# STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86 (For candidates admitted during the academic year 2006–07 & 2007–08)

### SUBJECT CODE: CH/PC/MS34 M.Sc. DEGREE EXAMINATION, NOVEMBER 2008 BRANCH IV- CHEMISTRY THIRD SEMESTER

REG.NO .....

COURSE PAPER	: MOLECULAR SPECTROSCOPY
TIME	: 30 MINUTES MAX.MARKS : 20
	SECTION – A (20x1=20) all the questions: hoose the correct answer:
1.	The chemical shift values are relative in nature.The reference that isnormally employed in NMR is
2.	Energy required for effecting nuclear spin transitions corresponds to a) Microwave region b) Infrared region c) $\gamma$ -rays d) None of the above
3.	Which of the following is NMR active nuclei? a) ${}^{16}O$ b) ${}^{12}C$ c) ${}^{31}P$ d) ${}^{14}N$
4.	The colour exhibited by Transition metal complexes is owing toa) Nuclear transitionsb) $n - \pi^*$ transitionsc) $\pi - \pi^*$ transitionsd) $d - d$ transitions
5.	The intensity of the bands in electromagnetic spectrum is governed bya) Fermi-Dirac distributionb) Bose-Einstein distributionc) Boltzmann distributiond) None of the above
II Fil	ll in the blanks:
6.	Only those vibrations are found to be IR active, whose oscillates during the vibration.
7.	Raman spectrum is a result of collision between photon matter.
8.	Spin-Spin coupling of nuclei through space in NMR is referred to as
9.	Coupling constant in NMR is expressed in
10.	A conjugated system requires energy for the $n-\pi^*$

transitions than an unconjugated system.

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# III Match the following:

- Planck's Constant Orientation of molecule in a magnetic field
  Polarizability Mass Spectrometry
- Polarizability M
  Anisotropy V
  - Vibrational Spectrum
- 14. Meta Stable Peak -
- 15. Zero point energy Raman effect
  - Joule-Second

Frequency

# **IV** Give reasons of the following:

- 16. Acetylenic protons are more shielded in NMR than ethylenic protons although the former are attached to a more electronegative SP carbon.
- 17. ESR spectrum shows hyperfine splitting where as NMR spectrum does not
- 18. The infrared and Raman spectra of methane molecule have no line in common
- 19. Non-linear molecule has 3N-6 vibrational degrees of freedom, while linear molecule has 3N-5
- 20. Acetone absorbs at 279nm in hexane where as the value of  $\lambda_{\rm max}$  in water is 264.5nm.

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COURSE PAPER	: MAJOR CORE : MOLECULAR SPECTROSCOPY	
TIME	: 2½ HOURS	MAX.MARKS: 80

## SECTION – B (5 x 8 = 40)

#### Answer any five questions:

1.	a)	The force constant for HF molecule is $9.7 \times 10^2 Nm^{-1}$ . Calculate the frequency of radiation to excite the molecules from $v = 0$ to $v = 1$ .		
	b)	Write notes on (i) Over tones (ii) Spinning side bands	(4) (4)	
2.	a)	The observed chemical shift of a proton is 300HZ from TMS and the operative frequency of the spectrometer is 100MHZ. Calculate chemical shift in terms of $\delta$ ( $\rho\rho m$ ).	the (4)	
	b)	Differentiate between stokes and Antistokes lines.	(4)	

3. a) Write the structural formulae for the compounds with the following molecular that show ONLY ONE SIGNAL in their PMR spectra (i)  $C_5H_{12}$  (ii)  $C_2H_6$  (iii)  $C_2H_6O$  (iv)  $C_2H_4$ 

() = 512	(1) = 36	() 22-60	(1) - 3 4
(v) $C_2H_4Br$	(vi) $C_4 H_6$	(vii) $C_8 H_{18}$	(viii) $C_4 H_8$ (4)

b) Bring out the applications of Raman spectroscopy. (4)

- 4. The bond length of NO molecule is  $1.151 \times 10^{-10} m$ . Calculate the frequencies in  $cm^{-1}$  for the pure rotational lines in the spectrum of NO corresponding to the following changes in the rotational quantum numbers  $J = 0 \rightarrow 1$ ;  $J = 1 \rightarrow 2$ ;  $J = 2 \rightarrow 3$ .
- 5. Identify the compound from the following data Molecular formula  $C_5H_4$ IR  $(\bar{\gamma} \ cm^{-1})$  : 3300(w), 2900 - 2840(m), 2110(m) UV  $(\lambda, nm)$  : no absorption above 200 nm PMR $(\delta, \rho pm)$  : 2.0, 3.1 (equal intensity)

6.	a)	Suggest the structure of a compound with molecular formula whose mass spectrum shows peaks at $\frac{m}{2}$ 15, 43, 57, 91, 3	
		whose mass spectrum shows peaks at $\frac{12}{2}$ 15, 45, 57, 51,	
	b)	Write a note on Mc Lafferty rearrangement.	(4) (4)
7.	W	hat are Woodward-Fieser rules? How can these be justified?	
			(2 x 20 = 40)
Answer	any	two questions:	
8.	a)	Discuss the distribution of intensities in first order splitting in Discuss AMX coupling with an example.	NMR.
	b)	Discuss the Principle of pure rotational spectroscopy and der expression for the spacing between lines.	ive the (10+10)
9.		Explain the origin of PQR branches in vibrational-roational sp Write notes on (i) Nuclear over houser effect (ii) 2D NMR	ectra.
	,		(10+10)
10.	a)	Explain the simplification of complex spectra by	
	b)	<ul><li>(i) shift reagents (ii) spin decoupling</li><li>Write a short notes on</li></ul>	
		(i) Frank – condon Principle	(10 + 10)
		(ii) Nitrogen rule in Mass Spectrum	(10+10)
11.	a)	Discuss the various modes of vibration with water molecule a example.	as an (6)
	b)	An organic compound (Molecular weight 108) is not acid, ca oxidized to a crystalline compound (m. pt. 122°C). It gives t spectral data: UV : $\lambda_{max} 255 \text{ mm}(\varepsilon_{max} = 202)$	
			=
		IR : $V_{\text{max}}^{cm^{-1}}$ 3402 (s, br), 3065 (w), 2888 (m), 1499 (w, sh) <sup>1</sup> HNMR : $\delta$ 3.90 4.60 7.26	) 1455 (m);
		Multiplicity s s s	
		Integration 1 : 2 : 5 Deduce the structure of the compound, justify the above obs	envations and
		predict the principal ions in its mass spectrum.	(14)

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