with increasing J	decreasing with increasing J	remains the same	can be either increasing or decreasing	decreasing with increasing J
In the case of non-rigid diatomic rotator, the reason for the separation between adjacent ines	increasing bond length during r	due to reduction in speed of	due to decreasing bond le	none of the above	increasing bond length during rotation due to centrifugal force
The vibrational excitation during rotation causes	increasing in B	reduction of B	no change	can either increase or decrease B	reduction of B
The molecular system where the moments of inertia are related as Ia not equal to Ib not equa	symmetric top	asymmetric top	linear	spherical top	asymmetric top
Nuclei with spin quantum number I ------ lack spherical symmetry	> 1	> 0	= 1	> 1/2	> 1/2
Pachen Back effect takes place in the presence of ----	very high electric field	very high magnetic field	weak electric field	weak magnetic field	very high magnetic field
When an atom with spin > placed in a weak magentic field, the spectral lines are split into ma	Pachen Back effect	Back-Goudsmit effect	Anomalous zeeman effec	normal zeeman effect	Anomalous zeeman effect
A prolate symmetric top molecule has the relation between their moments of inertia as	Ia < Ib = Ic	Ia = Ib < Ic	Ia > Ib = Ic	Ia = Ib > Ic	Ia < Ib = Ic
When an atom of Carbon dioxide which does not possess a permanent dipole moment and he	it shows rotational spectrum	it does not show rotational s	it may or may not show r	none of the above	it does not show rotational spectrum
A molecule whose moments of inertia are related as Ia = Ib > Ic is called	oblate symmetric top	prolate symmetric top	oblate asymmetric top	none of the above	prolate symmetric top
Rotation about the bond axis of a hetero nuclear diatomic molecule	gives rotation spectrum	gives no rotation spectrum	gives some weak lines	none of the above	gives no rotation spectrum
The quantity which measures the deviation in the charge distribution in the nucleus from sph	electric dipole moment	magnetic dipole moment	nuclear quadrupole mom	none of the above	nuclear quadrupole moment
The magnitude of the asymmetrical electric field surrounding the nucleus, due to electrons is	electric field gradient	magnetic field gradient	electric quadrupole mom	nuclear quadrupole moment	electric field gradient
The charge distribution in a nucleus with spin = 1/2 is	non-spherical	prolate	oblate	spherical	non-spherical
When an atom with total angular momentum J is placed in a magnetic field, the magnetic qua	2J+1	J	J+1	J-1	2J+1
The rotational selection rule is	dJ = + or - 1	dJ = 0, +1 or -1	dJ = 0	dJ = 0, +1, -1, +2, -2,.....	dJ = + or - 1
Out of the three types of energy of a molecule, the lowest energy is due to ----	vibration of the molecule	electronic transition of the m	rotation of the molecule	none of the above	rotation of the molecule
The total angular momentum of an atom is a vector sum of the ----	orbital angular momentum of t	orbital angular momentum o	orbital angular momentu	spin angular momentum of the electron and the spin angular m	orbital angular momentum of the electron, spin angular momentum of the electron and the spin angular momentum of the nucleus
Which of the following statements is not correct?	The robital angular momentum	S precesses around L	J and the nuclear spin ang	F precesses around I	F precesses around I
When the applied magnetic field is increased, the frequency of precession of the J vector arou	increases	decreases	remains the same	increases and then decreases	increases

SYLLABUS

IR spectroscopy: Practical aspects – Theory of I.R rotation vibration spectra of gaseous diatomic molecules – applications of I.R spectroscopy – Basic principles of F.T.I.R spectroscopy
Raman spectroscopy: Classical and Quantum theory of Raman effect - Rotation vibration Raman spectra of diatomic and polyatomic molecules – Applications - Laser Raman spectroscopy - Surface Enhanced Raman Scattering.

PRACTICAL ASPECTS:

We were discussing the sample holders, how we can take the sample in different containers and I had told you in the last class, that IR cells are constructed with sealed windows, which are separated by thin gaskets of copper and lead which are weighted with mercury; so, the whole assembly is securely clamped in a stainless still holder. As the mercury penetrates, a gasket it expands producing a tight seal. So, this is how we hold the sample. for films how do you take the infrared spectrum. So, for polymers, raisins and amorphous solids, the sample is usually dissolved in a volatile solvent and you evaporate the solvent, you will get a thin film of the material. So, a drop of the solution you can place it on the window and then seal the four edges as the solvent, evaporates a thin film of a homogeneous material is deposited which can be scan directly.

Theory of I.R rotation vibration spectra of gaseous diatomic molecules:

Molecular vibrations:

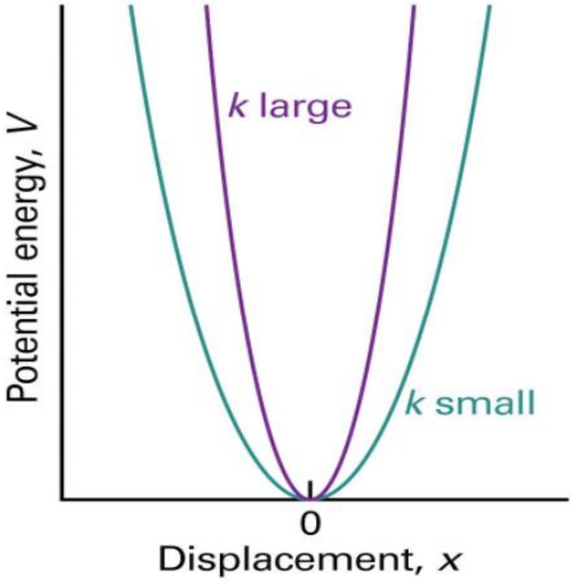


Figure 13-27
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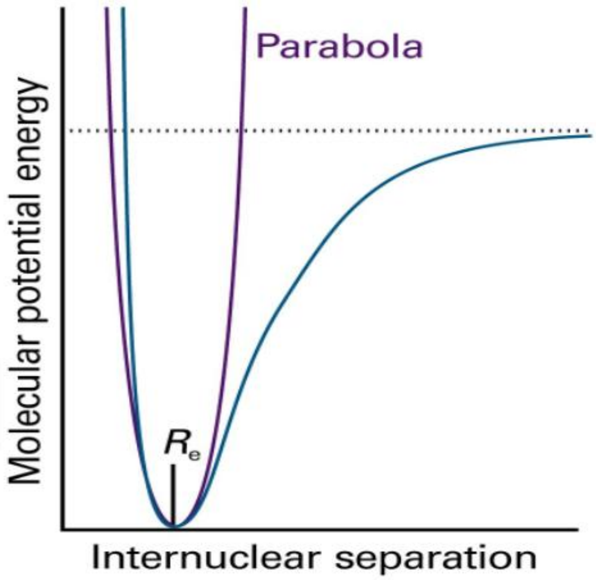

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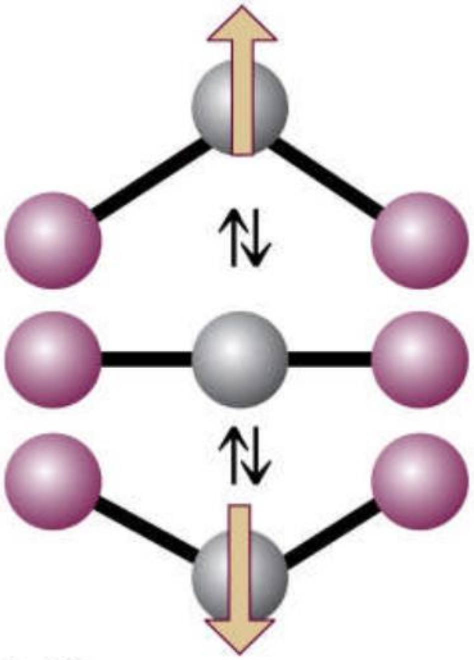
Typical potential energy curve of adiatomic molecule.Parabolic approximation close to Re.The steeper the walls of the potential, the stiffer the bond, the greater the force constant.

Selection rules:

Gross selection rule for a change invibrational state (absorption or emission):the electric dipole moment of the molecule(not necessarily permanent) must change when the atoms are displaced relative to one another.



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IR active molecules: heteronuclear diatomic.

IR inactive molecules: homonuclear diatomic. Not all the modes of polyatomic molecules are vibrationally active (e.g.: the symmetric stretch of CO2, in which the C –O–C bonds stretch and contract symmetrically is inactive.

Applications of I.R spectroscopy:

Infrared radiation lies between the visible and microwave portions of the electromagnetic spectrum.

Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves.

TheInfrared region is divided into: near, mid and far-infrared.

Near-infrared refers to the part of the infrared spectrum that is closest to visible light and far-infrared refers to the part that is closer to the microwave region.

Mid-infrared is the region between these two.

The primary source of infrared radiation is thermal radiation. (heat)

It is the radiation produced by the motion of atoms and molecules in an object. The higher the temperature, the more the atoms and molecules move and the more infrared radiation they produce.

Any object radiates in the infrared. Even an ice cube, emits infrared.

Humans,atnormalbodytemperature,radiatemoststronglyintheinfrared,atawavelengthofabout10microns(Amicronisthetermcommonlyusedinastronomyforamicrometeroronemillionthofameter).Intheimagetotheleft,**theredareas**arethe**warmest**,followedby**yellow,greenandblue(coolest)**.

The bonds between atoms in the molecule stretch and bend, absorbing infrared energy and creating the infrared spectrum.

Raman spectroscopy:

Classical theory correctly predicts that Raman scattering should beweaker than Rayleigh scattering and that there is a simple linear dependence of Raman scattering on incident intensity and on sample concentration. With classical theory, Stokes/anti-Stokes intensity ratio. However, Boltzmann distribution will be major factor in determining relative Stokes and anti-Stokes intensity. The excited vibrational state will be only thermally populated, and Stokes intensity will be much larger than anti-Stokes. Full quantum mechanical treatment of Raman spectroscopy has been derived with time-dependent perturbation theory. Expressions for polarizability tensors involve sums over excited electronic states.

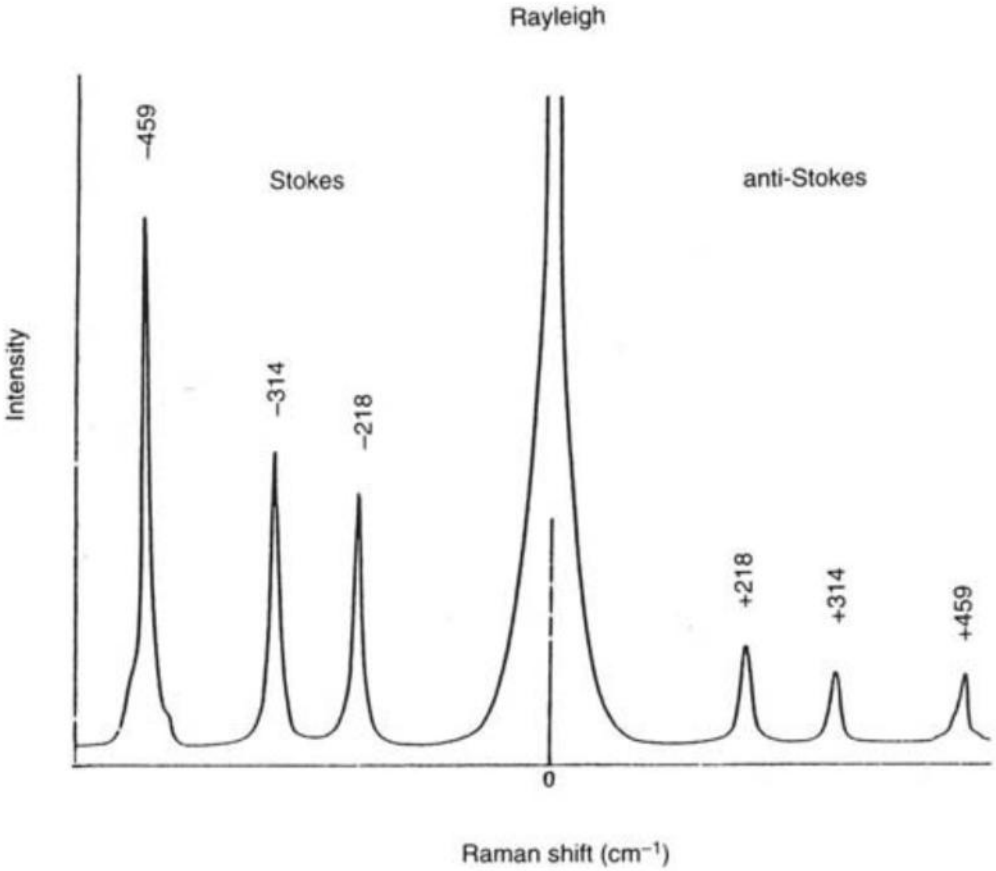
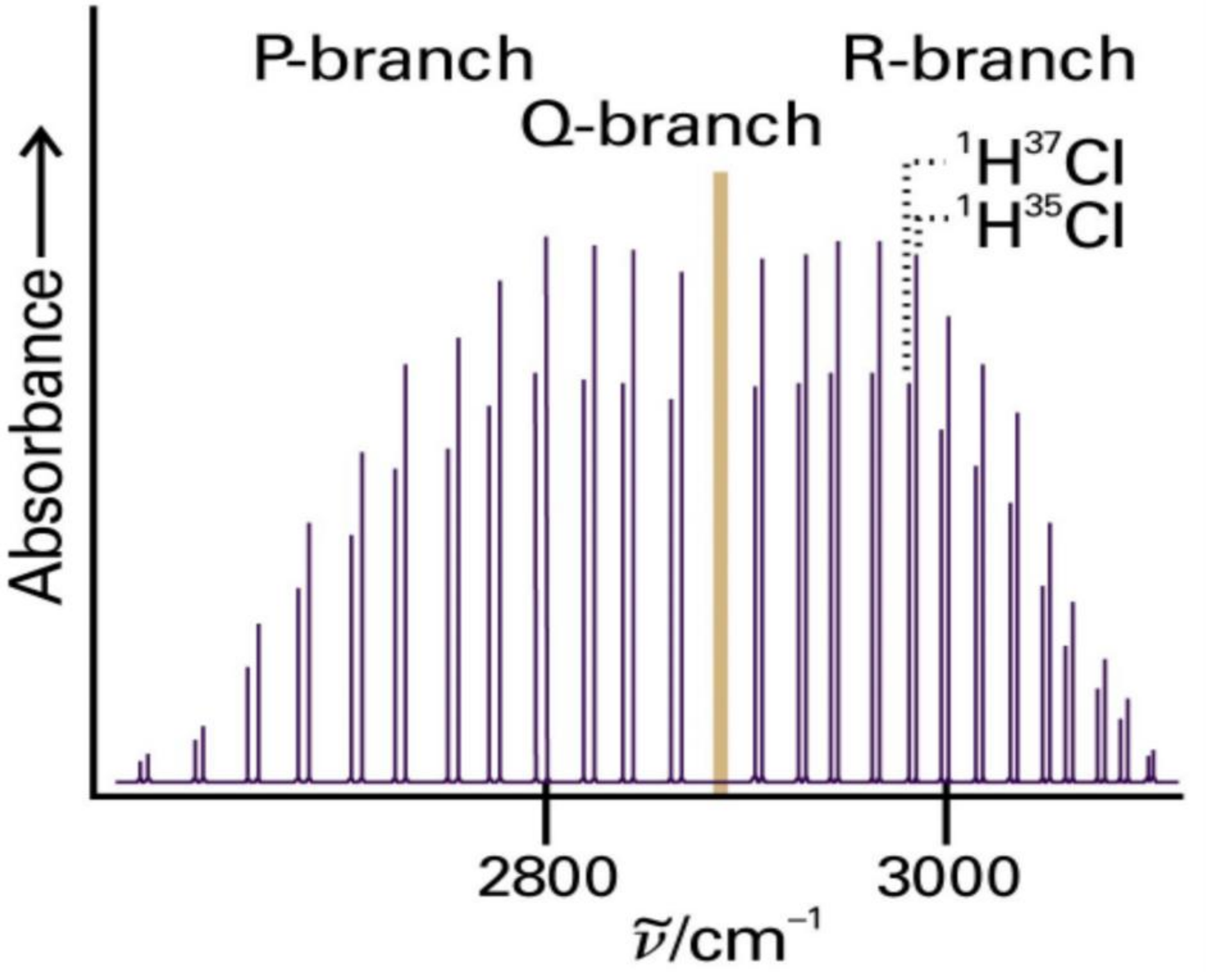


Figure 1-9 Raman spectrum of CCl_4 (488.0 nm excitation).

Rotation vibration Raman spectra of diatomic and polyatomic molecules:

Rotational change is expected since (classically) the transition leads to a sudden increase/decrease in instantaneous bond length. Therefore, rotation is retarded/accelerated by a vibrational transition.



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Detailed quantum mechanical analysis of simultaneous vibration and rotation changes shows that the rotational quantum number *J* changes by ±1 during the vibrational transition. If the molecule also possesses angular momentum bout its axis, then the selection rules.

1. What is the basic principle of IR spectra?
2. Explain the construction and working of FTIR spectroscopy with suitable examples.
3. Explain the following with of Raman spectra.
    i) Rotation vibration spectra of diatomic molecules.
    ii) Any two applications
4. Explain the construction and working of Laser Raman Spectroscopy.
5. Explain the theory of IR rotation vibration spectra of gaseous diatomic molecules.
6. Explain the construction and working of Surface enhanced Raman scattering Spectroscopy.
7. Explain the theory of IR rotation vibration spectra of gaseous diatomic molecules.
8. What is Raman effect?
9. Explain the construction and working of Laser Raman Spectroscopy.
10. Explain the basic principles of IR spectroscopy and its applications.
11. Explain the concept of rotation vibration Raman spectra of diatomic molecules.
12. The Raman line associated with a vibrational mode which is both Raman and Infrared active is found at 4600 Å when excited by light of wavelength 4358 Å. Calculate the wavelength of the corresponding infrared band.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641021
(For the candidates admitted from 2017 onwards)
DEPARTMENT OF PHYSICS
M. Sc. DEGREE EXAMINATION - APRIL 2018
Second Semester
PHYSICS
SPECTROSCOPY (17PHP204)
MULTIPLE CHOICE QUESTIONS

QUESTIONS	**OPTION 1**	**OPTION 2**	**OPTION 3**	**OPTION 4**	**ANSWER**
UNIT - II					
Change in electric dipole moment during vibration gives rise to absorption in	visible spectrum	NMR spectrum	IR spectrum	microwave spectrum	IR spectrum
Water molecule has ---- number of modes of vibraiton	9	4	3	5	3
Raman scattering occurs due to ---- of molecule	change in dipole moment	change in polarizability	change in magnetic dipo	change in quadrupole oment	change in polarizability
Glass is unsuitable as a lens for IR studies due to its ----	hardness	transmittence	dispersion	absorption	absorption
Mutual exclusion principle of Raman and IR spectra is applicable for	symmetric top molecules	asymmetric top molecules	molecules with centre of	diatomic molecules	molecules with centre of symmetry
Which of the following spectra is independent of the exciting frequency	Raman	IR	Microwave	Electronic spectra	Raman
Hot bands are IR absorption involving vibrational levels ----	v =0 to v = 1	v = 0 to v = 2	v = 1 to higher values of	v = 1 to v = 2 only	v = 1 to higher values of v
Unlike in the case of other branches of spectroscopy, Raman spectroscopy is a ---- process	scattering	absorption	emission	Fluorescence	scattering
For a linear molecule the relation between the moments of intertia is	Ia=Ib=Ic	Ia=0, Ib=Ic not equal to 0	Ia < Ib < Ic	Ia > Ib > Ic	Ia=0, Ib=Ic not equal to 0
The lines with frequency more than that of the exciting line in Raman spectra are called	Stokes lines	Rayleigh lines	antistokes lines	compton lines	antistokes lines
Virtual energy level concept is used to explain	IR absorption	Raman scattering	microwave absorption	none of the above	Raman scattering
When the virtual energy levels coincide with actual enregy level it is called	resonance raman scattering	inverse raman scattering	surface enhanced raman	none of the above	resonance raman scattering
IR spectroscopy involves	absorption	emission	scattering	stimulated emision	absorption
Out of the three types of energies of a molecule, rotational, vibrational and electronic, the	electronic	rotational	vibrational	vibrational-rotational	electronic
The most accurate method of determination of inter-nuclear distance, and bond angles in	IR	Raman	Microwave	UV	IR
Pure rotational raman lines can be observed only in	heavy molecules	light polyatomic molecules	heavy polyatomic molec	light diatomic molecules	light diatomic molecules
In IR spectra, the first overtone lines are due to transition from	v=0 to v=2	v=1 to v=2	v=0 to v=1	v=0 to v=3	v=0 to v=2
In the case of rotational raman spectra the selection rule dJ = 0 refers to	antistokes lines	stokes lines	both a and b	Rayleigh lines	Rayleigh lines
IR and Raman spectroscopy are said to be ----- to each other	complementary	opposite	repetition	inverse	complementary
Raman spectroscopy is due to -----	change in dipole moment	change in polarizability	change in magnetic dipo	none of the above	change in polarizability
Which of the following statements is not true?	Raman scattering cannot be e:	Microwave spectroscopy is	IR spectroscopy is an abs	Raman scattering is a scattering process	Raman scattering cannot be excited by any frequency
Classical theoretical expalnation of Raman effect could not explain	rotational raman lines	vibrational raman lines	rotation-vibration structu	intensity of stokes and antistokes lines	intensity of stokes and antistokes lines
Polarizability tensor has ----- components	7	3	9	5	9
Even though polarizability is a tensor of nine components, there are only ----- independent	6	8	3	7	6
In the case of anti Stokes Raman scattering	energy is absorbed by the mol	energy is given by the mole	both photon and molecu	no energy transfer	energy is given by the molecule to the photon
Zero point energy is the energy possessed by the molecule when it is in the	lowest vibrational level	lowest rotational level	lowest electronic level	none of the above	lowest vibrational level
Nernst Glower is normally used as a source of	Microwave radiation	IR radiation	Raman spectrum	UV spectrum	IR radiation
The number of vibrational modes for a linear molecule is	3N-6	3N-5	3N-3	3N	3N-5
A grating is uses the phenomenon of ----- to split the spectral lines into different frequenci	reflection	total internal reflection	diffraction	interference	diffraction
Rocksalt prisms are used to study	UV spectrum	IR spectrum	microwave spectrum	Electronic spectrum	IR spectrum
When two different frequencies of laser are used to study raman spectrum of a sample, it	these lines are not due to ram	these lines are also part of r	these lines are IR lines	none of the above	these lines are not due to raman scattering
The vibrational energy of a molecule when it is in the lowest vibrational level is known as	potential energy	zero point energy	knetic energy	none of the above	zero point energy
The value of the zero point energy is ----- where n0 is the frequency of the fundamental m	1/2 n0	n0	2n0	1/4 n0	1/2 n0
The vibrational transition between v=0 to v=1 isknown as	fundamental	first overtone	second overtone	hot band	fundamental
In the case of carbon dioxide, symmetric stretching is	raman active & IR inactive	raman active and IR active	raman inactive and IR ac	raman inactive and IR inactive	raman active & IR inactive
Resonance raman scattering occurs when	rotational level coincides with	electronic level coincides w	virtual energy level coinc	none of the above	virtual energy level coincides with original level
Far infrared region ranges from	4000 to 400 cm^-1	400 to 50 cm^-1	12500 to 4000 cm^-1	none of the above	4000 to 400 cm^-1
When vibrational quantum number increases, the separation between vibrational levels	increases	decreases	nemains the same	none of the above	increases
In vibration-rotation IR spectra, the selection rule for P-branch of lines is	dJ=+1	dJ=-1	dJ=0	dJ=+ or -1	dJ=+1
The raman lines with frequency less than the exciting frequency are known as	Rayleigh lines	stokes lines	antistokes lines	resonance lines	Rayleigh lines
Polarized raman spectra can be given by	single crystals only	liquids only	powder samples only	both single crystals and powder samples	single crystals only
In IR absorption spectra, the region between -------- is called as finger print region	less than 900 cm^-1	between 900 and 1450 cm^	1450 to 5000 cm^-1	above 5000 cm^-1	between 900 and 1450 cm^-1
In the case of water molecule all the three modes of vibrations are	IR and Raman active	IR active and Raman inactiv	IR inactive and Raman ac	IR inactive and Raman inactive	IR and Raman active
FTIR is normally used to study	far infrared spectrum	near IR spectrum	middle IR spectrum	all the above	far infrared spectrum
Laser used for Raman studies mainly due to its	coherence	high intensity	monochromaticity	directionality	middle IR spectrum
Conventional spectroscopy, where intensity is recorded with frquency is called	time domain spectroscopy	frequency domain spectros	intensity spectroscopy	none of the above	high intensity
Most common method of sample handling method for IR studies of solids is	pellet technique	mull technique	thin film technique	none of the above	pellet technique
Thermocouple is used as detector in ----- spectrometer	Raman	Microwave	IR	NMR	IR
The most common detector in a laser Raman spectrometer is -----	bolometer	thermocouple	photographic film	photomultiplier tube	photomultiplier tube
In FTIR technique, normally, the signal is converted from -----	time domail to frequency dom	frequency domain to time c	frequency to intensity	none of the above	time domail to frequency domain

Most intense IR absorption line is the one originating from v =	1	2	0	3	0
The anhamonicity of vibration of a diatomic molecule is due to	rigid nature of the bond	non-rigid nature of the bon	due to the charge of the	due to the mass of the atoms	rigid nature of the bond
The virtual energy level in the case of Raman spectra is -----	characteristic of the molecule	a combined effect of the m	depends only on the inci	none of the above	characteristic of the molecule
Rayleigh scattering is	inelastic process	elastic process	collision process	none of the above	inelastic process
In Raman spectra, anti-Stokes lines are	red shifted	blue shifted	no change	can be either red shifted or blue shifted	red shifted
The stokes lines of Raman spectra are	red shifted	blue shifted	no change	can be either red shifted or blue shifted	red shifted
Raman spectra can be obtained from	solids only	liquids only	gases only	solids, liquids and gases	solids, liquids and gases
In the case of molecules of centre of symmetry, the Raman active modes are not IR active	Pauli's exclusion principle	Frank Condon principle	Mutual exclusion princip	none of the above	Mutual exclusion principle
The polarisability ellipsoid of a linear molecule is	elliptical	spherical	ellipsoid	none of the above	spherical
The branch of rotational IR lines with selection rule dJ = 0 is called	Q branch	P branch	R branch	S branch	Q branch
Raman effect supports	corpuscular theory	wave theory	quantum theory	electromagnetic theory	quantum theory
In Raman spectrum, if λ is the wavelength of incident radiation, then the Anti-Stoke's lines	λ	λ + Δλ	λ - Δλ	λ2	λ - Δλ
Sun appears red at sun rise and sunset. This is due to scattering of	longer wavelengths	shorter wavelengths	lower frequencies	all frequencies	shorter wavelengths
In Raman spectrum, if λ is the wavelength of incident radiation, then the Stoke's lines will	λ	λ + Δλ	λ - Δλ	λ2	λ + Δλ
Tyndall effect is the scattering of the light by	air particles	solid particles	liquid particles	colloidal particles	colloidal particles
In 1928,Sir C.V.Raman was studying the	diffraction of light	interference	scattering of light	reflection of light	scattering of light
Coefficient of scattering of light in any medium is inversely proportional to the fourth pow	wavelength of light	frequency of light	velocity of light	none of these	wavelength of light
Raman lines had frequencies lower than that of the incident line are called	stokes lines	antistokes lines	both a and b	excitation line	stokes lines
Raman lines had frequencies higher than that of the incident line are called	stokes lines	antistokes lines	both a and b	excitation line	antistokes lines
Low frequency side and high frequency side Raman lines are referred to as	stokes lines	antistokes lines	stokes and antistokes lin	unmodified line	stokes and antistokes lines respectively
In Rayleigh scattering, there is a change in the intensity of the scattered light, there is no c	spectral character	wavelength	frequency	all the above	all the above
Rayleigh scattering is also called	incoherent scattering	coherent scattering	diffraction	compton scattering	coherent scattering
Light from a helium discharge tube filtered by nickel oxide glass gives a light of wavelengtl	3880Å	3888Å	3800Å	4888Å	3888Å
The apparatus used in the study of Raman effect in liquids was first designed by	Wood	Rayleigh	Raman	Newton	Wood
Raman got nobel prize in	1939	1932	1931	1930	1930
The modified frequencies observed in the scattering process was given the name	Compton effect	Raman effect	Scattering effect	Rayleigh scattering	Raman effect
Quinine sulphate solution contained in a novial glass vessel is used as a filter to obtain the	4350Å	4340Å	4300Å	4358Å	4358Å
Which filter is found to be a very satisfactory to get 4046Å	a solution of iodine in carbon t	quinine sulphate solution	nickel oxide glass	Copper oxide	a solution of iodine in carbon tetrachloride
The mercury arc is placed as close to the Raman tube as possible, which results in a large	intensity of the incident light	frequency of incident light	wavelength of the incide	velocity of the incident light	intensity of the incident light
Which reflector is used to enhance the intensity of illumination still further	semi-cylindrical aluminium	quartz	glass	none of these	semi-cylindrical aluminium
The chief features of a spectrograph, suited for the study of Raman spectra are	large light gathering power	special prisms of high resol	a short focus camera	all the above	all the above
The recording of the complete spectrum may require up to ten to fifteen hours, dependin	intensity of the incident light	the speed of the spectrogra	the intrinsic brilliance of	all the above	all the above
Which is available as transparent blocks	gypsum	quartz	a & b	benzene	a & b
Which of the following substance does not require container for the excitation of Raman e	gypsum	quartz	a & b	benzene	a & b
Raman effect can be obtained with solids which are in the form of loose crystal powders w	Baer & Menzies	Ananthakrishnan	Billroth,Kohlrausch & Rei	Raman	Baer & Menzies
A special type of spectrograph with two parts, each part having a prism and two lenses wi	Baer & Menzies	Ananthakrishnan	Billroth,Kohlrausch & Rei	Raman	Billroth,Kohlrausch & Reitz
In the case of gases, the intensity of the light scattered is normally	very weak	very strong	medium strong	weak	very weak
In the case of gases, wood employed a very long tube of	Calcite	Benzene	carbon tetrachloride	HCL gas	HCL gas
Who was the first to develop the technique of exciting Raman effect in gases under high p	Baer & Menzies	Ananthakrishnan	Rosetti	Raman	Rosetti
Rosetti was able to obtain the Raman spectra of several gases under pressure with the	2500Å line	2537Å line	2530Å line	2535Å line	2537Å line
Bhagavantam has constructed a Raman tube for gases which can stand pressures upto	30 atmospheres	40 atmospheres	50 atmospheres	60 atmospheres	50 atmospheres
Who obtained good spectrographs of Raman spectra of gases using the 3650Å,4046Å & 4:	Baer & Menzies	Ananthakrishnan	Bhagavantam	Raman	Bhagavantam
Raman effect has been observed & studied in	solids	liquids	gases	all the above	all the above
With benzene, the frequency shifts of the Raman lines correspond to an infra-red waveler	3μ	3.27μ	3.5μ	4μ	3.27μ
In absorption spectrum, benzene exhibits a	weak band	medium strong band	strong band	sharp band	strong band
The triad of stokes and antistokes lines equally spaced on either side of the exciting 4358Å	Calcite	Benzene	carbon tetrachloride	HCL gas	carbon tetrachloride
What bands are found in well purified water	two broad bands	one broad band	sharp band	weak band	two broad bands
Solutions of salts in water give Raman spectra characteristic of the	only salts	only water	both salts and water	either salts or water	both salts and water
The frequency shift of the Raman line of HCl gas corresponds to	3μ	3.27μ	3.46μ	4μ	3.46μ
Which shows the frequency shift equal to the frequency of Infra-red bands	HCl	carbondioxide	carbonmonoxide	oxygen	carbonmonoxide
Which of the following gas shows a frequency shift equal to the frequency difference of tv	HCl	carbondioxide	carbonmonoxide	oxygen	carbondioxide
The Raman lines obtained with crystals are sharp, becoming diffuse with rise of	intensity of the incident light	frequency	velocity	temperature	temperature
The two lines exist nearest to the exciting line have been identified with the oscillations of	calcite	diamond	HCl	water	calcite
Diamond exhibits a	broad line	very strong line	very sharp line	strong and sharp line	strong and sharp line
All the Raman lines move inward towards the parent line with	decrease of temperature	increase of temperature	increase of intensity	decrease of intensity	increase of temperature
The variations in intensity are of great significance in the study of	molecular structure	chemical constitution	shape and size	both a and b	both a and b
Which is used to separate the vertical and horizontal components in the scattered light	quartz crystal	calcite	double image prism	suitably oriented double image prism	suitably oriented double image prism
Crystalline quartz should not be used for	condenser	spectrographs	windows	all the above	all the above
Menzies has investigated the polarisation of the Raman lines in	solids	liquids	gases	all the above	liquids
For the vibrational Raman lines, the depolarisation factor varies from	0 to 0.86	0 to 0.70	0 to 0.80	0 to 0.60	0 to 0.86
A simple and satisfactory explanation on the quantum theory was put forwar by	Sir C.V.Raman	Prof.Smekal	Rayleigh	Bhagavantam	Prof.Smekal
Which would result in the appearance of the unmodified line in the scattered beam	The photon without absorbing	absorb part of the energy o	molecule imparts some (	all the above	The photon without absorbing energy
The frequency shift is the	difference between stokes and	difference between the inci	addition between the in	any of the above	difference between the incident and scattered lines
Raman spectra are determined by	the number of atoms in the m	the masses of the atoms	the strength of the chem	all the above	all the above

Carbon dioxide has two very strong bands in the infra-red absorption spectrum at	668 and 2349 cm-1	600 and 3349 cm-1	700 and 2349 cm-1	668 and 2900 cm-1	668 and 2349 cm-1
Nitrous oxide molecule has the same number of electrons as	CO2	CO	water	carbon disulphide	CO2
The band at 589cm-1 has not been recorded in the Raman spectrum of nitrous oxide due	weak frequency	weak intensity	strong intensity	strong frequency	weak intensity
nitrous oxide has a	unsymmetrical structure	symmetrical structure	center of symmetry	either a or b	unsymmetrical structure
According to theory, all triatomic molecules of bent symmetrical structure should give ris	two Raman lines	one Raman lines	no Raman lines	three Raman lines	three Raman lines
Depolarization factor is the ratio of the	Frequencies of the vertical anc	Frequencies of the horizont	Intensities of the horizor	Intensities of the vertical and horizontal compor	Intensities of the horizontal and vertical components
The natural frequency of vibration is given by	ν=1/2π(F)^1/2	ν=1/2π(F/μ)^1/2	ν=(F/μ)^1/2	ν=1/2π(μ/F)^1/2	ν=1/2π(F/μ)^1/2

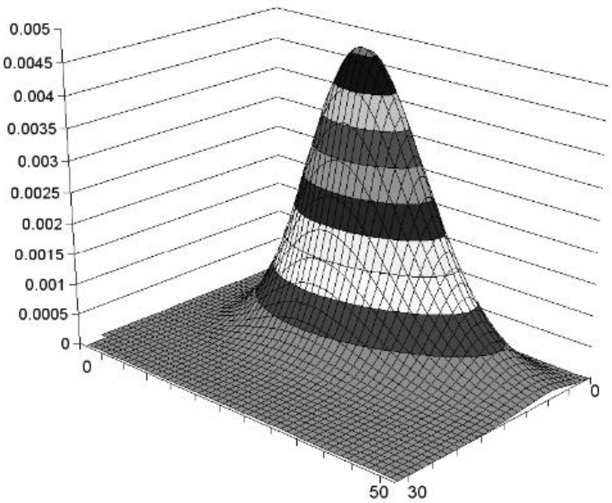
SYLLABUS

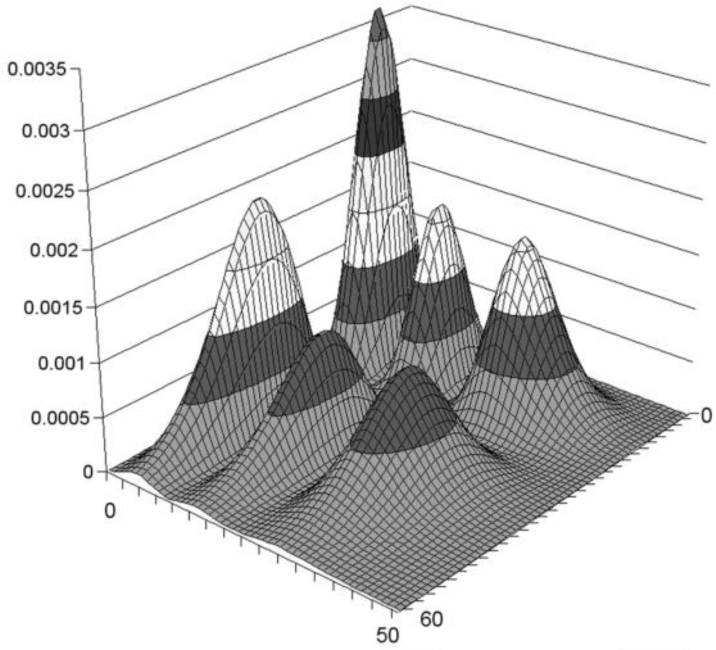
Electronic spectra: Electronic excitation of diatomic species - Vibrational analysis of diatomic molecules - Deslandre’s table - Intensity distribution Frank Condon principle - Rotational structure of electronic bands - Resonance and Normal Fluorescence – Intensities of transitions - Phosphorescence population of triplet state and intensity- Experimental methods - Applications of Fluorescence and phosphorescence.

Electronic excitation of diatomic species:

Despite its deficiencies the single-configuration description does provide an excellent description of the electronic wave function for small molecules. As we have seen, the bonding $1\sigma g$ orbital is singly occupied in H+2, but doubly occupied in the H2 molecule. We would then expect naively that the bond in H2 would be twice as strong a in the case of the H+2ion. A stronger bond corresponds to a deeper well in the potential V (R). The vibrational motion of a diatomic can be approximated as harmonic motion about the minimum in V (R), with a force constant.

Intensity distribution Frank Condon principle:





Intensity distribution Frank Condon principle:

These three different intensity distributions observed in the experiments can be explained by Franck-Condon principle. J. Franck in 1925 published a paper [Trans. Faraday Soc., Volume-21, Year-1925, Page-536] to describe this phenomenon with simple diagrammatical approach. Later on, in 1928 Condon gave the wave mechanical formulation on this idea [Physical Review, Volume-54, Year-1928, Page-858].

According to Franck:

"*The electron jump in a molecule takes place so rapidly in comparison to the vibrational motion of the nuclei that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump*".

Let us correlate this idea with the intensity three types of intensity pattern discussed before in figure-31.1, 31.2, 31.3.

The potential curves of the two electronic states are drawn in such way that their minima lie very nearly one above the other. The physical meaning is that in both the electronic states, the equilibrium internuclear distances are same. In absorption, the molecule is initially at the minimum vibrational state . If the transition takes place to (A→B), the change of the internuclear distance and momentum is small. The reason is transition is shown as vertical line (same internuclear distance) and both the vibrational levels are at zero point on the potential curve. This satisfies the requirement of the Franck-Condon principle. So, this transition will be highly probable. On the other hand, a transition from A → C is less probable because in this case, the internuclear distance changes after the jump. Further for a vertical transition (A→E) the velocity or momentum is appreciably changed. $0\upsilon''=0\upsilon'$

It should be noted that at poit E the kinetic energy is EB. At the turning points C and D, the velocity is zero as point A.

The minimum of the potential curve of the upper electronic state is shifted to higher intermolecular distance than that of the ground state. The physical meaning of this is that the bond length of the upper electronic state at the equilibrium is greater than that of the ground electronic state.

As we can see that the transition from minimum to minimum () is no longer the most probable because it does not satisfy the requirements of constant position during jump as prescribed by the Franck-Condon principle.

The most probable transition in this case will be from A → C. For this transition there is no change of nuclei positions (vertical line on the potential curve) and velocity during jump.

Since the equilibrium internuclear distance is different in this state the nuclei will start vibrating between C and D. So the vibrational state around the point C will have the most intense band. υ' For the higher and lower vibrational levels with respect to point C, the change will be gradually increase and thus the intensities of these levels will be gradually decreased with respect to the intense band. It is to be noted that the same intensity distribution will result when the upper potential curve will be shifted to the lower side with respect to the ground state.

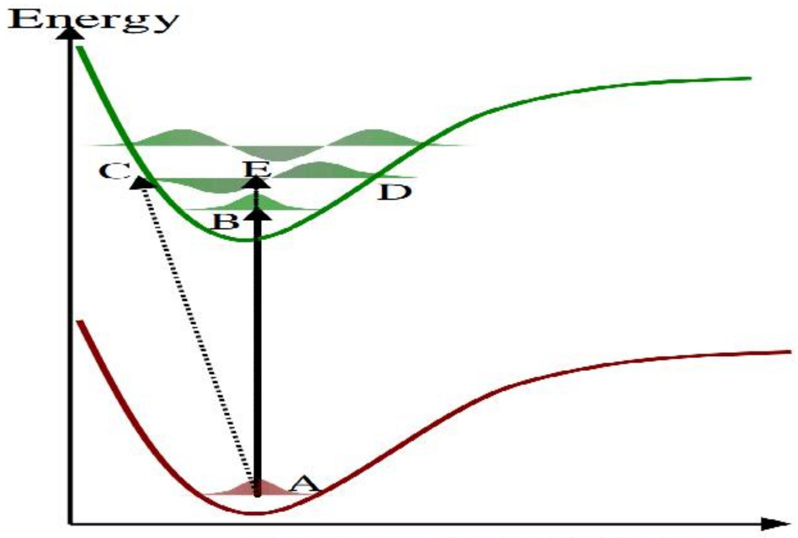


Figure-31.4

Rotational structure of electronic bands:

Because of their much larger mass, the nuclei in a molecule move much slower than electrons. This implies that the electrons can nearly immediately adjust their positions to the new nuclear configuration when the nuclei move. Although the electronic wave functions !(*r*, *R*) depend parametrically on the internuclear distance *R* they are barely affected by the velocity of the moving nuclei. The kinetic energy of the nuclearmotion *E*kin = 12. *M*v2 is small compared to that of the electrons. We therefore write the total Hamiltonian *H* in as the sum. The potential energy for the nuclear motion in the electronic state depends only on the nuclear distance *R*, not on the angles and *it is independent of the orientation of the molecule in space*. It is spherically symmetric. The wave functions however, may still depend on all three variables. we have neglected the influence of the electron motion on the rotation of molecules. In the axial symmetric electrostatic field of the two nuclei in the nonrotating molecule, the electrons precess around the space-fixed molecular z-axis. The angular momentum $\boldsymbol{L}(R)$ = /$\boldsymbol{l}i$ (R) of the electron shell, which depends on the separation R of the nuclei, has, however, a constant.

Resonance and Normal Fluorescence:

Resonance Raman (RR) spectroscopy and resonance fluorescence (RF) spectroscopy are two techniques for which the advent of lasers has generated renewed interest (2-11). In resonance Raman and resonance fluorescence, a molecule interacts with a photon which corresponds to an electronic transition. then re-emits which has changed by one or more vibrational and rotational quanta. Thus the soectrum of adiatomic a such as bromine or iodine in either process consists of an evenly spaced vibrational progression the levels of the excited electronic molecules. The basic experimental results, can he rationalized in terms of the molecular orbital, anharmonic oscillator, and rigid rotator quantum mechanical results of a diatomic molecule as developed in an undergraduate physical chemistry course. Useful information about the constants and molecular properties of the molecule in various electronic states can be obtained by detailed analysis of the fine structure of the overtone bands. Although a theoretical understanding of **RR** and RF and the relationship between them is still hewing developed, two competing interpretations of their relationship have been and will he summarized briefly. Resonance Raman spectroscopy **(5)** is an inelastic scattering process in which the incident (laser) photon "excites" the molecule to a virtual state in the vibrational-rotational continuum of the excited state, accompanied by instantaneous re-emission of a Raman scattered photon, that has lost several quanta of energy because the molecule returns to a ground electronic, but vibrationally excited, state (Fig. 2a). The resonance fluorescence involves excitation to a discrete vibrational-rotational level of an excited electronic state, which after a finite time interval fluoresces, returning the molecule to a vibrationally excited level of the ground electronic state (Fig. 2b). The different modes of absorption and re-emission for RF and RR spectroscopy result in different spectral characteristics which are summarized in table.. Although the two techniques are experimentally distinct under most conditions, some workers, have suggested a common origin for them. However, there remain serious questions about their relationship, which are still being investigated the selection rules for the RF and RR effects are very different from those for infrared and ordinary Raman spectroscopy, approximation, and ovenonei and rumhination hands appear weakly usually less than **1';** of the fundamental **u,** anharmonicitvefferts. In contrast. the RF and RR of comparable intensity to the fundamental, decreasing gradually for higher quantum numbers.

Intensities of transitions - Phosphorescence population of triplet state and intensity:

Fluorescence is a member of the ubiquitous **luminescence** family of processes in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical mechanism. Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed **photoluminescence**, which is formally divided into two categories, **fluorescence** and **phosphorescence**, depending upon the electronic configuration of the excited state and the emission pathway. Fluorescence is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval, termed the fluorescence lifetime. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime.

The fluorescence process is governed by three important events, all of which occur on timescales that are separated by several orders of magnitude. Excitation of a susceptible molecule by an incoming photon happens in femtoseconds (10E-15 seconds), while vibrational relaxation of excited state electrons to the lowest energy level is much slower and can be measured in picoseconds (10E-12 seconds). The final process, emission of a longer wavelength photon and return of the molecule to the ground state, occurs in the relatively long time period of nanoseconds (10E-9 seconds). Although the entire molecular fluorescence lifetime, from excitation to emission, is measured in only billionths of a second, the phenomenon is a stunning manifestation of the interaction between light and matter that forms the basis for the expansive fields of steady state and time-resolved fluorescence spectroscopy and microscopy. Because of the tremendously sensitive emission profiles, spatial resolution, and high specificity of fluorescence investigations, the technique is rapidly becoming an important tool in genetics and cell biology.

Several investigators reported luminescence phenomena during the seventeenth and eighteenth centuries, but it was British scientist Sir George G. Stokes who first described fluorescence in 1852 and was responsible for coining the term in honor of the blue-white fluorescent mineral fluorite (fluorspar). Stokes also discovered the wavelength shift to longer values in emission spectra that bears his name. Fluorescence was first encountered in optical microscopy during the early part of the twentieth century by several notable scientists, including August Köhler and Carl Reichert, who initially reported that fluorescence was a nuisance in ultraviolet microscopy. The first fluorescence microscopes were developed between 1911 and 1913 by German physicists Otto Heimstädt and Heinrich Lehmann as a spin-off from the ultraviolet instrument. These microscopes were employed to observe autofluorescence in bacteria, animal, and plant tissues. Shortly thereafter, Stanislav Von Provazek launched a new era when he used fluorescence microscopy to study dye binding in fixed tissues and living cells. However, it wasn't until the early 1940s that Albert Coons developed a technique for labeling antibodies with fluorescent dyes, thus giving birth to the field of immunofluorescence. By the turn of the twenty-first century, the field of fluorescence microscopy was responsible for a revolution in cell biology, coupling the power of live cell imaging to highly specific multiple labeling of individual organelles and macromolecular complexes with synthetic and genetically encoded fluorescent probes.

Applications of Fluorescence and phosphorescence:

Since the introduction of the polymerase chain reaction in the early 1980s perhaps no single technology has had a greater impact on molecular biology than fluorescence. Fluorescence-labeled oligonucleotides and dideoxynucleotide DNA sequencing
terminators have opened a seemingly limitless range of applications in PCR, DNA sequencing, microarrays, and in situ hybridization and have done so with vastly enhanced sensitivity and dramatically increased laboratory safety.

To begin, let us first distinguish fluorescence from luminescence. Luminescence is the production of light through excitation by means other than increasing temperature. These include chemical means (chemiluminescence), electrical discharges (electroluminescence), or crushing (triboluminescence). Fluorescence is a short-lived type of luminescence created by electromagnetic excitation. That is, fluorescence is generated when a substance absorbs light energy at a short (higher energy) wavelength and then emits light energy at a longer (lower energy) wavelength. The length of time between absorption and emission is usually relatively brief, often on the order of 10-9 to 10-8 seconds. The history of a single fluorescence event can be shown by means of a Jablonski Diagram, named for the Ukranian born physicist Aleksander Jablonski (Fig.1). As shown, in Stage 1 a photon of given energy h4ex is supplied from an outside source such as a laser or a lamp. The fluorescent molecule, lying in its ground energy state So, absorbs the energy creating an excited electronic singlet state S1'. This excited state will last for a finite time, usually one to ten nanoseconds (sec-9), during which time the fluorescent molecule (aka, fluorophore) undergoes conformational changes and can be subject to myriad potential interactions with its molecular environment. The first phase of Stage 2 is characterized by the fluorophore partially dissipating some of the absorbed energy creating a relaxed singlet state S1.

1. Describe Electronic excitation of diatomic species and Deslandre's table.
2. Explain the following, Rotational structure of electronic bands.
3. Define Normal Fluorescence
4. Give a note on vibrational analysis of diatomic molecules and Deslandre's table.
5. Explain the following
    i) Rotational structure of electronic bands
    ii) Applications of Fluorescence
6. Describe an Intensity distribution Frank Condon principle and Rotational structure of electronic bands.
7. Explain about the vibrational analysis of diatomic molecules.
8. What you meant by electronic excitation?
9. Describe Resonance and Normal fluorescence.
10. Describe Frank Condon principle and Rotational structure of electronic bands.
11. Explain the following, Rotational structure of electronic bands
12. Give an applications of Fluorescence
13. Electron spin resonance is observed for atomic hydrogen with an instrument operating at 9.5 GHz. If the g value for the electron in the hydrogen atom is 2.0026, what is the magnetic field applied? Bohr magnetron $\mu_B = 9.274 \times 10^{-24}$ $JT^{-1.}$
14. A free electron is placed in magnetic field of strength 1.3 T. Calculate the resonance frequency if g = 2.0023.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641021
(For the candidates admitted from 2017 onwards)
DEPARTMENT OF PHYSICS
M. Sc. DEGREE EXAMINATION - APRIL 2018
Second Semester
PHYSICS
SPECTROSCOPY (17PHP204)
MULTIPLE CHOICE QUESTIONS

QUESTIONS	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
The diagram representing the relation between the inter-nuclear distance and energy is	Morse curve	frequency spectrum	modulation curve	none of the above	Morse curve
In the case of microwave spectroscopy, the absorption takes place due to interaction bet	electric vector of the radiatio	magnetic vector and the el	electric vector of the ra	none of the above	electric vector of the radiation and magnetic dipole moment
The source of microwave radiation in microwave spectroscopy is normally	laser	mercury vapour lap	sodium vapour lamp	klystron	klystron
In a spectrometer, the devise used to split the spectral lines into its component frequenc	divider	selector	monochromator	recorder	monochromator
The most commonly used and most efficient monochromator is a spectrometer is	prism	lens	diffraction grating	none of the above	diffraction grating
The Morse curve depicts the variation of	internuclear distance with en	energy with internuclear di	vibraitonal energy with	none of the above	vibraitonal energy with internuclear distance
Which of the following statements is correct?	In a molecule, each electronic	In a molecule, each vibratio	In a molecule, each elec	In a molecule, each rotational level contains many vibrational levels and each vibrational level contains many elelctronic levels	In a molecule, each electronic level contains many vibrational levels and each vibrational level contains many rotational levels
Electronic spectra is given by	all molecules	only molecules with electri	only molecules with ma	only molecules with both electric and magnetic moments	all molecules
The change in vibrational quantum numbe acoompanying an electronic transition	has selection rule dv=0	has a selection rule dv = +	has selection rule dv=0,	is not governed by any selection rule	is not governed by any selection rule
In fluorescence, the frequency of emitted radiation is ----- that of incident radiation	higher than	lower than	same as	higher or lower than	lower than
The emission of radiation which may last for some time even after the removal of the ex	coherence	resonance	fluorescence	phosphorescence	phosphorescence
During electronic transition in a molecule the radiation normally fall in the	visible region	IR region	Microwave region	UV region	visible region
The condition for a molecule to give electronic spectra is	it should possess permanent	it sould possess permanent	it should possess both p	there is no such condition	there is no such condition
Electronic spectra may contain	vibrational and rotational stru	only vibrational structure	only rotational structure	no such components	vibrational and rotational structure
During an electronic transtion, the internuclear distance remains the same. This is called	mutual exclusion principle	Frank Condon principle	Deslander's principle	none of the above	Frank Condon principle
The intensity distribution of vibrational lines of electronic spectra is given by using	Deslander's table	Frank Condon principle	Population consideratio	none of the above	Frank Condon principle
The absorption and emission energy in the range 10 to about 10000 angstrom is restricte	electronic energy	vibrational energy	rotational enegy	translational energy	electronic energy
The group of lines resulting from transitions between the different rotational levels in tw	band	spectrum	spectral lines	none of the above	band
The time required for electronic transitions is about	10^-16 seconds	10^-14 seconds	10^-16 milliseconds	A few seconds	10^-16 seconds
The sum of all bands for transitions between two electronic levels is termed as	band origin	band system	band head	band lines	band system
During electronic transtions the internuclear distance	increases	decreases	remains the same	none of the above	remains the same
The P and R branches of spectral lines are represented by a diagram called	condon parabola	Fortrat parabola	Morse curve	none of the above	Fortrat parabola
For all electronic levels for which the electrons are paired, the spin is ----- and multiplicit	1 and 0	0 and 1	0 and 0	1 and 1	0 and 1
In triplet state, the probability of two electrons occuppying same state is	0	1	0.5	0.75	0
If during a spectral emission, the electron undergoing the transition does not change its	fluorescence	phosphorescence	scattering	raman shift	fluorescence
The emission process in which the electron taking part in the emission undergoes a chan	fluorescence	phosphorescence	delayed fluorescence	none of the above	phosphorescence
The process in which there occurs a delay between absorption and emission, but no char	fluorescence	phosphorescence	delayed fluorescence	raman shift	delayed fluorescence
Emission is a spontaneous process, generally, and absorption is a ----	stimulated	spontaneous	scattering	none of the above	stimulated
The diagram representing transitions between the various electronic and vibraitonal stat	Fortrat parabola	Condon parabola	Morse curve	Jablonski diagram	Jablonski diagram
In any non-degenerate molecular orbital, only two electrons of opposite spin can be acc	Pauli's exclusion principle	Frank Condon principle	Mutual exclusion princip	none of the above	Pauli's exclusion principle
The study of the physical and chemical properties of electronically excited atoms and mo	Physical chemistry	photochemistry	photonics	electrolysis	Physical chemistry
Which of the following statements is correct?	All electronically excited state	All electronicaly excited st	None of the electronical	All electronically excited states undergo stimulated emission	All electronicaly excited states do not give rise to observable emission
Some of the electronically excited states undego	relaxation	absorption	scattering	collision	relaxation
Fluorescence is a process in which the electron -----	emits energy as radiation and	emits energy as radiation a	does not emit energy as	does not emit energy as radiation and does not undergo change in spin	emits energy as radiation and does not undego change in spin
The principle involved in scintillators is	phosphorescence	fluorescence	delayed fluorescence	ionisation	fluorescence
Fluorescence emission is a ------ process	stimulated	scattering	spontaneous	none of the above	spontaneous
The process in which absorbed radiation is not emitted as radiation is called	spontaneous emission	stimulated emission	scattering	non-radiative transfer	non-radiative transfer
The electronic spectra fall within the range	10 to 10000 asgstrom	4000 to 12500 angstrom	50 to 400 cm^-1	none of the above	10 to 10000 asgstrom
Frank Condon principle states that during an electronic transition, the internucluear dist	changes	does not change	becomes double	becomes half	does not change
The triplet state is always ----- in energy than the corresponding state	higher	equal	lower	none of the above	lower
The electronic transition is spin forbidden, if the initial and final states have	same multiplicity	different multiplicity	less multiplicity	none of the above	different multiplicity
At very low pressures in the vapour phase, the electronically excited molecules may not	normal fluorescence	delayed fluorescence	resonance fluorescence	phosphorescence	normal fluorescence
Fortrat parabola represents ----- , represented by v - m plot	The P and R branches	P branche only	R branch only	S branch only	The P and R branches
If a molecule is excited to some vibrational level of S1 state under high pressure, the initi	normal fluorescence	delayed fluorescence	resonance fluorescence	phosphorescence	normal fluorescence
The difference in position of maximum of emission and of zero-zero transition on an ene	Stokes loss	anti stokes loss	collision loss	none of the above	anti stokes loss

SYLLABUS

NMR Spectroscopy: Quantum mechanical and Classical description - The Bloch equation - Relaxation process - the experimental technique - Principle and working of high resolution NMR Spectrometer - Chemical shift – Applications of NMR

NQR Spectroscopy: Fundamental requirements - General principle - Experimental detection of NQR frequencies – Interpretation and chemical explanation of NQR spectroscopy – Applications of NQR

Nuclear Magnetic Resonance Spectroscopy

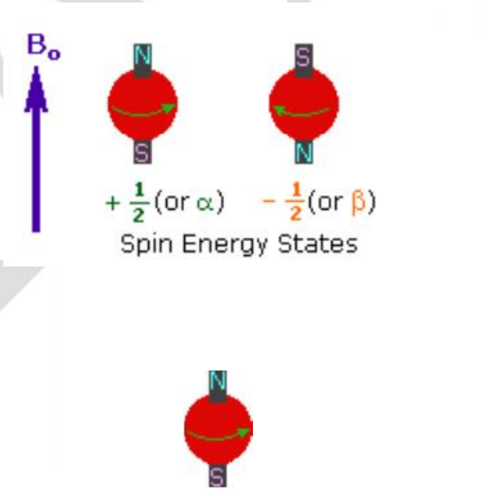
Background

Over the past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as nmr, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, nmr is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram. To be successful in using nmr as an analytical tool, it is necessary to understand the physical principles on which the methods are based.

The nuclei of many elemental isotopes have a characteristic spin (**I**). Some nuclei have integral spins (e.g. I = 1, 2, 3 ....), some have fractional spins (e.g. I = 1/2, 3/2, 5/2 ....), and a few have no spin, I = 0 (e.g. 12C, 16O, 32S, ...). Isotopes of particular interest and use to organic chemists are 1H, 13C, 19F and 31P, all of which have I = 1/2. Since the analysis of this spin state is fairly straight foreward, our discussion of NMR will be limited to these and other I = 1/2 nuclei.

The following features lead to the NMR phenomenon:

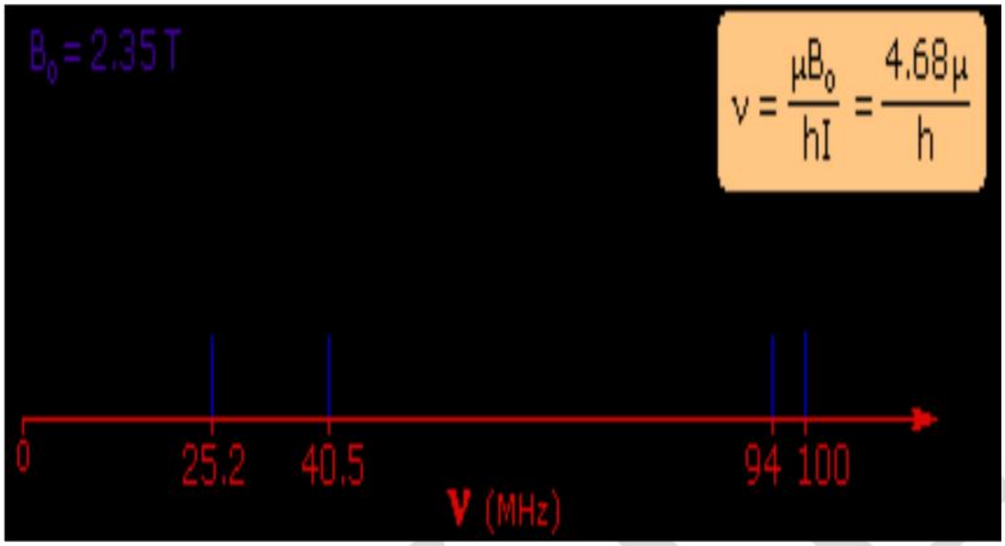
1. A spinning charge generates a magnetic field, as shown by the animation on the right. The resulting spin-magnet has a magnetic moment (**μ**) proportional to the spin.
2. In the presence of an external magnetic field (**B0**), two spin states exist, **+1/2** and **-1/2**. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field. Note that the arrow representing the external field points North.
3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to Bx a formula for the energy difference is given (remember I = 1/2 and μ is the magnetic moment of the nucleus in the field).



Strong magnetic fields are necessary for nmr spectroscopy. The international unit for magnetic flux is the tesla (**T**). The earth's magnetic field is not constant, but is approximately 10-4 T at ground level. Modern nmr spectrometers use powerful magnets having fields of 1 to 20 T. Even with these high fields, the energy difference between the two spin states is less than 0.1 cal/mole. To put this in perspective, recall that infrared transitions involve 1 to 10 kcal/mole and electronic transitions are nearly 100 time greater. For nmr purposes, this small energy difference (ΔE) is usually given as a frequency in units of MHz (106 Hz), ranging from 20 to 900 Mz, depending on the magnetic field strength and the specific nucleus being studied. Irradiation of a sample with radio frequency (rf) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the +1/2 state to the higher -1/2 spin state. Note that this electromagnetic radiation falls in the radio and television broadcast spectrum. Nmr spectroscopy is therefore the energetically mildest probe used to examine the structure of molecules. The nucleus of a hydrogen atom (the proton) has a magnetic moment μ = 2.7927, and has been studied more than any other nucleus. The previous diagram may be changed to display energy difference

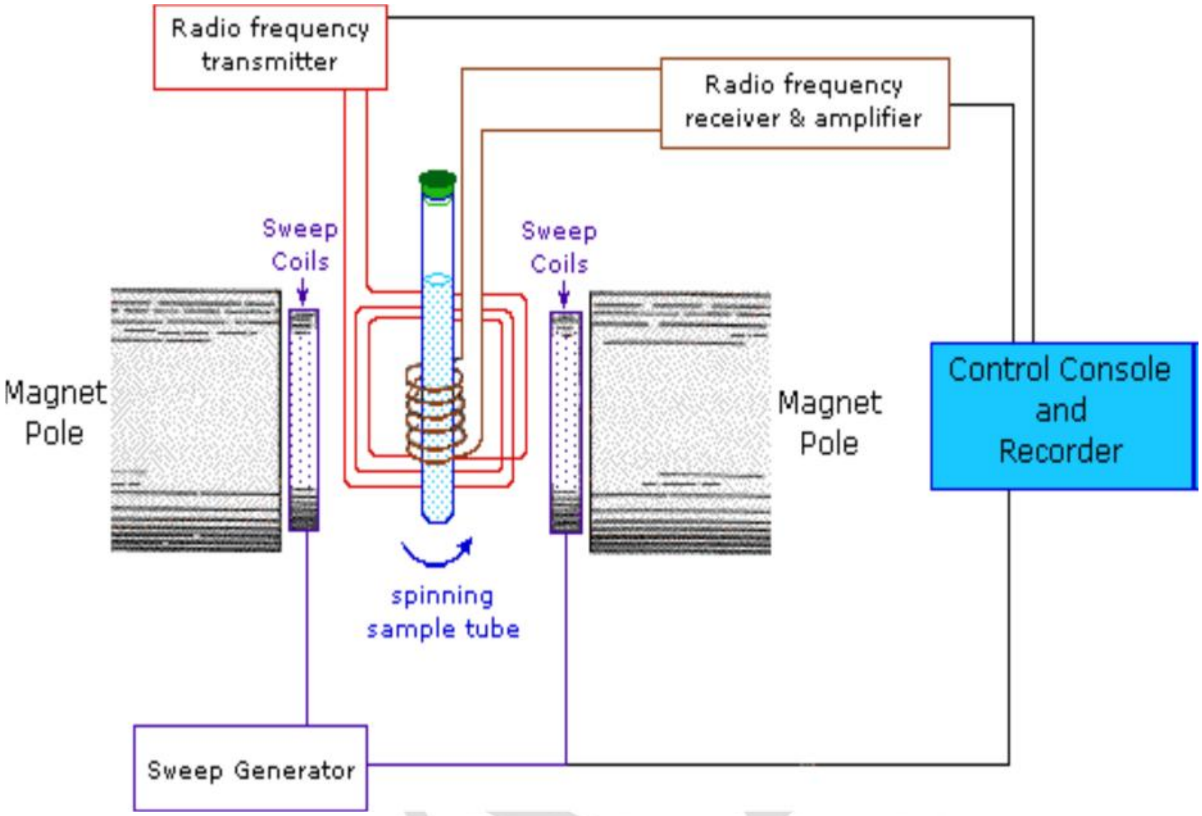
For spin 1/2 nuclei the energy difference between the two spin states at a given magnetic field strength will be proportional to their magnetic moments. For the four common nuclei noted above, the magnetic moments are: 1H μ = 2.7927, 19F μ = 2.6273, 31P μ = 1.1305 & 13C μ = 0.7022. These moments are in nuclear magnetos, which are 5.05078•10-27 JT-1. The following diagram gives the approximate frequencies that correspond to the spin state energy separations for each of these nuclei in an external magnetic field of 2.35 T. The formula in the colored box shows the direct correlation of frequency (energy difference) with magnetic moment (h = Planck's constant = 6.626069•10-34 Js).

s for the proton spin states (as frequencies) by mouse clicking anywhere within it.

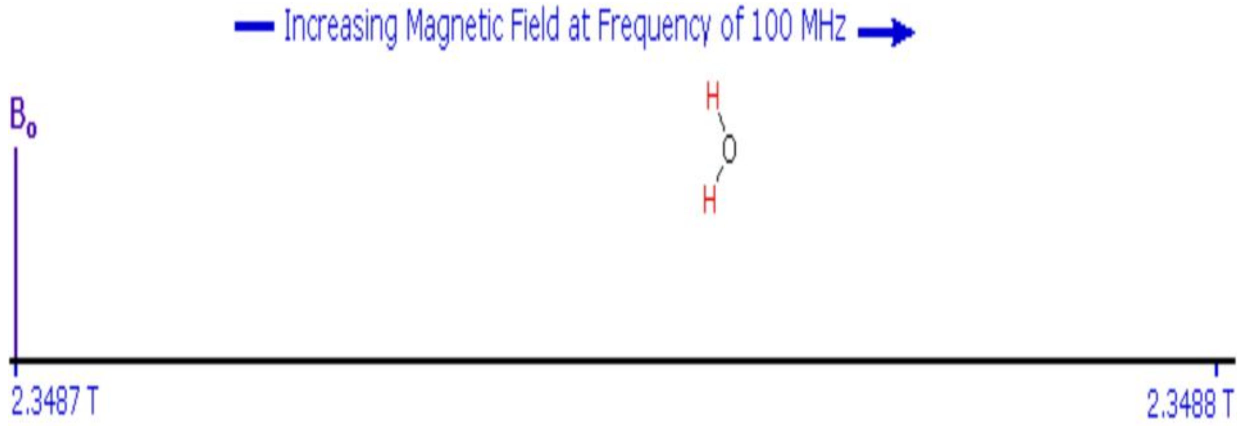


Proton NMR Spectroscopy

This important and well-established application of nuclear magnetic resonance will serve to illustrate some of the novel aspects of this method. To begin with, the nmr spectrometer must be tuned to a specific nucleus, in this case the proton. The actual procedure for obtaining the spectrum varies, but the simplest is referred to as the continuous wave (CW) method. A typical CW-spectrometer is shown in the following diagram. A solution of the sample in a uniform 5 mm glass tube is oriented between the poles of a powerful magnet, and is spun to average any magnetic field variations, as well as tube imperfections. Radio frequency radiation of appropriate energy is broadcast into the sample from an antenna coil (colored red). A receiver coil surrounds the sample tube, and emission of absorbed RF energy is monitored by dedicated electronic devices and a computer. An NMR spectrum is acquired by varying or sweeping the magnetic field over a small range while observing the rf signal from the sample. An equally effective technique is to vary the frequency of the rf radiation while holding the external field constant.



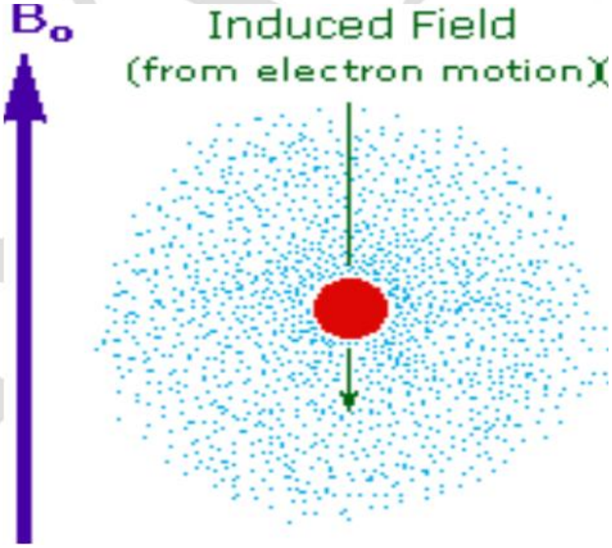
As an example, consider a sample of water in a 2.3487 T external magnetic field, irradiated by 100 MHz radiation. If the magnetic field is smoothly increased to 2.3488 T, the hydrogen nuclei of the water molecules will at some point absorb rf energy and a resonance signal will appear. An animation showing this may be activated by clicking the Show Field Sweep button. The field sweep will be repeated three times, and the resulting resonance trace is colored red. For visibility, the water proton signal displayed in the animation is much broader than it would be in an actual experiment.



Since protons all have the same magnetic moment, we might expect all hydrogen atoms to give resonance signals at the same field / frequency values. Fortunately for chemistry applications, this is not true. By clicking the Show Different Protons button under the diagram, a number of representative proton signals will be displayed over the same magnetic field range. It is not possible, of course, to examine isolated protons in the spectrometer described above; but from independent measurement and calculation it has been determined that a naked proton would resonate at a lower field strength than the nuclei of covalently bonded hydrogens. With the exception of water, chloroform and sulfuric acid, which are examined as liquids, all the other compounds are measured as gases.

Why should the proton nuclei in different compounds behave differently in the nmr experiment?

The answer to this question lies with the electron(s) surrounding the proton in covalent compounds and ions. Since electrons are charged particles, they move in response to the external magnetic field (Bo) so as to generate a secondary field that opposes the much stronger applied field. This secondary field **shields** the nucleus from the applied field, so Bo must be increased in order to achieve resonance (absorption of rf energy). As illustrated in the drawing on the right, Bo must be increased to compensate for the induced shielding field. In the upper diagram, those compounds that give resonance signals at the higher field side of the diagram (CH4, HCl, HBr and HI) have proton nuclei that are more shielded than those on the lower field (left) side of the diagram. The magnetic field range displayed in the above diagram is very small compared with the actual field strength (only about 0.0042%). It is customary to refer to small increments such as this in units of parts per million (ppm). The difference between 2.3487 T and 2.3488 T is therefore about 42 ppm. Instead of designating a range of NMR signals in terms of magnetic field differences (as above), it is more common to use a frequency scale, even though the spectrometer may operate by sweeping the magnetic field. Using this terminology, we would find that at 2.34 T the proton signals shown above extend over a 4,200 Hz range (for a 100 MHz rf frequency, 42 ppm is 4,200 Hz). Most organic compounds exhibit proton resonances that fall within a 12 ppm range (the shaded area), and it is therefore necessary to use very sensitive and precise spectrometers to resolve structurally distinct sets of hydrogen atoms within this narrow range. In this respect it might be noted that the detection of a part-per-million difference is equivalent to detecting a 1 millimeter difference in distances kilometer.



Chemical Shift

Unlike infrared and uv-visible spectroscopy, where absorption peaks are uniquely located by a frequency or wavelength, the location of different NMR resonance signals is dependent on both the external magnetic field strength and the RF frequency. Since no two magnets will have exactly the same field, resonance frequencies will vary accordingly and an alternative method for characterising and specifying the location of NMR signals is needed. This problem is illustrated by the eleven different compounds shown in the following diagram. Although the eleven resonance signals are distinct and well separated, an unambiguous numerical locator cannot be directly assigned to each.

One method of solving this problem is to report the location of an NMR signal in a spectrum relative to a reference signal from a standard compound added to the sample. Such a reference standard should be chemically unreactive, and easily removed from the sample after the measurement. Also, it should give a single sharp NMR signal that does not interfere with the resonances normally observed forganic compounds. Tetramethylsilane, $(CH_3)_4Si$, usually referred to as TMS, meets all these characteristics, and has become the reference compound of choice for proton and carbon NMR. Since the separation (or dispersion) of nmr signals is magnetic field dependent, one additional step must be taken in order to provide an unambiguous location unit. This is illustrated for the acetone, methylene chloride and benzene signals by clicking on the previous diagram. To correct these frequency differences for their field dependence, we divide them by the spectrometer frequency (100 or 500 MHz in the example), as shown in a new display by again clicking on the diagram. The resulting number would be very small, since we are dividing Hz by MHz, so it is multiplied by a million, as shown by the formula in the blue shaded box. Note that νref is the resonant frequency of the reference signal and νsamp is the frequency of the sample signal. This operation gives a locator number called the **Chemical Shift**, having units of parts-per-million (ppm), and designated by the symbol **δ** Chemical shifts for all the compounds in the original display will be presented by a third click on the diagram.

The compounds referred to above share two common characteristics:

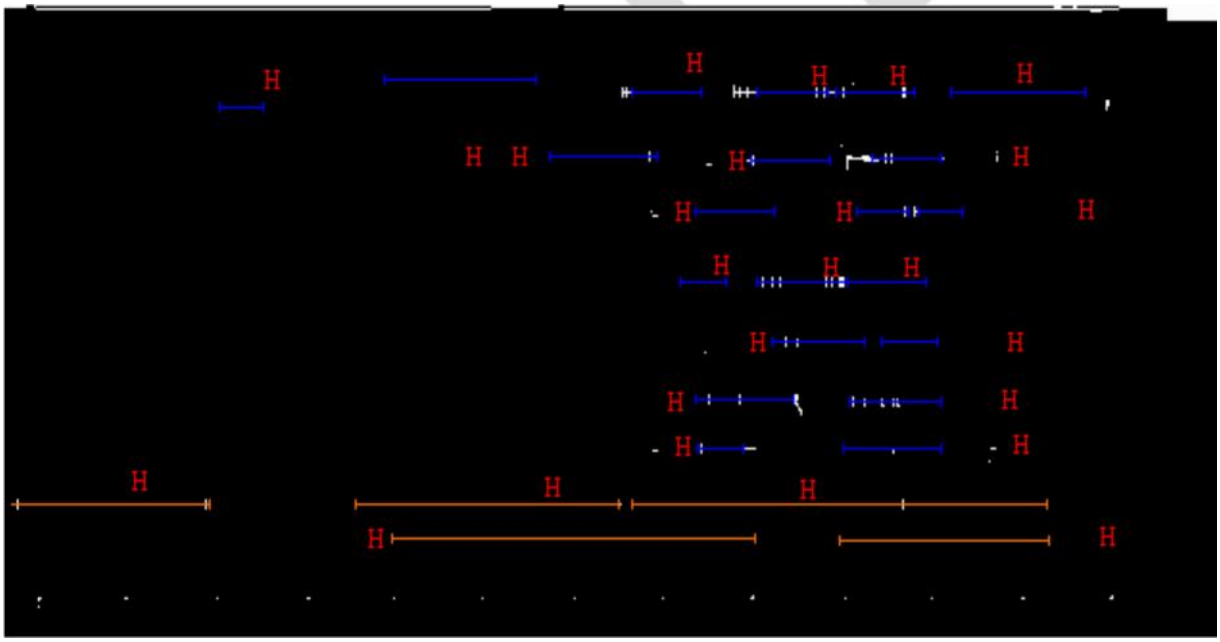
- The hydrogen atoms in a given molecule are all structurally equivalent, averaged for fast conformational equilibria.
- The compounds are all liquids, save for neopentane which boils at 9 °C and is a liquid in an ice bath.

The first feature assures that each compound gives a single sharp resonance signal. The second allows the pure (neat) substance to be poured into a sample tube and examined in a nmr spectrometer. In order to take the nmr spectra of a solid, it is usually necessary to dissolve it in a suitable solvent. Early studies used carbon tetrachloride for this purpose, since it has no hydrogen that could introduce an interfering signal. Unfortunately, CCl_4 is a poor solvent for many polar compounds and is also toxic. Deuterium labeled compounds, such as deuterium oxide (D2O), chloroform-d (DCCl3), benzene-d6 (C6D6), acetone-d6 (CD3COCD3) and DMSO-d6 (CD3SOCD3) are now widely used as nmr solvents. Since the deuterium isotope of hydrogen has a different magnetic moment and spin, it is invisible in a spectrometer tuned to protons.

From the previous discussion and examples we may deduce that one factor contributing to chemical shift differences in proton resonance is the **inductive effect**. If the electron density about a proton nucleus is relatively high, the induced field due to electron motions will be stronger than if the electron density is relatively low. The shielding effect in such high electron density cases will therefore be larger, and a higher external field (Bo) will be needed for the rf energy to excite the nuclear spin. Since silicon is less electronegative than carbon, the electron density about the methyl hydrogens in tetramethylsilane is expected to be greater than the electron density about the methyl hydrogens in neopentane (2,2-dimethylpropane), and the characteristic resonance signal from the silane derivative does indeed lie at a higher magnetic field. Such nuclei are said to be **shielded**. Elements that are more electronegative than carbon should exert an opposite effect (reduce the electron density); and, as the data in the following tables show, methyl groups bonded to such elements display lower field signals (they are deshielded). The deshielding effect of electron withdrawing groups is roughly proportional to their electronegativity, as shown by the left table. Furthermore, if more than one such group is present, the deshielding is additive (table on the right), and proton resonance is shifted even further downfield.

The general distribution of proton chemical shifts associated with different functional groups is summarized in the following chart. Bear in mind that these ranges are approximate, and may not encompass all compounds of a given class. Note also that the ranges specified for OH and NH protons (colored orange) are wider than those for most CH protons. This is due to hydrogen bonding variations at different sample concentrations.

Proton Chemical Shift Ranges



Nuclear Quadrupole Resonance Spectroscopy:

Nuclear quadrupole resonance (NQR) uses radio-frequency (RF) magnetic fields to induce and detect transitions between sublevels of a nuclear ground state, a description that also applies to nuclear magnetic resonance (NMR). NMR refers to the situation where the sublevel energy splitting is predominantly due to a nuclear interaction with an applied static magnetic field, while NQR refers to the case where the predominant splitting is due to an interaction with electric field gradients within the material. So-called “pure NQR” refers to the common case when there is no static magnetic field at all. That property may simply be the sample temperature, for use as an NQR thermometer [4, 5], or even whether or not a sample is present when NQR is used for materials detection [6]. On the other hand, NQR is also used to obtain detailed information on crystal symmetries and bonding, on changes in lattice constants with pressure, about phase transitions in solids, and other properties of materials of interest to solid state physicists and chemists.

The Nuclear Electric Quadrupole Interaction:

A non-zero electric quadrupole moment arises for nuclei that are classically described as prolate (“stretched”) or oblate (“squashed”) spheroids. The nuclear charge distribution has axial symmetry and the axis of symmetry coincides with the direction of the nuclear angular momentum and the nuclear magnetic dipole moment. In general, an electric quadrupole moment is described by a 3 - 3 symmetric, traceless tensor **Q**. For a nucleus such a tensor can be determined using a single value that describes how prolate or oblate the nucleus is, plus a description of the orientation of the nucleus. Since the charge distribution for a nucleus with spin 0 or ½ is spherical, such nuclei will have no electric quadrupole moment.

1. Write a note on NMR?
2. Write a note on NQR?
3. Describe chemical shift.
4. Write about high resolution NQR spectrometer with suitable diagram.
5. Discuss about classical description of NMR spectroscopy
6. Explain the construction and working of high resolution NMR spectrometer with suitable examples.
7. Explain the construction and working of high resolution NQR spectrometer with suitable examples.
8. The ^{14}N resonance of a compound showed 3 lines at 5.997, 3.501 and 2.496 MHz. Calculate the quadrupole coupling constant e^2qQ/h and η.

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(Under Section 3 of UGC Act 1956)
COIMBATORE – 641021
(For the candidates admitted from 2017 onwards)
DEPARTMENT OF PHYSICS
M. Sc. DEGREE EXAMINATION - APRIL 2018
Second Semester
PHYSICS
SPECTROSCOPY (17PHP204)
MULTIPLE CHOICE QUESTIONS

QUESTIONS	OPTION 1	OPTION 2	OPTION 3	OPTION 4	OPTION 5	OPTION 6	ANSWER
For sample to be NMR active, the spin of the nucleus must be	equal to zero	equal to 1/2	equal to + or - 1	greater than 1/2			greater than 1/2
In the super-regenerative NQR spectrometer, the oscillations are -----	insignificant	quenched	non quenched	significant			insignificant
The NMR and NQR frequencies fall in the	radio frequency region	visible region	UV region	microwave region			radio frequency region
In NQR experiment, the frequency of the input radiation must be	fixed	variable	can be either fixed or va	none of the above			variable
NQR is observed normally in	solids only	gas only	liquid only	in all the three			solids only
Nucei having ----- due to their spin, exhibit NMR spectrum	magnetic moments	electric dipole moment	electron spin	none of the above			magnetic moments
For nuclei with mass number odd and atomic number even or odd, the spin is	zero	half integer	integer	can be anything			half integer
In NQR the energy levels are ----- in nature	both electrical and megnetic	electrical	magnetic	none of these			electrical
In the equation for nuclear magnetic moment (mu)N = gamma*Ih*2pi, gamma is known	nuclear quadrupole moment	electric dipole moment	gyromagnetic ratio	none of the above			gyromagnetic ratio
In NMR, resonance condition can be obtianed by	eiher fixed magnetic field and	only by fixed magnetic fielc	only fixed frequency anc	by varying both magnetic field and frequency			eiher fixed magnetic field and varying frequency, or fixed frequency and varying magnetic field
The condition in which there is no net absorption or emission in the case of NMR is caled	resonance	relaxation	saturation	none of the above			saturation
The condition of saturation occurs when	the number of molecules in th	the number of molecules ir	the number of molecule	none of the above			the number of molecules in the upper and lower levels become equal
The condition of saturation is never reached due to the process called	relaxation	saturation	radiative transfer	non radiative transfer			relaxation
The process in which energy of the excited nucleus is transferred to another nucleus is ca	spin-spin relaxation	spin-lattice relaxation	excitation	absorption			spin-spin relaxation
The relaxation process is	stimulated	spontaneous	absorption	none of the above			spontaneous
In spin-spin relaxation, the energy of the excited nucleus is transferred to	another nucleus	electron	lattice of the crystal	none of the above			lattice of the crystal
The frequency of precession of the total angular momentum vector around the applied n	resonance frequency	emission frequency	Larmour frequency	none of the above			Larmour frequency
Spin lattice relaxation is	transverse	longitudinal	parallel	none of the above			longitudinal
Spin-spin relaxation is	transverse	longitudinal	parallel	none of the above			transverse
NQR is a branch of ----- frequency spectroscopy which is closely related to NMR	radio frequency	UV frequency	Microwave frequency	visible frequency			radio frequency
In NQR spectroscopy,	an external magnetic field is a	an external electric field is	no external field is appli	external magnetic or electric field is applied			no external field is applied
In NQR spectroscopy, the absorption takes place in the	UV region	IR region	RF region	none of the above			RF region
In NQR spectroscopy	frequency of the radiation has	frequency of the radiation	external magnetic field i	both magnetic field and frequency to be varied			frequency of the radiation has to be varied
In NQR, different energy levels are caused due to the interaction between	the nuclear quadrupole mome	the electric field gradient a	the nuclear quadrupole	none of the above			the nuclear quadrupole moment of the nucleus and the electric field gradient
In NQR, the energy levels are -----in nature and the transitions are ----- type	electrical and magnetic	magnetic and electric	electric and electric	magnetic and magnetic			electrical and magnetic
In NMR, the energy levels are ----- in nature, and the transitions are ----- type	electrical and magnetic	magnetic and electric	electric and electric	magnetic and magnetic			electric and electric
The ESR spectrum falls in the	microwave region	rf region	UV region	IR region			microwave region
ESR is observed only in species having	paired electrons	one or more unpaired elec	nuclear quadrupole mor	none of the above			one or more unpaired electons
The magnetic moment of the electron is due to its	orbital motion only	spin only	both orbital motion as w	none of the above			both orbital motion as well as spin
For molecules with even atomic number and mass number, has nuclear spin	half integer	integer	zero	none of the above			zero
For molecules with odd atomic number and even mass number, the nuclear spin is	half integer	integer	zero	none of the above			integer
The resonance condition in NMR is ____	$h\nu = g_N\mu_N B_0$	$E = -\mu.B_0$	$\Delta E = 2\ \mu.B_0$	None of the above			$h\nu = g_N\mu_N B_0$
In the relation $h\nu = g_N\mu_N B_{0,}$ g_N is known as ___	Lange g factor	Nuclear g factor	Molecular g factor	None of the above			Nuclear g factor
In the relation $h\nu = g_N\mu_N B_{0,}$ μ_N is known as ___	Bohr magneton	Magnetic moment	Nuclear magneton	None of the above			Nuclear magneton
In both NMR and NQR absorption of radiation takes place only if ____ is achieved	resonance	saturation	relaxation	none of the above			resonance

SYLLABUS

ESR Spectroscopy: Basic principles of ESR - Experiments – ESR spectrometer reflection cavity and microwave bridge – ESR spectrum hyperfine structure - Study of free radicals – Applications of ESR

MOSSBAUER Spectroscopy: The Mossbauer effect- the recoilless emission and absorption of - Mossbauer spectrum – Experimental methods- Hyperfine interaction - Chemical Isomer Shift – Magnetic hyperfine and electric quadrupole interaction.

ESR Spectroscopy:

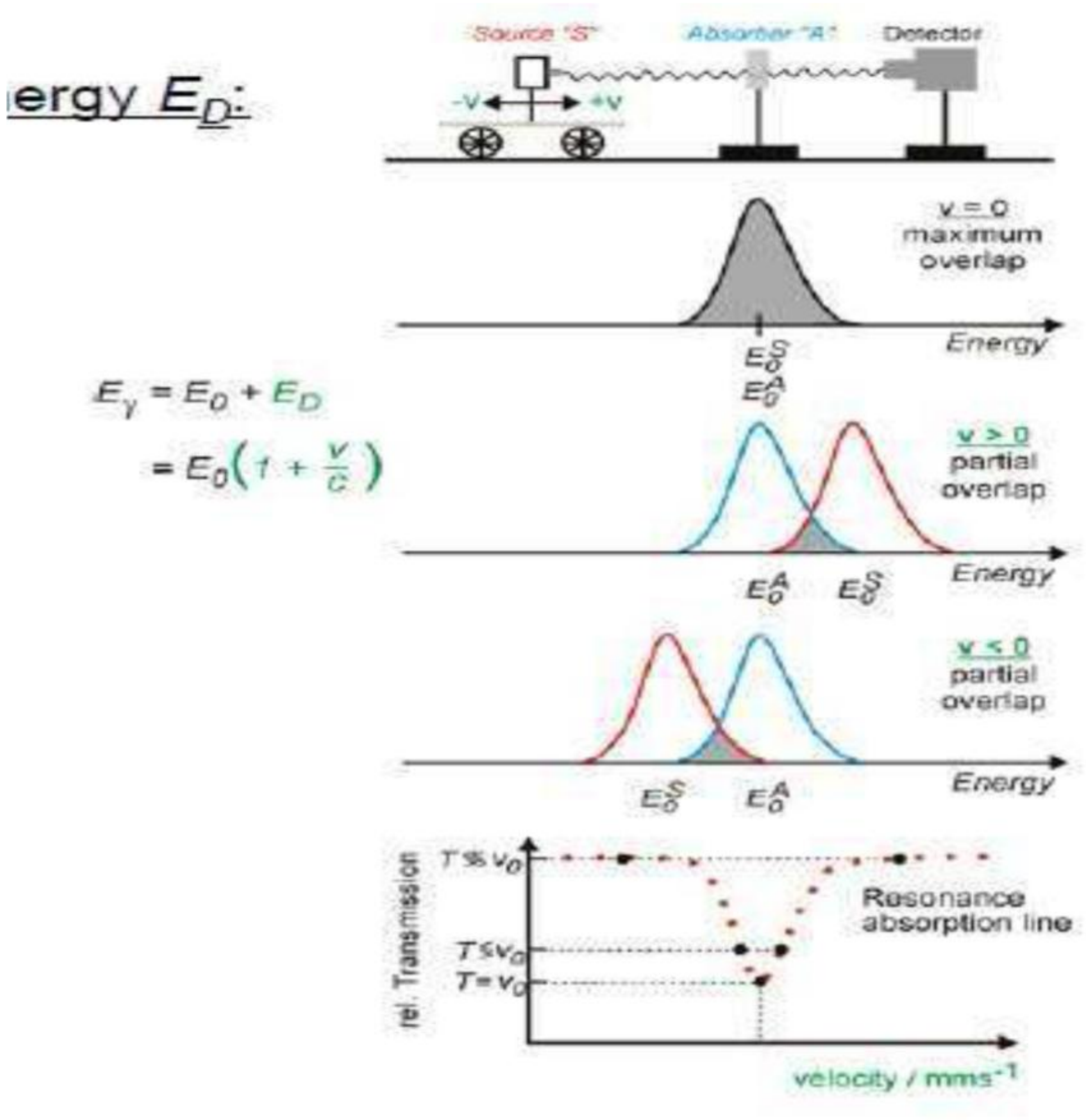
Electron Spin Resonance (ESR) spectroscopy, also referred to as Electron Paramagnetic Resonance (EPR) spectroscopy, is a versatile, nondestructive analytical technique based on the absorption of microwave radiation in presence of an applied field by paramagnetic species. When any species that contains unpaired electron(s) is subjected to a static magnetic field, the interaction between the magnetic moment of the electron and the applied magnetic field splits the spin energy levels (Zeeman splitting), and transitions between these spin levels are induced by applying suitable microwave radiation perpendicular to the magnetic field. Further interactions will depend on the presence of other factors such as the nuclear spins present in both the origin and other neigbours. The resulting absorption of the microwave radiation is modulated to record the first derivative of the absorption. Conventionally, EPR spectra are recorded as first derivative rather than absorption to improve the resolution. In fact, second derivative operation is also possible when needed to get better resolution of complex splitting patterns.

The block diagram of JES200 ESR spectrometer available at SAIF, IITM is shown below. This is a continuous wave (CW) ESR spectrometer that employs field modulation and phase sensitive detection. The Microwave Bridge consists of the Gundiode (as source of radiation) and the Detector. Both X-band (8.75 - 9.65 GHz) and Q-band (35.5GHz) frequency units are available. The sample is placed in a resonant cavity which admits microwaves through an iris. The cavity is located in the middle of an electromagnet and helps to amplify the weak signals from the sample. Other components such as an attenuator, field modulator and amplifier are also included to enhance the performance of the instrument. X- Band Electron Nuclear DOuble Resonance (ENDOR) facility is also available to study the nature of hyperfine interactions of very low magnitude, noting that this may be used only after complete understanding of the electronic structure of the molecule.

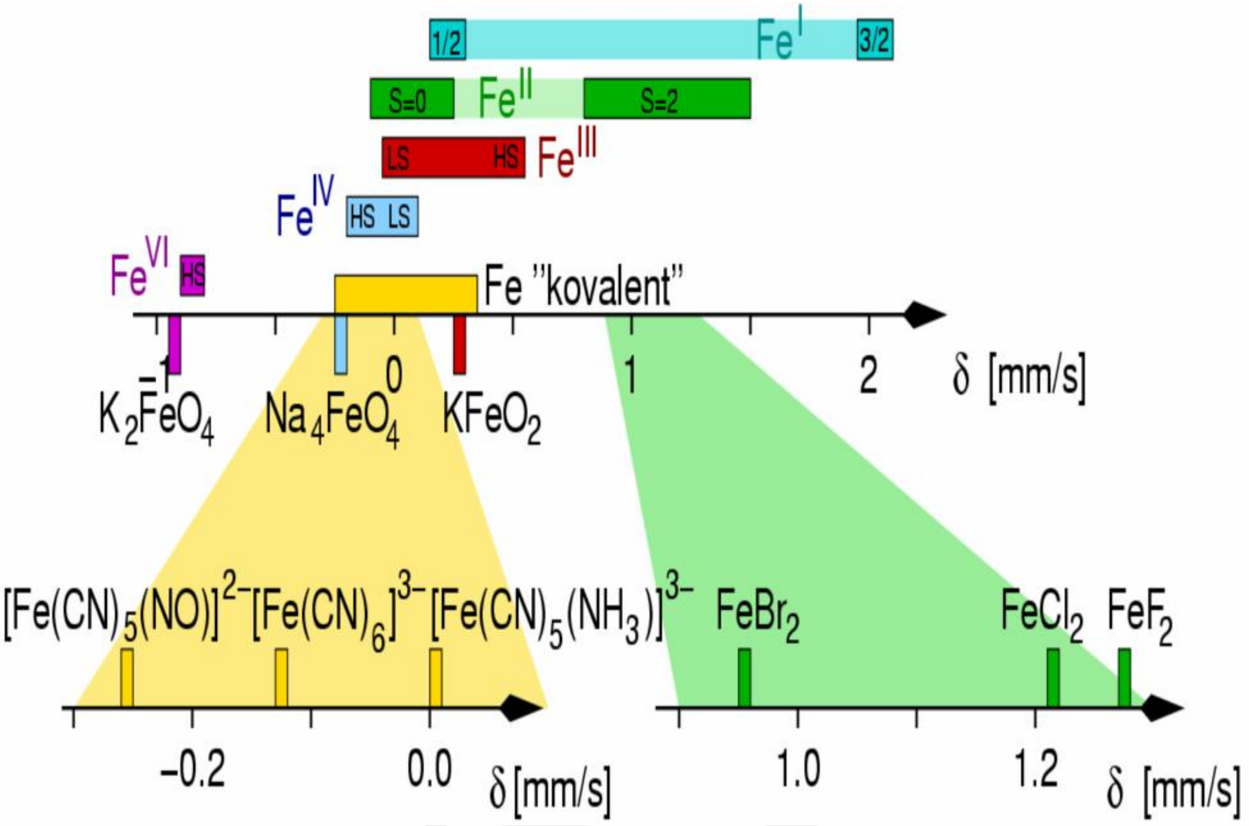
The ESR parameters that are monitored include the measurement of the g factor at the centre of the spectrum and the hyperfine splitting due to interaction with nuclei having spin $I \neq 0$. Zero-field splitting (or fine structure) characteristic of transition metal complexes and other species with two or more unpaired electrons ($S \geq 1$) can be observed in solid samples.

MOSSBAUER Spectroscopy:

Theory of Mossbauer spectroscopy:



Common samples for Mossbauer spectroscopy:

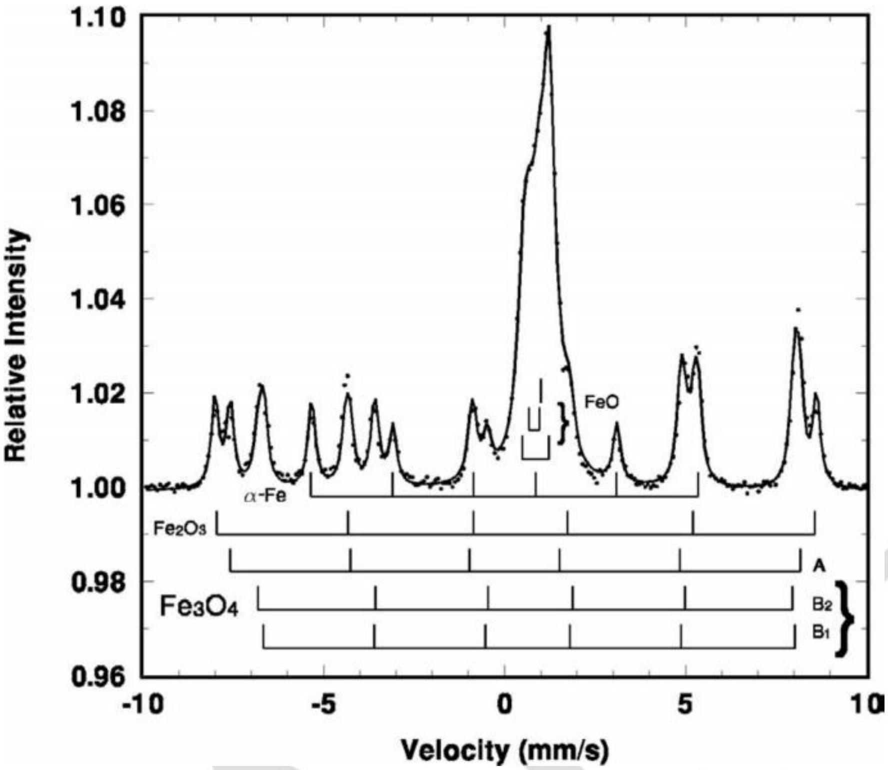


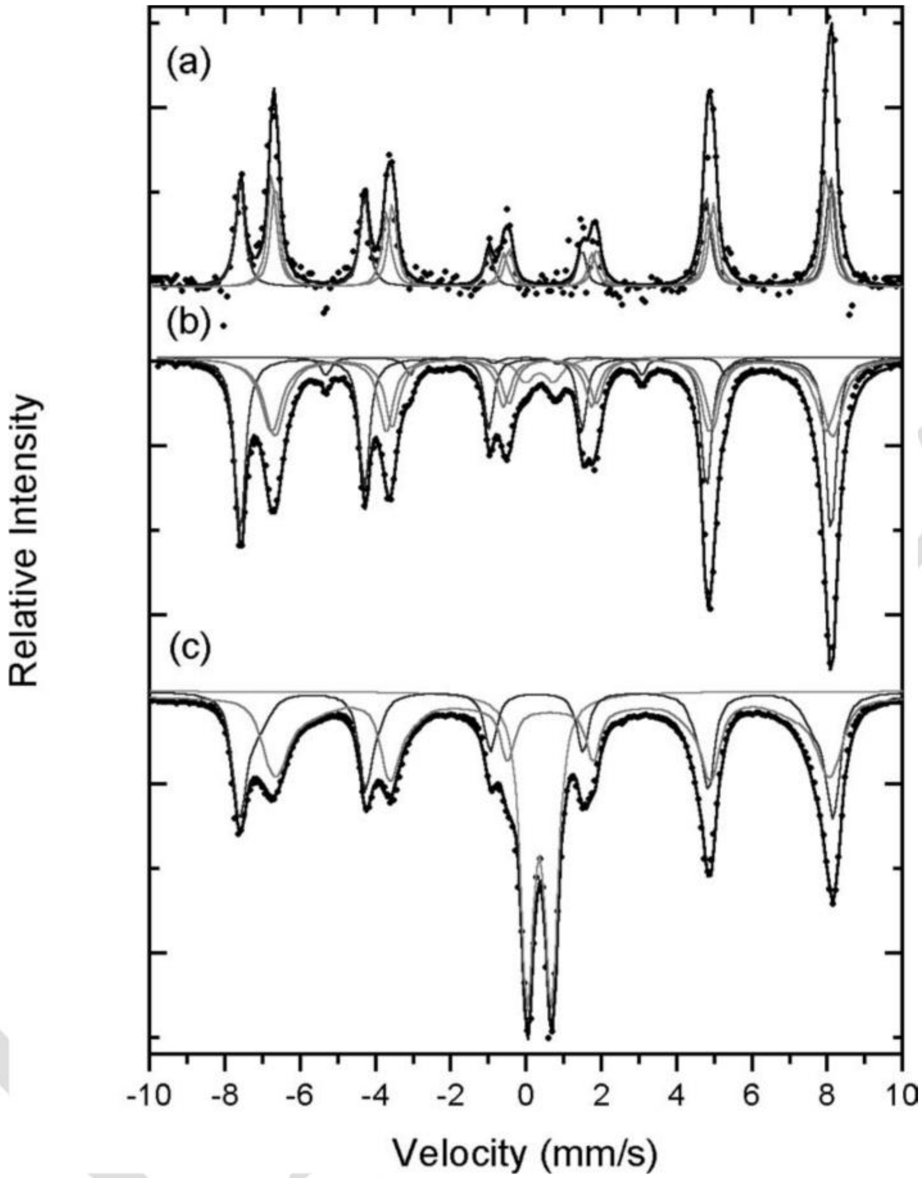
Corrosion, deterioration, and weathering of materials are age-long problems thathave faced mankind for millennia. From the world's ancient man-made and natural monoliths to today's most modern buildings, bridges and transportation facilities, the longevity of structures are closely controlled by the environments in which they are located. Having little control over these local environments, we must carefully select the materials that are best suited to the conditions to which they are exposed. Often this requires a protective coating to be applied to the material of choice. History shows however that our predecessors have often lacked the ability to predict the interaction of structures with their surroundings, and today we see deterioration of historic icons and the loss cultural relics that mark the development and achievements of humanity.

APPLICATION OF MÖSSBAUER SPECTROSCOPY:

The monitoring and evaluation of the corrosion performance of bridges and other steel structures have been extremely limited over the past 40 years. It may be considered that the serious corrosion and deterioration problems that are presently being experienced in steel and concrete bridges that are less than 25 years old, have resulted from the lack of knowledge of the performance of coated and uncoated structural steels and rebar in the adverse environments in which they are often located. Under the guidelines of the American Society for Testing and Materials, ASTM, and the International Organization for Standardization, ISO, it is common to evaluate the corrosion properties of steel, by exposing steel coupons at environmentally monitored test sites worldwide, for periods typically up to 30 years.

The test sites are classified as rural, industrial or marine according to their levels of the common airborne pollutants containing chlorides and sulfides [5]. The classification of corrosively of a test site is calculated by measuring the daily chloride and sulfide depositions as well as the time-of-wetness, which is defined as the time for which the relative humidity exceeds 80% [6]. At regular intervals, often starting at 1 year, some of the steel coupons are retrieved, the corrosion products removed, and the steel mass loss measured. Plots of mass-loss with exposure time permit the corrosion rates of the steels to be determined for their particular exposure site and its corrosivity classification.


Relative Intensity
1.10
1.08
1.06
1.04
1.02
1.00
0.98
0.96
-10
-5
0
5
10
Velocity (mm/s)
FeO
α-Fe
Fe2O3
A
Fe3O4
B2
B1



Atmospheric corrosion: protective corrosion coatings:

Structural steels can be separated into two main categories, carbon steel and alloyedsteel. Carbon steel must be used in situations where it is very well protected from exposure to both water and oxygen, and this is usually achieved by painting the clean bare surface. With time the coating will fail due to direct environmental exposure, or become porous and allow the steel beneath to corrode. For bridges, roadside guide-rails, and other large structures, this results in significant and regular repair, replacement and maintenance costs, as well as environmental problems with coating removal. If left uncoated in a normal atmospheric environment, carbon steel will corrode and the rust layer will peel from the substrate, exposing more steel to the atmosphere. The rust layer therefore offers very little protection to the carbon steel that continually loses mechanical strength and will eventually fail.

1. Explain the following;
    i) Basic principles of ESR
    ii) ESR spectrum hyperfine structure
2. What is Mossbauer effect? Explain the construction and working of Mossbauer spectrometer with suitable examples.
3. Write a note on ESR spectrum hyperfine structure
4. Write a note on Applications of ESR
5. Explain the construction and working of Mossbauer spectrometer with suitable examples.
6. Write about the high resolution ESR spectroscopy and its applications.
7. What is Mossbauer effect? Explain the following
    i) Chemical Isomer Shift
    ii) Magnetic hyperfine interaction
8. Explain the construction and working of high resolution ESR spectroscopy and its applications.
9. What is ESR spectroscopy and describe about it?
10. Explain the following, Magnetic hyperfine interaction and Electric quadrupole interaction
11. A Mossbauer nucleus ^{57}Fe makes the transition from the excited state of energy 14.4 keV to the ground state. What is recoil velocity?

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QUESTIONS	OPTION 1	OPTION 2	OPTION 3	OPTION 4	OPTION 5	OPTION 6	ANSWER
The origin of ESR lies in the ____	spin of the electron	spin of the nucleus	orbital motion of the ele	none of the above			spin of the electron
The orientation of the magnetic dipole with respect to the applied magnetic field are	not quantized	can be anything	quantized	in the direction of the applied field			quantized
The fact that the applied magnetic field tries to orient the magnetic moment of the elect	the magnetic moment to be c	the magnetic moment of th	the magnetic moment t	none of the above			the magnetic moment of the electron to precess around the applied magnetic field
The spin of the electron can have values _____	+1/2 only	-1/2 only	±1/2	None of the above			±1/2
The hyperfine structure of the ESR spectrum is due to	the interaction of the unpaire	interaction of the magnetic	interaction of the orbita	none of the above.			the interaction of the unpaired electron with the magnetic moments of nuclei within its orbital
The mechanism by which interaction occurs due to the unpaired electron density at the	spin-spin interaction	spin-lattice interaction	Fermi or Contact interac	None of the above			Fermi or Contact interaction
The phenomena concerned with nuclear resonant absorption and fluorescence is called	Mossbauer spectroscopy	ESR spectroscopy	NMR spectroscopy	NQR spectroscopy			Mossbauer spectroscopy
The daughter nuclei in the highly excited state, produced during a radioactive decay, con	visible photons	x-ray photons	γ-ray photons	none of the above			γ-ray photons
The high energy γ-ray photon emitted by a nuclear transition excites a nucleus in the gro	absorption	the recoil energy	instrument not sensitive	none of the above			the recoil energy
The recoilless absorption of the γ-ray photon is responsible for _____	ESR absorption	NMR absorption	Mossbauer effect	NQR absorption			Mossbauer effect
The strength of the resonant absorption is determined by the ________	overlap profile of the source	the peak of the absorption	the peak of the emissior	none of the above.			overlap profile of the source and absorber
The excited state of a nucleus has a mean life time of the order of ___	10^{-6} s	10^{-16}s	10^{-6} ms	10^{6} s			10^{-6} s
The highest energy for which a Mossbauer effect is known is _____	100 keV	187 keV	187 MeV	None of the above			187 keV
Mossbauer effect involves absorption of	x-rays	g-rays	UV rays	IR rays			g-rays
The detector normally used to detect Mossbauer spectrum is _____	PMT	Thermocouple	Scintillator	Klystron			Scintillator
In Mossbauer experiment if the environment of emitting and absorbing nuclei are differe	Isotope shift	Wave length shift	Isomer shift	None of the above			Isomer shift
The Isomer shift is due to the interaction between _____	the nuclear charge distributio	the nuclear quadrupole mc	the nuclear magnetic m	none of the above			the nuclear charge distribution and electron charge distribution
Unlike in the other branches of spectroscopy Mossbauer spectroscopy involves ____	Source-absorber pair	absorber alone	source alone	other samples			Source-absorber pair
Splitting of Mossbauer lines are due to the interaction between _____	nuclear quadrupole moment	nuclear magnetic moment	nuclear magnetic mome	none of the above			nuclear quadrupole moment and electric field gradient
The isomer shift in Mossbauer spectrum is a direct function of ___	p-electron density at the nucl	s-electron density at the nu	proton density in the nu	none of the above			s-electron density at the nucleus
The relative movement between the source and absorber in a Mossbauer spectroscopy	reduction in intensity	Doppler shift	Increase in intensity	None of the above			Doppler shift
Electron spin resonance is also known as ____	nuclear magnetic resonance	electron paramagnetic resc	nuclear quadrupole resc	none of the above			electron paramagnetic resonance
The magnetic moment of the electron is due to combined effect of ___	spin and charge	spin and mass	mass and charge	charge alone			spin and charge
The magnetic moment of the electron is given by $\mu_s = - g\mu_B S$, where g is	Lande g factor	Nuclear g factor	Electron g factor	None of the above			Electron g factor
The angular momentum due to spin and the magnetic moment are in ___	opposite directions	same directions	perpendicular to each o	any orientation			opposite directions
For an electron since S = ½, the value of m_s is ____	½	- ½	± ½	1			± ½
Spectrometers used for ESR studies in the frequency range of ~9.5 GHz are known as ___	Q-band spectrometers	X-band spectrometers	S-band spectrometers	None of the above			X-band spectrometers
Q band spectrometers are operated at frequencies of the order of ____	~9.5 GHz	~35 GHz	~9.5 MHz	~35 MHz			~35 GHz
The hyperfine Structure of ESR spectrum is due to ___	nuclear spin	electron spin	dipole-dipole interactior	none of the above			dipole-dipole interaction
ESR involves ________	absorption	emission	scattering	radiation			absorption