



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – APRIL 2024

PCH3MC03 – MOLECULAR SPECTROSCOPY

Date: 06-04-2024

Dept. No.

Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

SECTION A – K1 (CO1)

Answer ALL the questions

(5 x 1 = 5)

1 Answer the following

- Among the following molecules which has $I_a = 0$ and $I_b = I_c$: chloroacetylene, methane, vinyl chloride.
- Which type of molecule obeys the rule of mutual exclusion principle?
- Mention the importance of meta stable peaks.
- What is a chromogen? When does it become a dye?
- Name the energy shift in Mossbauer spectroscopy observed when the electronic configuration around the absorber and source nuclei are different.

SECTION A – K2 (CO1)

Answer ALL the questions

(5 x 1 = 5)

2 Answer the following

- Write the relationship between thermochemical and spectroscopic dissociation energies.
- How are isotopic peaks useful for the study of organic compounds?
- The precessional frequency of ^{13}C nucleus will be _____, if that of proton is 600 MHz at 14.1 tesla.
- What is Nuclear Overhauser effect?
- Mention the parameter which measures the deviation of nuclear charge distribution from spherical symmetry in NQR spectroscopy.

SECTION B – K3 (CO2)

Answer any THREE of the following

(3 x 10 = 30)

- (a) Why are Q-branch lines in the vibrational spectrum of linear molecules found to be very intense?

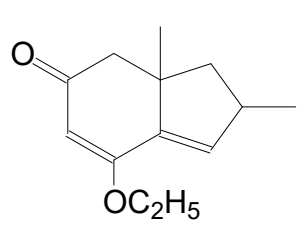
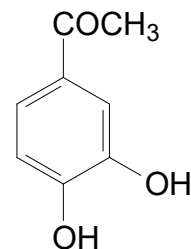
(b) The successive line separation in $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ are 3.8435 and 3.6735 cm^{-1} , respectively. Calculate the isotopic mass of ^{13}C . (5+5)
- (a) What are the types of fragmentation peaks obtained in mass spectrometry? Mention their significance.

(b) Explain the working principle of ESI mass spectrometry. Mention its merits. (5+5)
- Write a short note on the following.

a) Fluorescence spectroscopy b) pH variation study using UV visible spectroscopy (5+5)
- Explain the following techniques in detail with suitable examples.

i) COSY ii) HETCOR (5+5)
- The Mossbauer spectrum of $\text{K}_4[\text{Fe}(\text{CN})_6]$ consists of a single line but $\text{K}_4[\text{Fe}(\text{CN})_5\text{NO}]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ consist of two lines each. Explain.

SECTION C – K4 (CO3)

	Answer any TWO of the following	(2 x 12.5 = 25)
8	(a) Obtain the expression for finding the most populated rotational level of a rigid rotor. (b) Discuss the effect of inter and intra molecular hydrogen bonding on the position of vibrational frequency of O-H in a compound.	(7.5+5)
9	(i) Why Stokes lines are more intense than anti-Stokes lines? (ii) What is the recoil energy of ^{57}Fe nucleus if the energy of the emitted γ -rays from the first excited state is 14.4 keV?	(7.5+5)
10	(a) Describe tandem mass spectrometry with a specific example. (b) Calculate the λ_{max} of the following compounds.	(5.5) (4+3)
	i)  ii) 	
11	a) Write a short note on ^{31}P NMR spectroscopy. What will be the spectral pattern of HPF_2 molecule? b) Calculate the ESR hyperfine splitting of benzene and ethyl radicals.	(2.5+4)+(3+3)

SECTION D – K5 (CO4)

	Answer any ONE of the following	(1 x 15 = 15)
12	(a) Calculate the room temperature population of NO in $v = 1$ relative to $v = 0$. Given that the fundamental wave number is 2169 cm^{-1} . (b) Explain the theory of NQR spectroscopy. (c) The fundamental band, first and second overtones of a molecule appear at 2886 , 5668 and 8347 cm^{-1} respectively. Determine the vibrational wave number and anharmonicity constant of the molecule.	(4+6+5)
13	(a) Identify the compound from the following spectral data. Mol Formula: $\text{C}_3\text{H}_7\text{NO}$ UV: 238 nm , $\epsilon = 10500 \text{ l mol}^{-1} \text{ cm}^{-1}$ IR: 3428 (m) , $2940\text{-}2855 \text{ (w)}$, 1618 (s) , 1452 (w) NMR: 8.18 ppm, s (1H) ; 2.70 ppm, s (3H) ; 1.9 ppm, s (3H) . (b) Enumerate the various techniques used to refine complex NMR spectra into first order spectra.	(7) (8)

SECTION E – K6 (CO5)

	Answer any ONE of the following	(1 x 20 = 20)
14	(a) Explain the appearance of P and R branch lines in the vibrational spectrum of a diatomic rotor obeying Born-Oppenheimer approximation. (b) Diagrammatically represent the in plane and out of plane deformations observed in a molecule. (c) Determine the number of NQR transitions for ${}^5\text{B}^{11}$ ($I=3/2$) assuming the asymmetry parameter, $\eta=0$.	(10+4+6)
15	(a) What are the advantages of ${}^1\text{H}$ coupled ${}^{13}\text{C}$ NMR over ${}^1\text{H}$ decoupled ${}^{13}\text{C}$ NMR technique? Explain with an example. (b) Draw the mass spectral fragmentation patterns of (i) toluene (ii) methylcyclohexylketone	

(c) Write a short note on MRI imaging.

(6+9+5)
