STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted during the academic year 2004-05 & thereafter)

SUBJECT CODE: CH/MO/SP64

B.Sc. DEGREE EXAMINATION, APRIL 2008
BRANCH IV - CHEMISTRY
SIXTH SEMESTER

Reg. No ……..

COURSE : MAJOR – OPTIONAL
PAPER : SPECTROSCOPY
TIME : 30 MINUTES **MAX. MARKS : 30**

SECTION – A
TO BE ANSWERED ON THE QUESTION PAPER ITSELF.
ANSWER ALL THE QUESTIONS. **(30x1=30)**

I. Choose the correct answer:

1. Which of the molecule can show pure rotational spectrum?
   a) H_2 b) Cl_2 c) CO_2 d) SO_2

2. Electronic band spectra are observed in the region
   a) uv-visible b) infra red c) nmr d) esr

3. The frequency of visible radiation is greater than
   a) ir b) γ-rays c) X-rays d) uv

4. The selection rule of the transition in rotational energy levels for a diatornic molecule in the raman spectrum is
   a) $\Delta J = \pm 1$ b) $\Delta J = 0, \pm 2$ c) $\Delta J = +2$ d) $\Delta J = \pm 2, \pm 1$

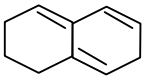
5. The number of equivalent protons in nmr for 2-chloropropane is
   a) 4 b) 1 c) 2 d) 3

6. Groups which modify the position of absorption relative to the chromophore in electronic spectra are
   a) cytochromes b) bathochromes c) hypsochromes d) auxochromes

7. ^{13}C has a spin quantum number
   a) zero b) one c) $\frac{1}{2}$ d) $\frac{3}{2}$

8. The esr spectrum of p-benzoquinone contains
   a) quintet b) quartet c) doublet d) triplet

9. The g-value for a free electron is
   a) 1.008 b) 2.0023 c) 2.016 d) 2.0362

10. The compound  contains
    a) one exocyclic bond b) one endo and one exo
    c) two endo cyclic bonds d) two exocyclic bonds

11. The molecular ion peak in a mass spectrum corresponds to the
    a) base peak b) metastable peak c) parent peak d) stableion peak

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12. TMS used as a reference in nmr is
    a) trimethyl silane b) tetramethyl silane
    c) tetramethyl sylphoxide d) tertiary butyl methyl silicone

13. Which of the following molecules will show esr
    a) N_2 b) O_2 c) H_2 d) Cl_2

14. Conjugation of carbonyl with C = C leads to the carbonyl stretching frequency being
    a) increased b) decreased c) remains unaltered d) broadened

15. McLafferty peak for $CH_3CH_2CH_2CH_2CHO$ occurs at $\frac{m}{e}$.
    a) 44 b) 57 c) 70 d) 28

I1 Match the following :

16.	Finger print region	a) Microwave
17.	Metastable ions	b) Infrared
18.	Chemical Shift	c) Raman spectra
19.	Scattering of light	d) Mass Spectra
20.	Klystron source	e) NMR
		f) Mossbauer

III Fill in the blanks:

21. The standard used in esr is _____.

22. $n - \pi^*$ transitions are _____ in energy than $\pi - \pi^*$ transitions.

23. The expansion for TMS is _____.

24. γ – ray resonance spectroscopy is the other name for _____.

25. The parent ion of aromatic compounds is _____ than aliphatic compounds.

IV Answer in one or two sentences:

26. What is a metastable peak?

27. What is gyromagnetic ratio?

28. Define chemical shift.

29. Why cis-stilbene absorbs at a shorter wavelength compared to trans-stilbene?

30. What is Born-Oppenheimer approximation?

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SECTION – B

ANSWER ANY FIVE QUESTIONS: **5X6=30**

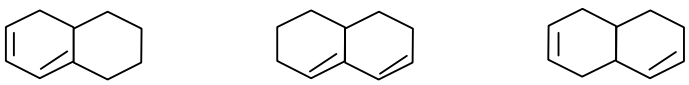
1. Explain the rule of mutual exclusion with suitable examples.
2. a) List any three factors which affect the magnitude of g values in epr.
   b) The fundamental vibrational frequency of $^{1}H^{35}Cl$ is $2890cm^{-1}$. Calculate the fundamental vibrational frequency of $^{2}D^{35}Cl$. (3+3)
3. State and explain the nitrogen rule with two examples.
4. Discuss how Raman spectra complements IR..
5. Write a note on Franck Condon principle.
6. What are isotope peaks & their significance.
7. Sketch and explain the nmr spectrum of m-cresol.

SECTION – C

ANSWER ANY TWO QUESTIONS: **2X20=40**

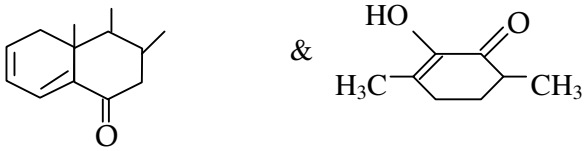
8. How will you distinguish the following by suitable spectral methods.
   a) Benzoic acid and benzyl alcohol (infrared)
   b) Benzyl alcohol and o-cresol (mass spectrum)
   c) Fe^{2+} and Fe^{3+} using mossbauer
   d) Cu^{2+} and Cu^{+} using esr.

9. a) Explain the types of electronic transitions in organic molecules. What is the effect of polar and nonpolar solvents on these transitions.
   b) Arrange the following in the increasing order of λ_{max} giving their λ_{max} using Woodward Fieser rules.



(1) (2) (3)

   c) Calculate the λ_{max} for the following enones.



(8+6+6)

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10. Write briefly on
    a) Retro Diels Alder rearrangement
    b) Mass spectrum of benzylchloride
    c) Shielding & deshielding protons (6+6+8)

11. a) How is IR spectra useful in studying hydrogen bonding
    b) Discuss McLafferty rearrangement with two suitable examples.
    c) The pure rotational (microwave) spectrum of CN consists of a series of equally spaced lines separated by $3.7978 cm^{-1}$. Calculate the internuclear distance of the molecule. The molar masses are $^{12}C = 12.011$ $^{14}N = 14.007\ gmol^{-1}$ (8+6+6)