CLASS: I MSC PHYSICS

COURSE NAME: SPECTROSCOPY

COURSE CODE: 18PHP204

UNIT I

BATCH-2018-2020

SYLLABUS

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 Classical and Quantum theory of Raman effect - Rotation vibration Raman spectra of diatomic and polyatomic molecules – Applications - Laser Raman spectroscopy

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:



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.



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 farinfrared refers to the part that is closer to the microwave region.

Mid-infrared is the region between these two.

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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, at normal body temperature, radiatemost strongly in the infrared, at a wavelength of about 10 microns (Amicronis the term commonly used in a stronomy for a micrometer or no million the fame of the stronomy of the

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 be weaker 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

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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.







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.



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.

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POSSIBLE QUESTIONS

- 1. What is the basic principle of IR spectra?
- 2. Explain the construction and working of FTIR spectroscopy with suitable examples.

UNIT I

- 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.

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QUESTIONS

In normal atomic spectra ----- changes its orbit by absorbing radiation Transition from a lower to upper level causes An atom can absorb -----The principal gantum of the ground electronic state is A photographic record of a spectrum is called The spectral lines of hydrogen atom where the transitions end at n = 2 level, form The study of both frequency and intensity of spectral lines is known as ----For an energy level of principal quantum number n, the azimuthal quantum number can bay For principal quantum number n = 3, the values of azimuthal quantum number l are Hamiltonian of a system represents For any real physical system represented by a Shrodinger wave equation, the eigen values In the case of atomic spectra, the principal quantum numbers of two levels must be such that The splitting of spectral lines in the case of alkali metals was explained by considering For s orbital of electron the value of l is Zeeman effect is splitting of spectral lines in the presence of The decoupling of nuclear spin angular momentum vector I and the total angular momentun For normal Zeeman effect, there are ----- lines when observed parallel to the magnetic field The sodium D line is a member of -----Anomalous Zeeman effect occurs in atoms whose S is In normal zeeman effect, pi lines are -----Which of the spectral series of hydrogen atom does not show fine structure? Anomalous Zeeman effect occurs in the presense of a Hyperfine structure in atomic spectra is observed due to The intensity of a spectral line mainly depends on Hyperfine structure of rotational lines are due to The molecule with permanent electric or magnetic dipole moment absorb Stark modulation spectrometer is used to study In normal zeeman effect, there are ------ lines when observeed perpendicular to the magneti The decoupling of L and S vectors due to the application of very high magnetic field is caled The frequency of radiation absorbed due to rotational motion of molecules fall in the ---- reg The product eQq is known as The quantity eQ is known as the ----- of the nucleus The nuclear magneton (mu)N is ----- times the Bohr magneton (mu)B The angular momentum associated with the orbital quantum number L is given by The microwave region of the electromagnetic spectrum is between -----The criterion for absorption of microwave is that the molecule should possess For an asymmetric top molecule the moments of inertia are related as In the case of a diatomic rigid rotator, the separation between nearby rotational lines is

If the first line in a microwave absorption spectrum of a diaomic (rigid) rotator is observed at In the case of a diatomic rigid rotator, the energy difference between ground level and first r In the case of non-rigid diatomic rotator, the separation between adjacent spectral lines In the case of non-rigid diatomic rotator, the reason for the separation between adjacent ine The vibrational excitation during rotation causes

The molecular system where the moments of inertia are related as la not equal to lb not equ Nuclei with spin quantum number I ------ lack spherical symmetry

Pachen Back effect takes place in the presence of ----

When an atom with spin > placed in a weak magentic field, the spectral lines are split into m A prolate symmetric top molecule has the relation between their moments of inertia as

When an atom of Carbon dioxide which does not possess a permanent dipole moment and h

A molecule whose moments of inertia are related as Ia = Ib > Ic is called

Rotation about the bond axis of a hetero nuclear diatomic molecule

The quantity which measures the deviation in the charge distribution in the nucleus from spl The magnitude of the asymmetrical electric field surrounding the nucleus, due to electrons i: The charge distribution in a nucleus with spin = 1/2 is

When an atom with total angular momentum J is placed in a magnetic field, the magnetic qu The rotational selection rule is

Out of the three types of energy of a molecule, the lowest energy is due to ----

The total angular momentum of an atom is a vector sum of the ----

Which of the following statements is not correct?

When the applied magnetic field is increased, the frequency of precession of the J vector arc

OPTION 1	OPTION 2	OPTION 3	OPTION 4
Valence electrons	electron in the inner orbit	nucleus	proton
	absorption of radiation	Scattering of radiation	
any amount of energy	only energy equal to the dif	i only energy less than the	only energy greater tha
		-1	
spectrogram	spectrograph Dreaket earlies	spectrometer	spectroscope
Lymann series	Bracket series	Prund series	Baimer series
spectroscopy	spectral study	spectrophotometry	spectrography
n+1 values	n-1 values	n values	n ² values
1,2,3,4	-3,-2,0,1,2,3	0,1,2	1,3,5,7
total energy of the system	only kinetic energy of the sy	only potential energy of t	none of the above
must be real and positive	can be complex but positive	can be real but negative	can be anything
they follow the selection rule of	I they follow the selection rul	they follow the selection	dn may be any positive
orbital motion of the electron	spin of the electron	spin of the atom	spin of the nucleus
0	1	2	3
electric field	magnetic field	electric and magnetif fiel	none of the above
Pachen Back effect	Back-Goudsmit effect	Stark effect	Anomalous Zeeman eff
2	3	5	A large number of lines
the principal siries	the diffuse series	the sharp series	the fundamental series
greater than 1/2	equal to zero	less than zero	greater than zero
polarized in the direction of the	polarized perpendicular to t	circularly polarized	non-polarized
Balmer series	Bracket series	Pfund series	Lymann series
strong magnetic field	electric field	weak magnetic field	both electric and magne
spin of the electron	spin of the nucleus	presence of isotope	temperature
number of electron in the aton	the atomic number of the el	the atomic mass of the e	I the number of atoms in
nuclear quadrupole moment	rotaion of the molecule	rotation of the atom	dipole moment
infrared radiation	microwave radiation	UV radiation	radio waves
IR spectrum	microwave spectrum	Raman spectrum	Fluorescence
2	3	4	0
Pachen Back effect	Stern Gerlach effect	Stark effect	Back-Goudsmith effect
IR	UV	X-ray	Microwave
electric dipole moment	magnetic dipole moment	Quadrupole coupling con	total magnetic moment
guadrupole moment	electric dipole moment	electric field strength	Magnetic field strength
1836	1/1836	2	none of the above
L	L(L+1)	L(L+1)*h/(2pi)	[L(L+1)h/(2pi)}^1/2
1 mm and 300 mm	1mm and 30 mm	400 cm and 1200 cm	300 mm to 900 mm

either a permanent electric or ra permanent electric dipole a permanent magnetic di none of the above

la = lb = lc	la = lb not equal to lc	la not equal to lb = lc	Ia not equal to Ib not ec
В	3B	2B	4B
4B	6B	8B	10B
2B	4B	6B	8B
increases with increasing J	decreasing with increasing J	remains the same	can be either increasing
increasing bond length during	due to reduction in speed or	due to decreasing bond l	none of the above
increasing in B	reduction of B	no change	can either increase or d
symmetric top	asymmetric top	linear	spherical top
> 1	> 0	= 1	> 1/2
very high electric field	very high magnetic field	weak electric field	weak magnetic field
Pachen Back effect	Back-Goudsmit effect	Anomalous zeeman effect	normal zeeman effect
la < lb = lc	la = lb < lc	la > lb = lc	la = lb > lc
it shows rotational spectrum	it does not show rotational	it may or may not show r	none of the above
oblate symmetric top	prolate symmetric top	oblate asymmetric top	none of the above
gives rotation spectrum	gives no rotation spectrum	gives some weak lines	none of the above
electric dipole moment	magnetic dipole moment	nuclear quadrupole mor	none of the above
electric field gradient	magnetic field gradient	electric quadrupole mom	nuclear quadrupole mo
non-spherical	prolate	oblate	spherical
2J+1	J	J+1	J-1
dJ = + or - 1	dJ = 0, +1 or -1	dJ = 0	dJ = 0, +1, -1, +2, -2,
vibration of the molecule	electronic transition of the r	rotation of the molecule	none of the above
orbital angular momentum of t	orbital angular momentum	orbital angular momentu	spin angular momentun
The robital angular momentum	S precesses around L	J and the nuclear spin an	F precesses around I
increases	decreases	remains the same	increases and then decr

ANSWER

	Valence electrons
	absorption of radiation
n the difference between two levels	only energy equal to the difference between two levels
	1
	spectrograph
	Balmer series
	spectrophotometry
	n values
	0,1,2
	total energy of the system
	must be real and positive
integer	dn may be any positive integer
	spin of the electron
	0
	magnetic field
ect	Pachen Back effect
	2
	the principal siries
	greater than zero
	polarized in the direction of the applied field
	Lymann series
etic field	weak magnetic field
	spin of the nucleus
the initial energy level	the number of atoms in the initial energy level
57	nuclear quadrupole moment
	microwave radiation
	microwave spectrum
	3
	Pachen Back effect
	Microwaye
	Quadrupole coupling constant
	quadrupole moment
	1/1836
	$[1/(1+1)b/(2ni)]^{1/2}$
	1 mm and $30 mm$
	either a permanent electric or magnetic dipole moment
	entrer a permanent electric or magnetic alpole moment

jual to lb	la not equal to lb not equal to lb
	2B
	8B
	6B
; or decreasing	decreasing with increasing J
	increasing bond length during rotation due to centrifugal force
ecrease B	reduction of B
	asymmetric top
	> 1/2
	very high magnetic field
	Anomalous zeeman effect
	la < lb = lc
	it does not show rotational spectrum
	prolate symmetric top
	gives no rotation spectrum
	nuclear quadrupole moment
ment	electric field gradient
	non-spherical
	2J+1
	dJ = + or - 1
	rotation of the molecule
n of the electron and the spin angular n	r orbital angular momentum of the electron, spin angular moment
	F precesses around I
reases	increases

:um of the electron and the spin angular momentum of the nucleus

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SYLLABUS

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

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 H , H , H , and H . This is the spectrum of Balmer series for Hydrogen.

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

Hydrogen Spectrum Diagram



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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

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longest wavelength of 656.3 nm is designated to H and followed by next wavelength of 486.3 nm which was designated to H. 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.

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

Where **R** is Rydberg constant with a value of 1.097×107 per meter and n = 3,4,5,... The H line corresponds to n = 3 and then H line to n = 4 and so on. The series limit corresponds to n = -3 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,

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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:

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

The precession angular velocity (Larmor frequency) is

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

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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.

$$\begin{split} \omega_{electron\,spin} &= \frac{2\mu_e B}{\hbar} = \frac{2 \cdot 2 \cdot \frac{1}{2} (5.79 \times 10^{-5} eV / T) (1T)}{6.58 \times 10^{-16} eV \cdot s} = 1.7608 \times 10^{11} s^{-1} \\ v &= \frac{\omega}{2\pi} = 28.025 \, GHz \quad Larmor \, frequency \\ \omega_{proton\,spin} &= \frac{2\mu_p B}{\hbar} = \frac{2(2.79)(3.15 \times 10^{-8} eV / T) (1T)}{6.58 \times 10^{-16} eV \cdot s} = 2.6753 \times 10^8 s^{-1} \\ v &= \frac{\omega}{2\pi} = 42.5781 \, MHz \quad Larmor\, frequency \end{split}$$

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.

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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.

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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 1/4 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.



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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.



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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).

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POSSIBLE QUESTIONS

- 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.

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QUESTIONS

UNIT - II

Change in electric dipole moment during vibration gives rise to absorption in Water molecule has ---- number of modes of vibraiton Raman scattering occurs due to ---- of molecule Glass is unsuitable as a lens for IR studies due to its ----Mutual exclusion principle of Raman and IR spectra is applicable for Which of the following spectra is independent of the exciting frequency Hot bands are IR absorption involving vibrational levels ----Unlike in the case of other branches of spectroscopy, Raman spectroscopy is a ---- process For a linear molecule the relation between the moments of intertia is The lines with frequency more than that of the exciting line in Raman spectra are called Virtual energy level concept is used to explain When the virtual energy levels coincide with actual enregy level it is called IR spectroscopy involves Out of the three types of energies of a molecule, rotational, vibrational and electronic, the lc The most accurate method of determination of inter-nuclear distance, and bond angles in m Pure rotational raman lines can be observed only in In IR spectra, the first overtone lines are due to transition from In the case of rotational raman spectra the selection rule dJ = 0 refers to IR and Raman spectroscopy are said to be ----- to each other Raman spectroscopy is due to -----Which of the following statements is not true? Classical theoretical expalnation of Raman effect could not explain Polarizability tensor has ----- components Even though polarizability is a tensor of nine components, there are only ----- independent c In the case of anti Stokes Raman scattering Zero point energy is the energy possessed by the molecule when it is in the Nernst Glower is normally used as a source of The number of vibrational modes for a linear molecule is A grating is uses the phenomenon of ----- to split the spectral lines into different frequencies Rocksalt prisms are used to study When two different frequencies of laser are used to study raman spectrum of a sample, it w The vibrational energy of a molecule when it is in the lowest vibrational level is known as The value of the zero point energy is ----- where n0 is the frequency of the fundamental moc The vibrational transition between v=0 to v=1 isknown as In the case of carbon dioxide, symmetric stretching is Resonance raman scattering occurs when Far infrared region ranges from When vibrational quantum number increases, the separation between vibrational levels

In vibration-rotation IR spectra, the selection rule for P-branch of lines is The raman lines with frequency less than the exciting frequency are known as Polarized raman spectra can be given by In IR absorption spectra, the region between ------ is called as finger print region In the case of water molecule all the three modes of vibrations are FTIR is normally used to study Laser used for Raman studies mainly due to its Conventional spectroscopy, where intensity is recorded with frquency is called Most common method of sample handling method for IR studies of solids is Thermocouple is used as detector in ----- spectrometer The most common detector in a laser Raman spectrometer is -----In FTIR technique, normally, the signal is converted from -----Most intense IR absorption line is the one originating from v = The anhamonicity of vibration of a diatomic molecule is due to The virtual energy level in the case of Raman spectra is -----Rayleigh scattering is In Raman spectra, anti-Stokes lines are The stokes lines of Raman spectra are Raman spectra can be obtained from In the case of molecules of centre of symmetry, the Raman active modes are not IR active ar The polarisability ellipsoid of a linear molecule is The branch of rotational IR lines with selection rule dJ = 0 is called Raman effect supports In Raman spectrum, if λ is the wavelength of incident radiation, then the Anti-Stoke's lines w Sun appears red at sun rise and sunset. This is due to scattering of In Raman spectrum, if λ is the wavelength of incident radiation, then the Stoke's lines will ha Tyndall effect is the scattering of the light by In 1928, Sir C.V. Raman was studying the Coefficient of scattering of light in any medium is inversely proportional to the fourth power Raman lines had frequencies lower than that of the incident line are called Raman lines had frequencies higher than that of the incident line are called Low frequency side and high frequency side Raman lines are referred to as In Rayleigh scattering, there is a change in the intensity of the scattered light, there is no cha Rayleigh scattering is also called Light from a helium discharge tube filtered by nickel oxide glass gives a light of wavelength The apparatus used in the study of Raman effect in liquids was first designed by Raman got nobel prize in The modified frequencies observed in the scattering process was given the name Quinine sulphate solution contained in a novial glass vessel is used as a filter to obtain the lir Which filter is found to be a very satisfactory to get 4046Å The mercury arc is placed as close to the Raman tube as possible, which results in a large Which reflector is used to enhance the intensity of illumination still further The chief features of a spectrograph, suited for the study of Raman spectra are The recording of the complete spectrum may require up to ten to fifteen hours, depending li Which is available as transparent blocks Which of the following substance does not require container for the excitation of Raman effe Raman effect can be obtained with solids which are in the form of loose crystal powders was A special type of spectrograph with two parts, each part having a prism and two lenses with In the case of gases, the intensity of the light scattered is normally In the case of gases, wood employed a very long tube of

Who was the first to develop the technique of exciting Raman effect in gases under high pre Rosetti was able to obtain the Raman spectra of several gases under pressure with the Bhagavantam has constructed a Raman tube for gases which can stand pressures upto Who obtained good spectrographs of Raman spectra of gases using the 3650Å,4046Å & 4358 Raman effect has been observed & studied in

With benzene, the frequency shifts of the Raman lines correspond to an infra-red wavelengt In absorption spectrum, benzene exhibits a

The triad of stokes and antistokes lines equally spaced on either side of the exciting 4358Å li What bands are found in well purified water

Solutions of salts in water give Raman spectra characteristic of the

The frequency shift of the Raman line of HCl gas corresponds to

Which shows the frequency shift equal to the frequency of Infra-red bands

Which of the following gas shows a frequency shift equal to the frequency difference of two

The Raman lines obtained with crystals are sharp, becoming diffuse with rise of

The two lines exist nearest to the exciting line have been identified with the oscillations of the Diamond exhibits a

All the Raman lines move inward towards the parent line with

The variations in intensity are of great significance in the study of

Which is used to separate the vertical and horizontal components in the scattered light

Crystalline quartz should not be used for

Menzies has investigated the polarisation of the Raman lines in

For the vibrational Raman lines, the depolarisation factor varies from

A simple and satisfactory explanation on the quantum theory was put forwar by

Which would result in the appearance of the unmodified line in the scattered beam

The frequency shift is the

Raman spectra are determined by

Carbon dioxide has two very strong bands in the infra-red absorption spectrum at

Nitrous oxide molecule has the same number of electrons as

The band at 589cm-1 has not been recorded in the Raman spectrum of nitrous oxide due to nitrous oxide has a

According to theory, all triatomic molecules of bent symmetrical structure should give rise to Depolarization factor is the ratio of the

The natural frequency of vibration is given by

OPTION 1	OPTION 2	OPTION 3	OPTION 4
visible spectrum	NMR spectrum	IR spectrum	microwave spectrum
9	4	3	5
change in dipole moment	change in polarizability	change in magnetic dipol	change in quadrupole o
hardness	transmittence	dispersion	absorption
symmetric top molecules	asymmetric top molecules	molecules with centre of	diatomic molecules
Raman	IR	Microwave	Electronic spectra
v =0 to v = 1	v = 0 to v = 2	v = 1 to higher values of v	v = 1 to v = 2 only
scattering	absorption	emission	Fluorescence
la=lb=lc	la=0, lb=lc not equal to 0	la < lb < lc	la > lb > lc
Stokes lines	Rayleigh lines	antistokes lines	compton lines
IR absorption	Raman scattering	microwave absorption	none of the above
resonance raman scattering	inverse raman scattering	surface enhanced raman	none of the above
absorption	emission	scattering	stimulated emision
electronic	rotational	vibrational	vibrational-rotational
IR	Raman	Microwave	UV
heavy molecules	light polyatomic molecules	heavy polyatomic molect	light diatomic molecule
v=0 to v=2	v=1 to v=2	v=0 to v=1	v=0 to v=3
antistokes lines	stokes lines	both a and b	Rayleigh lines
complementary	opposite	repetition	inverse
change in dipole moment	change in polarizability	change in magnetic dipol	none of the above
Raman scattering cannot be ex	Microwave spectroscopy is	IR spectroscopy is an abs	Raman scattering is a sc
rotational raman lines	vibrational raman lines	rotation-vibration structu	intensity of stokes and រ
7	3	9	5
6	8	3	7
energy is absorbed by the mole	energy is given by the mole	c both photon and molecu	l no energy transfer
lowest vibrational level	lowest rotational level	lowest electronic level	none of the above
Microwave radiation	IR radiation	Raman spectrum	UV spectrum
3N-6	3N-5	3N-3	3N
reflection	total internal reflection	diffraction	interference
UV spectrum	IR spectrum	microwave spectrum	Electronic spectrum
these lines are not due to rama	a these lines are also part of r	these lines are IR lines	none of the above
potential energy	zero point energy	knetic energy	none of the above
1/2 n0	n0	2n0	1/4 n0
fundamental	first overtone	second overtone	hot band
raman active & IR inactive	raman active and IR active	raman inactive and IR act	raman inactive and IR ir

rotational level coincides with velectronic level coincides wi virtual energy level coincinone of the above

4000 to 400 cm^-1	400 to 50 cm^-1	12500 to 4000 cm^-1	none of the above
increases	decreases	nemains the same	none of the above
dJ=+1	dJ=-1	0=Lp	dJ=+ or -1
Rayleigh lines	stokes lines	antistokes lines	resonance lines
single crystals only	liquids only	powder samples only	both single crystals and
less than 900 cm^-1	between 900 and 1450 cm^.	1450 to 5000 cm^-1	above 5000 cm^-1
IR and Raman active	IR active and Raman inactive	IR inactive and Raman ac	IR inactive and Raman i
far infrared spectrum	near IR spectrum	middle IR spectrum	all the above
coherence	high intensity	monochromaticity	directionality
time domain spectroscopy	frequency domain spectrosc	intensity spectroscopy	none of the above
pellet technique	mull technique	thin film technique	none of the above
Raman	Microwave	IR	NMR
bolometer	thermocouple	photographic film	photomultiplier tube
time domail to frequency doma	frequency domain to time d	frequency to intensity	none of the above
1	2	0	3
rigid nature of the bond	non-rigid nature of the bond	due to the charge of the	due to the mass of the a
characteristic of the molecule	a combined effect of the mo	depends only on the incid	none of the above
inelastic process	elastic process	collision process	none of the above
red shifted	blue shifted	no change	can be either red shifte
red shifted	blue shifted	no change	can be either red shifte
solids only	liquids only	gases only	solids, liquids and gases
Pauli's exclusion principle	Frank Condon principle	Mutual exclusion principl	none of the above
elliptical	spherical	ellipsoid	none of the above
O branch	P branch	R branch	S branch
corpuscular theory	wave theory	quantum theory	electromagnetic theory
λ	$\lambda + \Lambda \lambda$	λ - Λλ	λ2
longer wavelengths	shorter wavelengths	lower frequencies	all frequencies
λ	$\lambda + \Lambda \lambda$	λ - Λλ	λ2
air particles	solid particles	liquid particles	colloidal particles
diffraction of light	interference	scattering of light	reflection of light
wavelength of light	frequency of light	velocity of light	none of these
stokes lines	antistokes lines	both a and b	excitation line
stokes lines	antistokes lines	both a and b	excitation line
stokes lines	antistokes lines	stokes and antistokes line	unmodified line
spectral character	wavelength	frequency	all the above
incoherent scattering	coherent scattering	diffraction	compton scattering
3880Å	3888Å	3800Å	4888Å
Wood	Ravleigh	Raman	Newton
1939	1932	1931	1930
Compton effect	Raman effect	Scattering effect	Ravleigh scattering
4350Å	4340Δ	4300Å	4358Å
a solution of iodine in carbon to	quinine sulphate solution	nickel oxide glass	Conner oxide
intensity of the incident light	frequency of incident light	wavelength of the incider	velocity of the incident
semi-cylindrical aluminium		alace	none of these
large light gathering power	special prisms of high resolu	a short focus camera	all the above
intensity of the incident light	the special prisitis of fight resolv	the intrinsic brilliance of t	all the above
	une speed of the spectrograp		honzono
gypsum	quartz	a & u a & h	bonzono
Boor & Monzios	yuai 12 Apanthakrishnan	a & U Dillroth Kohlrousch & Doi	Paman
Daer & Manzies	Ananthakrishnan	Dimouri, Normausch & Kel	Nailidii
Daer & IVIENZIES	Ananthakrishnan	Billroth, Konirausch & Rei	Kaman

verv weak	verv strong	medium strong	weak
, Calcite	Benzene	carbon tetrachloride	HCL gas
Baer & Menzies	Ananthakrishnan	Rosetti	Raman
2500Å line	2537Å line	2530Å line	2535Å line
30 atmospheres	40 atmospheres	50 atmospheres	60 atmospheres
Baer & Menzies	Ananthakrishnan	Bhagavantam	Raman
solids	liquids	gases	all the above
3μ	3.27µ	- 3.5μ	4μ
weak band	medium strong band	strong band	sharp band
Calcite	Benzene	carbon tetrachloride	HCL gas
two broad bands	one broad band	sharp band	weak band
only salts	only water	both salts and water	either salts or water
3μ	3.27μ	3.46μ	4μ
HCI	carbondioxide	carbonmonoxide	oxygen
HCI	carbondioxide	carbonmonoxide	oxygen
intensity of the incident light	frequency	velocity	temperature
calcite	diamond	HCI	water
broad line	very strong line	very sharp line	strong and sharp line
decrease of temperature	increase of temperature	increase of intensity	decrease of intensity
molecular structure	chemical constitution	shape and size	both a and b
quartz crystal	calcite	double image prism	suitably oriented double
condenser	spectrographs	windows	all the above
solids	liquids	gases	all the above
0 to 0.86	0 to 0.70	0 to 0.80	0 to 0.60
Sir C.V.Raman	Prof.Smekal	Rayleigh	Bhagavantam
The photon without absorbing	absorb part of the energy of	molecule imparts some c	all the above
difference between stokes and	difference between the inci	addition between the inc	any of the above
the number of atoms in the mo	the masses of the atoms	the strength of the chem	all the above
668 and 2349 cm-1	600 and 3349 cm-1	700 and 2349 cm-1	668 and 2900 cm-1
CO2	CO	water	carbon disulphide
weak frequency	weak intensity	strong intensity	strong frequency
unsymmetrical structure	symmetrical structure	center of symmetry	either a or b
two Raman lines	one Raman lines	no Raman lines	three Raman lines
Frequencies of the vertical and Frequencies of the horizont. Intensities of the horizon Intensities of the vertical			Intensities of the vertica
v=1/2π(F)^1/2	v=1/2π(F/μ)^1/2	v=(F/µ)^1/2	v=1/2π(μ/F)^1/2

OPTION 5	OPTION 6	ANSWER
		IR spectrum
		3
ment		change in polarizability
		absorption
		molecules with centre of symmetry
		Raman
		v = 1 to higher values of v
		scattering
		la=0, lb=lc not equal to 0
		antistokes lines
		Raman scattering
		resonance raman scattering
		absorption
		electronic
		IR
S		light diatomic molecules
		v=0 to v=2
		Rayleigh lines
		complementary
		change in polarizability
attering process	;	Raman scattering cannot be excited by any frequency
antistokes lines		intensity of stokes and antistokes lines
		9
		6
		energy is given by the molecule to the photon
		lowest vibrational level
		IR radiation
		3N-5
		diffraction
		IR spectrum
		these lines are not due to raman scattering
		zero point energy
		1/2 n0
		fundamental
nactive		raman active & IR inactive
		virtual energy level coincides with original level

	4000 4 400 4 4
	4000 to 400 cm^-1
	Increases
	dJ=+1
	Rayleigh lines
powder samples	single crystals only
	between 900 and 1450 cm^-1
nactive	IR and Raman active
	far infrared spectrum
	middle IR spectrum
	high intensity
	pellet technique
	IR
	photomultiplier tube
	time domail to frequency domain
	0
atoms	rigid nature of the bond
	characteristic of the molecule
	inelastic process
d or blue shifted	red shifted
d or blue shifted	red shifted
i	solids, liquids and gases
	Mutual exclusion principle
	spherical
	Q branch
	quantum theory
	λ - Δλ
	shorter wavelengths
	$\lambda + \Delta \lambda$
	colloidal particles
	scattering of light
	wavelength of light
	stokes lines
	antistokes lines
	stokes and antistokes lines respectively
	all the above
	coherent scattering
	3888Å
	Wood
	1930
	Raman effect
	1258Å
	a solution of iodine in carbon tetrachloride
light	intensity of the incident light
light	somi cylindrical aluminium
	all the above
	all the above
	a & b a & b
	a x u Poor & Monzies
	Billroth,Konirausch & Reitz

	very weak
	HCL gas
	Rosetti
	2537Å line
	50 atmospheres
	Bhagavantam
	all the above
	3.27μ
	strong band
	carbon tetrachloride
	two broad bands
	both salts and water
	3.46μ
	carbonmonoxide
	carbondioxide
	temperature
	calcite
	strong and sharp line
	increase of temperature
	both a and b
e image prism	suitably oriented double image prism
	all the above
	liquids
	0 to 0.86
	Prof.Smekal
	The photon without absorbing energy
	difference between the incident and scattered lines
	all the above
	668 and 2349 cm-1
	CO2
	weak intensity
	unsymmetrical structure
	three Raman lines
al and horizontal components	Intensities of the horizontal and vertical components
	v=1/2π(F/μ)^1/2
UNIT III

CLASS: I MSC PHYSICS

COURSE NAME: SPECTROSCOPY

COURSE CODE: 18PHP204

BATCH-2018-2020

SYLLABUS

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 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.

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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 = 0

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. 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

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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.



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 Ekin = 12. Mv2 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

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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 L(R) = /li(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 reemission 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

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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

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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,

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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

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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.

POSSIBLE QUESTIONS

- 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 $\mu_B = 9.274 \times 10^{-24} \text{ JT}^{-1}$.
- 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 PHYSICS SPECTROSCOPY (17PHP204) MULTIPLE CHOICE QUESTIONS

QUESTIONS

The diagram representing the relation between the inter-nuclear distance and energy is calle In the case of microwave spectroscopy, the absorption takes place due to interaction betwee The source of microwave radiation in microwave spectroscopy is normally In a spectrometer, the devise used to split the spectral lines into its component frequencies The most commonly used and most efficient monochromator is a spectrometer is The Morse curve depicts the variation of Which of the following statements is correct? Electronic spectra is given by The change in vibrational quantum numbe accompanying an electronic transition In fluorescence, the frequency of emitted radiation is ----- that of incident radiation The emission of radiation which may last for some time even after the removal of the excitat During electronic transition in a molecule the radiation normally fall in the The condition for a molecule to give electronic spectra is Electronic spectra may contain During an electronic transtion, the internuclear distance remains the same. This is called The intensity distribution of vibrational lines of electronic spectra is given by using The absorption and emission energy in the range 10 to about 10000 angstrom is restricted to The group of lines resulting from transitions between the different rotational levels in two vi The time required for electronic transitions is about The sum of all bands for transitions between two electronic levels is termed as During electronic transtions the internuclear distance The P and R branches of spectral lines are represented by a diagram called For all electronic levels for which the electrons are paired, the spin is ----- and multiplicity is -In triplet state, the probability of two electrons occuppying same state is If during a spectral emission, the electron undergoing the transition does not change its spin The emission process in which the electron taking part in the emission undergoes a change i The process in which there occurs a delay between absorption and emission, but no change Emission is a spontaneous process, generally, and absorption is a ----The diagram representing transitions between the various electronic and vibraitonal states v In any non-degenerate molecular orbital, only two electrons of opposite spin can be accomm The study of the physical and chemical properties of electronically excited atoms and molecu Which of the following statements is correct? Some of the electronically excited states undego Fluorescence is a process in which the electron -----The principle involved in scintillators is Fluorescence emission is a ----- process The process in which absorbed radiation is not emitted as radiation is called The electronic spectra fall within the range

Frank Condon principle states that during an electronic transition, the internucluear distance

The triplet state is always ----- in energy than the corresponding state

The electronic transition is spin forbidden, if the initial and final states have

At very low pressures in the vapour phase, the electronically excited molecules may not sufficient parabola represents ----- , represented by v - m plot

If a molecule is excited to some vibrational level of S1 state under high pressure, the initially The difference in position of maximum of emission and of zero-zero transition on an energy

OPTION 1	OPTION 2	OPTION 3	OPTION 4
en			
Morse curve	frequency spectrum	modulation curve	none of the above
electric vector of the radiation	magnetic vector and the ele	electric vector of the radi	none of the above
laser	mercury vapour lap	sodium vapour lamp	klystron
divider	selector	monochromator	recorder
prism	lens	diffraction grating	none of the above
internuclear distance with ener	energy with internuclear dis	vibraitonal energy with ir	none of the above
In a molecule, each electronic l	In a molecule, each vibration	In a molecule, each electi	In a molecule, each rota
all molecules	only molecules with electric	only molecules with mag	only molecules with bot
has selection rule dv=0	has a selection rule dv = + or	has selection rule dv=0, +	is not governed by any :
higher than	lower than	same as	higher or lower than
coherence	resonance	fluorescence	phosphorescence
visible region	IR region	Microwave region	UV region
it should possess permanent el	it sould possess permanent	it should possess both pe	there is no such condition
vibrational and rotational struc	only vibrational structure	only rotational structure	no such components
mutual exclusion principle	Frank Condon principle	Deslander's principle	none of the above
Deslander's table	Frank Condon principle	Population consideration	none of the above
electronic energy	vibrational energy	rotational enegy	translational energy
band	spectrum	spectral lines	none of the above
10^-16 seconds	10^-14 seconds	10^-16 milliseconds	A few seconds
band origin	band system	band head	band lines
increases	decreases	remains the same	none of the above
condon parabola	Fortrat parabola	Morse curve	none of the above
1 and 0	0 and 1	0 and 0	1 and 1
0	1	0.5	0.75
fluorescence	phosphorescence	scattering	raman shift
fluorescence	phosphorescence	delayed fluorescence	none of the above
fluorescence	phosphorescence	delayed fluorescence	raman shift
stimulated	spontaneous	scattering	none of the above
Fortrat parabola	Condon parabola	Morse curve	Jablonski diagram
Pauli's exclusion principle	Frank Condon principle	Mutual exclusion principl	none of the above
Physical chemistry	photochemistry	photonics	electrolysis
All electronically excited states	All electronicaly excited stat	None of the electronically	All electronically excited
relaxation	absorption	scattering	collision
emits energy as radiation and o	emits energy as radiation an	does not emit energy as r	does not emit energy as
phosphorescence	fluorescence	delayed fluorescence	ionisation
stimulated	scattering	spontaneous	none of the above

spontaneous emission 10 to 10000 asgstrom changes higher same multiplicity normal fluorescence The P and R branches normal fluorescence Stokes loss

stimulated emission 4000 to 12500 angstrom does not change equal different multiplicity delayed fluorescence P branche only delayed fluorescence anti stokes loss

scattering 50 to 400 cm^-1 becomes double lower less multiplicity resonance fluorescence phosphorescence R branch only resonance fluorescence phosphorescence collision loss

non-radiative transfer none of the above becomes half none of the above none of the above S branch only none of the above

OPTION 5 OPTION 6	ANSWER
	Morse curve electric vector of the radiation and magnetic dipole moment klystron monochromator
	diffraction grating
	vibraitonal energy with internuclear distance
ational level contains many vib	rational kin a molecule, each electronic level contains many vibrational lev
th electric and magnetic mome	nts all molecules
selection rule	is not governed by any selection rule
	lower than
	phosphorescence
	visible region
on	there is no such condition
	vibrational and rotational structure
	Frank Condon principle
	Frank Condon principle
	electronic energy
	band
	10^-16 seconds
	band system
	remains the same
	Fortrat parabola
	0 and 1
	0
	fluorescence
	phosphorescence
	delayed fluorescence
	stimulated
	Jablonski diagram
	Pauli's exclusion principle
	Physical chemistry
d states undergo stimulated er	nission All electronicaly excited states do not give rise to observable emi relaxation
s radiation and does not under	go chang emits energy as radiation and does not undego change in spin fluorescence
	spontaneous

non-radiative transfer 10 to 10000 asgstrom does not change lower different multiplicity normal fluorescence The P and R branches normal fluorescence anti stokes loss 'els and each vibrational level contains many rotational levels

ssion

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COURSE NAME: SPECTROSCOPY

COURSE CODE: 18PHP204

UNIT IV BATCH-202

BATCH-2018-2020

SYLLABUS

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

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. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), 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.

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The following features lead to the NMR phenomenon:

- 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 (\mathbf{T}). The earth's magnetic field is not constant, but is approximately 10-

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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 (E) 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 $\mu = 2.7927$, 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: $1H \mu = 2.7927$, $19F \mu = 2.6273$, $31P \mu = 1.1305 \& 13C \mu = 0.7022$. These moments are in nuclear magnetos, which are $5.05078 \cdot 10.27$ 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 = $6.626069 \cdot 10.34$ Js).

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

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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.

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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

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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.



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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, (CH₃)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 ref is the resonant frequency of the reference signal and samp is the frequency of the sample signal. This operation gives a locator number called the **Chemical Shift**, having units of parts-permillion (ppm), and designated by the symbol Chemical shifts for all the compounds in the original display will be presented by a third click on the diagram.

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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, CCl₄ 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

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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



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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 $\frac{1}{2}$ is spherical, such nuclei will have no electric quadrupole moment.

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POSSIBLE QUESTIONS

- 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 ¹⁴N 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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QUESTIONS

For sample to be NMR active, the spin of the nucleus must be In the super-regenerative NQR spectrometer, the oscillations are -----The NMR and NQR frequencies fall in the In NQR experiment, the frequency of the input radiation must be NQR is observed normally in Nucei having ----- due to their spin, exhibit NMR spectrum For nuclei with mass number odd and atomic number even or odd, the spin is In NQR the energy levels are ----- in nature In the equation for nuclear magnetic moment (mu)N = gamma*Ih*2pi, gamma is known as In NMR, resonance condition can be obtianed by The condition in which there is no net absorption or emission in the case of NMR is caled The condition of saturation occurs when The condition of saturation is never reached due to the process called The process in which energy of the excited nucleus is transferred to another nucleus is callec The relaxation process is In spin-spin relaxation, the energy of the excited nucleus is transferred to The frequency of precession of the total angular momentum vector around the applied mag Spin lattice relaxation is Spin-spin relaxation is NQR is a branch of ----- frequency spectroscopy which is closely related to NMR In NQR spectroscopy, In NQR spectroscopy, the absorption takes place in the In NQR spectroscopy In NQR, different energy levels are caused due to the interaction between In NQR, the energy levels are ----- in nature and the transitions are ----- type In NMR, the energy levels are ----- in nature, and the transitions are ----- type The ESR spectrum falls in the ESR is observed only in species having The magnetic moment of the electron is due to its For molecules with even atomic number and mass number, has nuclear spin For molecules with odd atomic number and even mass number, the nuclear spin is The resonance condition in NMR is In the relation $hv = g_N \mu_N B_{0,g_N}$ is known as ____ In the relation $hv = g_N \mu_N B_0$, μ_N is known as _____

In both NMR and NQR absorption of radiation takes place only if _____ is achieved

OPTION 1	OPTION 2	OPTION 3	OPTION 4
equal to zero	equal to $1/2$	equal to + or - 1	greater than 1/2
insignificant	quenched	non quenched	significant
radio fraguoneu region	visible region	IIV region	microwayo rogion
fixed	visible region	ov region	none of the above
		liquid anhu	in all the three
	gas only		in all the three
magnetic moments	electric dipole moment	electron spin	none of the above
zero	nalt integer	integer	can be anything
both electrical and megnetic	electrical	magnetic	none of these
nuclear quadrupole moment	electric dipole moment	gyromagnetic ratio	none of the above
eiher fixed magnetic field and	only by fixed magnetic field	only fixed frequency and	by varying both magnet
resonance	relaxation	saturation	none of the above
the number of molecules in th	ethe number of molecules in	the number of molecules	none of the above
relaxation	saturation	radiative transfer	non radiative transfer
spin-spin relaxation	spin-lattice relaxation	excitation	absorption
stimulated	spontaneous	absorption	none of the above
another nucleus	electron	lattice of the crystal	none of the above
resonance frequency	emission frequency	Larmour frequency	none of the above
transverse	longitudinal	parallel	none of the above
transverse	longitudinal	parallel	none of the above
radio frequency	UV frequency	Microwave frequency	visible frequency
an external magnetic field is ap	o an external electric field is a	no external field is applie	external magnetic or ele
UV region	IR region	RF region	none of the above
frequency of the radiation has	frequency of the radiation h	external magnetic field is	both magnetic field and
the nuclear quadrupole mome	r the electric field gradient ar	the nuclear quadrupole r	none of the above
electrical and magnetic	magnetic and electric	electric and electric	magnetic and magnetic
electrical and magnetic	magnetic and electric	electric and electric	magnetic and magnetic
microwave region	rf region	UV region	IR region
paired electrons	one or more unpaired elected	nuclear quadrupole mom	none of the above
orbital motion only	spin only	both orbital motion as w	none of the above
half integer	integer	zero	none of the above
half integer	integer	zero	none of the above
$hv = g_N \mu_N B_0$	E = -μ.Β ₀	$\Delta E = 2 \mu . B_0$	None of the above
Lange g factor	Nuclear g factor	Molecular g factor	None of the above
Bohr magneton	Magnetic moment	Nuclear magneton	None of the above
resonance	saturation	relaxation	none of the above

OPTION 5	OPTION 6	ANSWER
		greater than 1/2
		insignificant
		radio frequency region
		variable
		solids only
		magnetic moments
		half integer
		electrical
		gyromagnetic ratio
ic field and free	quency	eiher fixed magnetic field and varying frequency, or fixed freque
		saturation
		the number of molecules in the upper and lower levels become ϵ
		relaxation
		spin-spin relaxation
		spontaneous
		lattice of the crystal
		Larmour frequency
		longitudinal
		transverse
		radio frequency
ectric field is ap	plied	no external field is applied
		RF region
frequency to b	be varied	frequency of the radiation has to be varied
		the nuclear quadrupole moment of the nucleus and the electric f
		electrical and magnetic
		electric and electric
		microwave region
		one or more unpaired electons
		both orbital motion as well as spin
		zero
		integer
		$hv = g_N \mu_N B_0$
		Nuclear g factor
		Nuclear magneton
		resonance

ncy and varying magnetic field

equal

[:]ield gradient

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COURSE NAME: SPECTROSCOPY

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SYLLABUS

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

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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 = 0. Zero-field splitting (or fine structure) characteristic of transition metal complexes and other species with two or more unpaired electrons (S = 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.
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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.



Prepared by Dr. S. KARUPPUSAMY, Asst. Prof, Dept. of PHYSICS, KAHE Page 6 of 9



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

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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.

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POSSIBLE QUESTIONS

- 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
- A Mossbauer nucleus ⁵⁷Fe makes the transition from the excited state of energy 14.4 keV to the ground state. What is recoil velocity?

KARPAGAM ACADEMY OF HIGHER EDUCATION (Under Section 3 of UGC Act 1956) COIMBATORE – 641021 (For the candidates admitted from 2017 onwards) DEPARTMENT OF PHYSICS PHYSICS SPECTROSCOPY (18PHP204) MULTIPLE CHOICE QUESTIONS

QUESTIONS

The origin of ESR lies in the

The orientation of the magnetic dipole with respect to the applied magnetic field are The fact that the applied magnetic field tries to orient the magnetic moment of the electron The spin of the electron can have values The hyperfine structure of the ESR spectrum is due to The mechanism by which interaction occurs due to the unpaired electron density at the nucl The phenomena concerned with nuclear resonant absorption and fluorescence is called The daughter nuclei in the highly excited state, produced during a radioactive decay, comes The high energy y-ray photon emitted by a nuclear transition excites a nucleus in the ground The recoilless absorption of the γ-ray photon is responsible for ____ The strength of the resonant absorption is determined by the The excited state of a nucleus has a mean life time of the order of _____ The highest energy for which a Mossbauer effect is known is _____ Mossbauer effect involves absorption of The detector normally used to detect Mossbauer spectrum is In Mossbauer experiment if the environment of emitting and absorbing nuclei are different, The Isomer shift is due to the interaction between Unlike in the other branches of spectroscopy Mossbauer spectroscopy involves Splitting of Mossbauer lines are due to the interaction between ____ The isomer shift in Mossbauer spectrum is a direct function of _____ The relative movement between the source and absorber in a Mossbauer spectroscopy expe Electron spin resonance is also known as The magnetic moment of the electron is due to combined effect of The magnetic moment of the electron is given by $\mu_s = -g\mu_B S$, where g is The angular momentum due to spin and the magnetic moment are in For an electron since $S = \frac{1}{2}$, the value of m_s is _____ Spectrometers used for ESR studies in the frequency range of ~9.5 GHz are known as Q band spectrometers are operated at frequencies of the order of _____ The hyperfine Structure of ESR spectrum is due to _____ ESR involves

OPTION 1	OPTION 2	OPTION 3	OPTION 4		
spin of the electron	spin of the nucleus	orbital motion of the elec	none of the above		
not quantized	can be anything	quantized	in the direction of the a		
the magnetic moment to be ca	the magnetic moment of the	the magnetic moment to	none of the above		
+1/2 only	-1/2 only	±1/2	None of the above		
the interaction of the unpaired interaction of the magnetic interaction of the orbital none of the above.					
spin-spin interaction	spin-lattice interaction	Fermi or Contact interact	None of the above		
Mossbauer spectroscopy	ESR spectroscopy	NMR spectroscopy	NQR spectroscopy		
visible photons	x-ray photons	γ-ray photons	none of the above		
absorption	the recoil energy	instrument not sensitive	none of the above		
ESR absorption	NMR absorption	Mossbauer effect	NQR absorption		
overlap profile of the source ar the peak of the absorption c the peak of the emission none of the above.					
10 ⁻⁶ s	10 ⁻¹⁶ s	10 ⁻⁶ ms	10 ⁶ s		
100 keV	187 keV	187 MeV	None of the above		
x-rays	g-rays	UV rays	IR rays		
PMT	Thermocouple	Scintillator	Klystron		
Isotope shift	Wave length shift	Isomer shift	None of the above		
the nuclear charge distribution the nuclear quadrupole mor the nuclear magnetic mo none of the above					
Source-absorber pair	absorber alone	source alone	other samples		
nuclear quadrupole moment ar nuclear magnetic moment a nuclear magnetic momer none of the above					
p-electron density at the nucleis-electron density at the nuc proton density in the nuc none of the above					
reduction in intensity	Doppler shift	Increase in intensity	None of the above		
nuclear magnetic resonance	electron paramagnetic reso	nuclear quadrupole reso	none of the above		
spin and charge	spin and mass	mass and charge	charge alone		
Lande g factor	Nuclear g factor	Electron g factor	None of the above		
opposite directions	same directions	perpendicular to each ot	any orientation		
1/2	- 1/2	± 1/2	1		
Q-band spectrometers	X-band spectrometers	S-band spectrometers	None of the above		
~9.5 GHz	~35 GHz	~9.5 MHz	~35 MHz		
nuclear spin	electron spin	dipole-dipole interaction	none of the above		
absorption	emission	scattering	radiation		

OPTION 5	OPTION 6	ANSWER
pplied field		spin of the electron quantized
		the magnetic moment of the electron to precess around the app $\pm 1/2$
		the interaction of the unpaired electron with the magnetic mome Fermi or Contact interaction
		Mossbauer spectroscopy
		γ-ray photons
		the recoil energy
		Mossbauer effect
		overlap profile of the source and absorber
		10 ⁻⁶ s
		187 keV
		g-rays
		Scintillator
		Isomer shift
		the nuclear charge distribution and electron charge distribution Source-absorber pair
		nuclear quadrupole moment and electric field gradient
		s-electron density at the nucleus
		Doppler shift
		electron paramagnetic resonance
		spin and charge
		Electron g factor
		opposite directions
		± ½
		X-band spectrometers
		~35 GHz
		dipole-dipole interaction
		absorption

lied magnetic field

ents of nuclei within its orbital