STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2023–2024)

M.Sc. DEGREE EXAMINATION, NOVEMBER 2024
BRANCH IV- CHEMISTRY
THIRD SEMESTER

COURSE : CORE
PAPER : MOLECULAR SPECTROSCOPY
SUBJECT CODE : 23CH/PC/MS34
TIME : 3 HOURS MAX.MARKS :100

Q. No.	SECTION A Answer all the questions (10 x 1 =10 marks)	CO	KL
1.	The molecule which is IR inactive and Raman active is a) HCl b) N_2 c) SO_2 d) protein	CO1	K1
2.	The region of group frequency (IR) for >C=C< stretching is a) 3700-2500cm^{-1} b) 2500-2000cm^{-1} c) 2000-1600cm^{-1} d) 1600-1450cm^{-1}	CO1	K1
3.	M+2 peaks are observed in the mass spectrum of the compounds containing one of the following elements a) F b) I c) Br d) N	CO1	K1
4.	The natural abundance of ^{13}C is about a) four times less than 1H b) 0.11% of the total carbon c) 1.1% of the total carbon d) 99% of the total carbon	CO1	K1
5.	Which molecular electronic transition requires the most energy? a) $\sigma \rightarrow \sigma^*$) b) $\pi \rightarrow \pi^*$ c)$n \rightarrow \pi^*$ d) $n \rightarrow \sigma^*$	CO1	K1
6.	What type of 2D-NMR spectrum indicates which carbon atoms are coupled to which hydrogen atoms? a) DEPT b) APT c) COSY d) HETCOR	CO1	K1
7.	The mass spectrum of alcohols often fails to exhibit detectable M peaks, but instead show relatively large _____ peaks a) M+1 b) M+2 c) M-17 d) M-18	CO1	K1
8	The nuclear relaxation characterized by T1 relaxation is not a) spin-lattice relaxation b) longitudinal relaxation c) spin-spin relaxation d) relaxation along z-axis	CO1	K1
9.	In the mass spectrum of Benzaldehyde, the base peak is observed at m/e _____ a) 105 b) 106 c) 77 d) 51	CO1	K1
10.	The ^{19}F NMR spectrum of ClF_3 shows a) doublet and triplet for a T-shaped structure b) singlet for a trigonal planar structure c) singlet for a trigonal pyramidal structure d) doublet and singlet for a T-shaped structure.	CO1	K1

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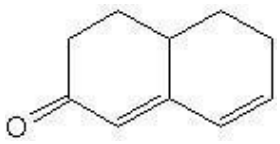
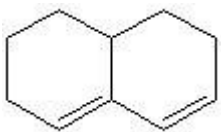
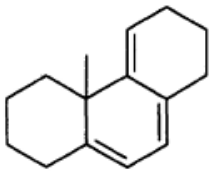
Q. No.	SECTION B Answer all the questions (10 x 1 =10 marks)	CO	KL
11.	In NMR spectra for a triplet, the relative peak areas are in the ratio_____.	CO2	K2
12.	An organic compound containing an odd number of nitrogen atoms will have a molecular ion with an _____ mass number	CO2	K2
13.	What is Born-Oppenheimer approximation?	CO2	K2
14.	State Stevenson's rule.	CO2	K2
15	The region of the IR spectrum, which contains the most complex vibrations (600-1400 cm^{-1}) is called the _____ region of the spectrum.	CO2	K2
16.	The IR spectrum of ethanol (CH_3CH_2OH) shows strong absorption at 3420(broad), 2922, 2842 and 1050cm^{-1}. The band assigned to the OH stretching is _____.	CO2	K2
17.	Arrange the following bonds in the decreasing order of vibrational frequency νC-X C-O, C-I, C-C, C-H, C-Br, C-Cl	CO2	K2
18.	Predict the number of signals in the PMR spectra of the following compounds $CH_3CH=CH_2$	CO2	K2
19.	Calculate the Double Bond equivalence for $C_{10}H_{14}O$.	CO2	K2
20.	State rule of Mutual Exclusion Principle.	CO2	K2

Q. No.	SECTION C Answer any four of the following (4x6 =24 marks)	CO	KL
21.	Calculate the λmax for the following compounds i.  ii.   iii. (2+2+2)	CO3	K3
22.	a) Why anti-Stokes lines are less intense than Stokes lines? b) Indicate the number of peaks in the off-resonance decoupled ^{13}C NMR spectra 2-butanone (3+3)	CO3	K3
23.	a) What is Fieser Kuhn equation b) Explain the excited and ground state term symbol for Hydrogen	CO3	K3
24.	a) Distinguish between fundamental vibrations and overtones b) Discuss the various stretching and bending vibrations which arise in the IR spectrum of an aromatic compound. (3+3)	CO3	K3
25.	Outline the advantages of 2D NMR technique.	CO3	K3

Q. No.	SECTION D Answer any four of the following (4x 8=32 marks)	CO	K4
26.	a) Elucidate nuclear overhauser effect. b) Explain McLafferty rearrangement with an example. (4+4)	CO4	K4
27.	a) Discuss the applications of ^{19}F and ^{31}P NMR spectroscopic techniques b) Explain why the aldehydic proton appears much downfield in the PMR spectrum (4+4)	CO4	K4
28.	a) Using mass spectrometry how will you distinguish 2-pentanone and 3-pentanone? b) Explain vicinal and geminal coupling constants with suitable examples (4+4)	CO4	K4
29.	a) An organic compound of molecular formula C_8H_8O exhibits m/z 120,105,77,43. Determine the structure of the compound b) Sketch the fundamental modes of Vibration of CO_2 and predict which modes will be IR active and which will be Raman active. (4+4)	CO4	K4
30.	a) Explain the classical quantum theory of Raman effect .b) Determine the structure of SO_2 and N_2O using Raman Spectroscopy. (4+4)	CO4	K4

Q.No.	SECTION E Answer any two of the following (2x 12 =24 marks)	CO	K L
31.	a) Assign the structure and justify your answer for the compound of molecular formula $C_9H_{10}O_2$ with the following data UV: λmax:268,264,262 nm IR: ν=1745,1225and 749 cm^{-1} ^{1}HNMR: δ7.22(5H,s),5.00(s,2H), 1.96(s,3H) MS: m/z 150. b) What is meant by chemical shift? Discuss on the shielding and deshielding of protons (7+5) OR a) An organic compound of molecular formula $C_8H_8O_2$ with the following data Mass: m/z 136,91 and 45 UV: λmax:229 and 257nm; IR: ν=1710 cm^{-1} ^{1}HNMR: δ7.2(s 5H) ,3.5(s,2H) and 10.5(s,1H) b) Explain the following terms: i) base peak ii) isotope peak iii) molecular ion peak. (7+5)	CO5	K5

32.	a). The C=O stretching frequencies are as follows $RCONH_2 \approx 1680\ cm^{-1}$, $RCOOH \approx 1715\ cm^{-1}$, $RCOR \approx 1725\ cm^{-1}$, $RCHO \approx 1735\ cm^{-1}$, Discuss the trend observed b) The compound having the molecular formula C_7H_8 gave the following PMR data 1.13δ (3H, s) and 7.22δ (5H, s). Assign the structure of the compound c) Explain the solvent effect on π- π^* and n- π^* transitions in organic compounds (4+4+4) OR a) An organic compound of molecular formula C_4H_8O exhibits the following IR and NMR spectral data IR: ν=1715cm^{-1}(s) ^{1}HNMR: δ1.06(t, 3H) ,2.14(s,3H) and 2.43(q,2H) Deduce the structure of the compound and predict the principal fragment ion for the base peak b) Outline the importance of Stark effect (7+5)	CO5	K5