LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **APRIL 2025**

PCH3MC03 – MOLECULAR SPECTROSCOPY

Date: 29-04-2025 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 PM

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Answer the following**	
a)	What are hot bands?	
b)	How does an auxochrome exert bathochromic shift on chromophores?	
c)	Predict the number of signals in the $^{13}C\{^{1}H\}$ NMR spectrum of (*R*)-4-methylpentan-2-ol.	
d)	How are primary and secondary amines distinguished by infrared spectral analysis?	
e)	What is meant by recoilless transition?	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**Answer the following**	
a)	Sketch the different kinds of in-plane bending vibrations of polyatomic molecules.	
b)	What are the projectiles used in the MALDI desorption ionization techniques?	
c)	Predict the number of signals expected for the benzene radical anion.	
d)	What is the reference compound used in EPR spectral analysis?	
e)	Write the major difference between NMR and NQR in the splitting of nuclear energy levels.	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	(a) Sketch the energy level diagrams and selection rules for harmonic and anharmonic oscillators. (5) (b) The equilibrium vibrational frequency and anharmonicity constant for HI molecule are 2309.5 cm^{-1} and 0.0172 respectively. Calculate the wave numbers of fundamental, first and second overtone transitions. (5)	
4	(a) State and explain mutual exclusion principle with an example. (4) (b) Predict the number of EPR signals observed in $[Cu(bpy)_3]^{2+}$. Given that I value of Cu = 3/2; N = 1 and bpy = 2,2'-bipyridyl. (6)	
5	(a) How will you distinguish the three disubstituted dibromobenzenes on the basis of the proton decoupled CMR spectra? (b) Explain McLafferty rearrangement with suitable examples. (5 + 5)	
6	(a) In the 400 MHz ^{1}H NMR spectrum, an organic compound exhibited a doublet. The two lines of the doublet are at δ 2.35 and 2.38 ppm. Calculate the coupling constant (J) value. (4) (b) Explain the following: (i) Hyperfine splitting (ii) Kramer's degeneracy (3 + 3)	
7	(a) What do you mean by Quadrupole splitting in Mossbauer spectroscopy? (b) Discuss Mossbauer spectrum of nitroprusside ion, $[Fe(CN)_5NO]^{2-}$. (4+6)	

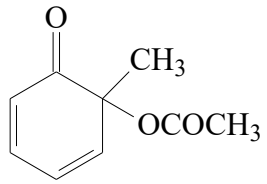
SECTION C – K4 (CO3)

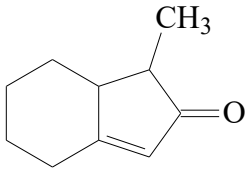
Answer any TWO of the following **(2 x 12.5 = 25)**

8 (a) Describe the appearance of P and R branch lines in the vibrational-rotational spectra of diatomic molecules obeying Born-Oppenheimer approximation.
(b) Find the vibrational wave number of HCl having a rotational constant of 10.593 cm^{-1} and centrifugal distortion constant of 5.3×10^{-4} cm^{-1}. (8.5 + 4)

9 (a) Calculate the possible number of EPR signals for the following:
(i) naphthalene radical (ii) $^{13}CH_3\cdot$
(b) How will you differentiate the following compounds by IR spectrometry?
CH_3CH_2CHO and $CH_2=CHCH_2OH$ (4 + 4 + 4.5)

10 (a) Calculate the absorption maxima for the following compounds. (4+4)

(i) 

(ii) 

(b) Explain the various factors affecting the electronic transitions. (4.5)

11 (a) The NQR spectrum of solid PCl_5 shows 10 NQR lines – Justify. (8)
(b) The exciting radiation used in recording Raman spectrum is 5650 Å. Calculate the wavelength of anti-Stokes lines if the Stokes lines observed at 5810 Å. (4.5)

SECTION D – K5 (CO4)

Answer any ONE of the following **(1 x 15 = 15)**

12 (a) Explain the influence of rotation on parallel and perpendicular vibrations of linear polyatomic molecules. (7)
(b) Discuss the magnetic hyperfine interaction in Mossbauer spectroscopy with an example. (8)

13 (a) Explain the following: (i) Population densities of nuclear spin states (ii) ^1H Free induction decay
(b) Predict the fragmentation pattern of cyclohexanol and justify your answer. (4 + 4 + 7)

SECTION E – K6 (CO5)

Answer any ONE of the following **(1 x 20 = 20)**

14 (a) Discuss any three factors affecting vibrational frequencies with examples. (8)
(b) The rotational constant of ICl is 0.114 cm^{-1}. Find the transition which gives the most intense spectral line at 300 K. (4)
(c) Determine the number of NQR transitions and their energies for $_7N^{14}$ (I=1) assuming the asymmetry parameter, η=0. (8)

15 (a) An organic compound C_9H_{12} gave the following spectral data:
UV: λ_{max} 268 nm, ε_{rnax} 480.
IR: absorption bands at 3065-2910, 1608 and 1473 cm^{-1}. PMR: δ 2.26 (9H, s) and 6.79 (3H, s).
^{13}C NMR (Off-resonance decoupled): One quartet, one doublet and one singlet.
DEPT 135: Two positive peaks.
Explaining the spectral data, derive the structure of the compound. (15)

(b) Explain the theory of fluorescence spectrometry. (5)
