LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2024**

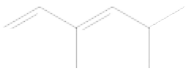
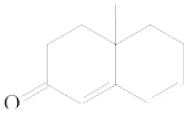
PCH3MC03 – MOLECULAR SPECTROSCOPY

Date: 12-11-2024 Dept. No. Max. : 100 Marks

Time: 01:00 pm-04:00 pm

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Answer the following**	
a)	Why are spherical top rotors microwave inactive?	
b)	What type of absorption shift is found when aniline is in less polar solvent and/or in acidic solution?	
c)	What is retro Diels-Alder cleavage in mass spectral analysis?	
d)	If two signals differ by 1.5 ppm in a 60 MHz spectrometer, calculate the difference observed (in Hz) in a 100 MHz spectrometer.	
e)	State the law of conservation of momentum applied in Mossbauer spectroscopy.	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**Answer the following**	
a)	How are thermochemical and spectroscopic dissociation energies related?	
b)	State the rule of mutual exclusion principle.	
c)	How are *o*-hydroxybenzaldehye and *p*-hydroxybenzaldehye differentiated using IR spectrometry?	
d)	Why EPR signals are presented as a first derivative absorption spectrum?	
e)	Draw the shape of nucleus having $I > ½$ and $eQ < 0$.	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	(a) Using Morse's curve, explain the vibrational transitions in anharmonic oscillator and derive the expressions for $\Delta\varepsilon$ of fundamental band, first and second overtones. (5) (b) Calculate the rotational constant of $D^{35}Cl$ using the inter nuclear distance of 127.5 pm. (5)	
4	(a) Justify the following. (6) (i) $C{=}O_{str}$ frequency of benzamide and methyl benzoate are different. (ii) Glycol in dilute CCl_4 shows two $O{-}H_{str}$ frequencies. (iii) Anhydrides show two $C{=}O_{str}$ frequencies around 1850-1750 cm^{-1} with a separation of 65 cm^{-1}. (b) Explain the Stevenson's rule of probable fragmentation in Mass spectral analysis.	
5	(a) A certain transition involves an energy change of 4.005×10^{-22} $Jmol^{-1}$. If there are 1000 molecules in the ground state, what is the approximate equilibrium population of the excited state at temperatures of i) 29 K and ii) 2900 K? (b) Calculate the number of EPR signals expected for the coordination compound $[Co_3(CO)_9Rh]$. Given that I value of Co = 7/2, Rh = ½; Atomic number of Co is 27. (6 + 4)	
6	Explain SIMS, FAB and MALDI desorption ionization techniques with suitable examples. (10)	
7	Define isomer shift in Mössbauer spectroscopy and explain the contributions of nuclear and chemical terms to determine the position of isomer shift.	

SECTION C – K4 (CO3)

	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	(a) Discuss the factors governing the intensity of rotational spectral lines and derive the expression for the maximum populated rotational level. (9) (b) Calculate the room temperature population of CO in v = 1 relative to v = 0. Given that the fundamental wave number is 2169 cm^{-1}. (3.5)	
9	(a) Apply Woodword –Fieser rule and calculate the λ_{max} value of for the following compounds. (4+4) i)  ii)  (b) Explain McLafferty rearrangement with suitable examples. (4.5)	
10	(a) Explain the following: (i) Hyperfine splitting (ii) Kramer's degeneracy (3 + 3) (b) Reaction of $C_6H_5CH=CH_2$ with HBr gives a mixture of regioisomers **A** (major) and **B** (minor). The ^1H NMR spectrum of the mixture shows four signals, amongst others, at δ 5.17, 3.53, 3.15 and 2.00 ppm with relative integration of 2:1:1:6, respectively. Calculate mole ratio of A & B. (6.5)	
11	(a) Discuss the effect of magnetic field on NQR transitions with an example. (8) (b) Calculate the spacing between successive rotational Raman lines in the spectrum of H_2 molecule if the bond length of H_2 is 0.07417 nm. (4.5)	

SECTION D – K5 (CO4)

	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Explain the microwave spectrum of prolate and oblate symmetric top molecules with the help of the selection rules and energy level diagrams. (8) (b) How will you distinguish high and low spin Fe (II) complexes by Mossbauer spectroscopy? (7)	
13	(a) Predict the fragmentation pattern of ethyl benzene and justify your answer. (7) (b) Explain the various factors affecting the electronic transitions. (8)	

SECTION E – K6 (CO5)

	Answer any ONE of the following	**(1 x 20 = 20)**
14	(a) Discuss PR contours which explain the difference in the spacing between the rotational lines in P and R branches. (8) (b) Explain the intensity of Stokes and anti-Stokes lines based on quantum theory. (5) (c) Determine the number of NQR transitions and their frequencies, for $_5B^{11}$ (I = 3/2) assuming the asymmetry parameter, η = 0. (7)	
15	(a) Explain the following spectral data systematically and deduce the structure of an organic molecule with an empirical formula C_8H_8O: **UV**: λ_{max} 278 and 319 nm. **IR**: Significant absorption bands at 3070-3010, 2970-2860, 1685, 1605, 1580 and 1450 cm^{-1} **PMR**: δ(ppm) 2.1 (3H, s) and 7.5 (5H, m). **^{13}C NMR**: δ (ppm) 198 and 137 (two singlets), 134, 129 and 128 (three doublets) and 26 (one quartet). **DEPT-135**: four positive peaks; MS: m/e 120 (M^+), 105, 77, 51 and 43. (15) (b) Explain magnetic anisotropy using acetylene and benzene as examples. (5)	
