STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted from the academic year 2004–05 & thereafter)

SUBJECT CODE: CH/PC/MS43

M. Sc. DEGREE EXAMINATION, APRIL 2007
BRANCH IV- CHEMISTRY
FOURTH SEMESTER

REG.NO …….

COURSE : CORE
PAPER : MOLECULAR SPECTROSCOPY
TIME : 30 MINUTES **MAX. MARKS :20**

SECTION – A
TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

Choose the correct answer from the given alternatives: (10x1=10)

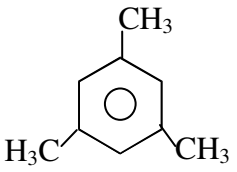
1. Cyclohexane has its λ_{max} in the region 120-200nm. This absorption is due to the transition.
   a) $n \rightarrow \pi^*$ b) $n \rightarrow \sigma^*$ c) $\sigma \rightarrow \sigma^*$ d) $\pi \rightarrow \pi^*$

2. In a mass spectrum, the M+2 peak will be observed if the compound contains an atom of
   a) hydrogen b) bromine c) nitrogen d) carbon

3. The nuclear spin value of the $^{14}N_7$ nucli will be
   a) 0 b) ½ c) 1 d) 3

4. Which of the following contains non-equivalent protons?
   a) 1,2,4,5 – Tetrachtorobenzene
   b) 2,2,3,3 – Tetramethylbutane
   c) 1,2 – Dichloroethane
   d) 1,3 – Dibromopropane.

5. How many signals would be seen in the proton NMR spectra of mesitylene,



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   a) 2 b) 4 c) 9 d) 12

6. Which of the following molecules have lowest vibrational stretching frequency?
   a) $^1H^{35}Cl$ b) $^2H^{35}Cl$ c) $^1H^{36}Cl$ d) $^1H^{37}Cl$

7. The selection rule for the rotational Raman spectroscopy is
   a) $\Delta J = 0$ b) $\Delta J = \pm 1$ c) $\Delta J = \pm 2$ d) $\Delta J = 0, \pm 1$

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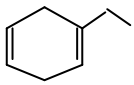
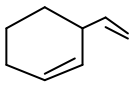
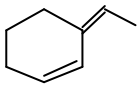
8. Identify the compound for which the molecular ion peak is not detectable in its mass spectral analysis.
   a) Acetone b) Ethanal c) toluene d) t-butanol

9. The vibrational wave number $(\bar{\gamma})$ of $^{12}C\equiv^{12}C$ is $2060cm^{-1}$. Its force constant value is
   a) $1.5\times10^{6}\ g\ s^{-2}$ b) $1.0\times10^{6}\ g\ s^{-2}$ c) $1.0\times10^{5}\ g\ s^{-2}$ d) $5.0\times10^{5}\ g\ s^{-2}$

10. Which of the following will have longest wavelength electronic absorption?
    a)  b)  c)  d) 

II Fill in the following with most appropriate word/phrase: (5x1=5)

11. Atoms or group of atoms which do not by themselves absorb in UV – VIS region but enhance the intensity of absorption of other groups active in this region are called _____.
12. Due to spin-spin interactions, in the proton NMR spectrum of propane the methyl protons and the methylene protons will appear as a _____ and _____ respectively.
13. All the IR active vibrations of N_2O are active in Raman spectroscopy also. Hence, N_2O is a _____ molecule.
14. The light source for the ultra violet region used in UV-VIS spectrophotometers is _____ lamp.
15. The force constant value for the C-C bond is _____ than that of a C=C bond.

III Answer the following in one or two lines: (5x1=5)

16. The CH_3 protons and the CHO protons in ethanol occur at $\delta = 2.2$ and $\delta = 9.8$ respectively. What will be the difference in local magnetic field between the two regions of the molecule for an applied field of 1.5T ?

17. In Raman spectrum, Stokes lines are intense than the anti-Stokes line. Why?

18. What are hot bands, in IR spectra?

19. The molar absorptivity (ε) of a molecule X at 450 nm is 20000 mol L^{-1} cm^{-1}. What do you understand from this statement?

20. State 'Laporte rule'.

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TIME : 2 HOURS & 30 MINUTES **MAX. MARKS: 80**

SECTION – B

Answer any five questions : **5 x 8 = 40**

1. Define 'moment of inertia'. How are the polyatomic molecules classified based on their moments of inertia? Give one example for each class.

2. The exciting source in a Raman experiment is at 5460A and the stokes line occurs at 5520A. Calculate the wave length of the anti-stokes line.

3. Explain the origin and the salient features of charge transfer spectra, with suitable examples.

4. What is 'relaxation' in NMR spectroscopy? Discuss the nature and an application of the different relaxation processes.

5. a) Explain the principles of fourier transformation as applied to spectroscopy.
   b) Sketch the ^{13}C NMR peaks of propanone and identify the peaks.

6. The mass spectrum of secondary butyl isopropyl ether shows peaks (lines) at $m/z = 41,43,57,87,101 \& 116$. Considering appropriate fragmentation pattern, identify the species responsible for each of these lines.

7. What is Retro-Diels Alder rearrangement? Discuss the application of mass spectrometry to it.

SECTION – C

Answer any two questions : **2x20=40**

8. a) Discuss the origin of stokes and anti-stokes lines, based on classical theory. (8)
   b) Explain the application of vibrational spectroscopy in the determination of (i) force constants (ii) molecular shapes and (iii) functional groups, choosing a specific example in each case. (3x4=12)

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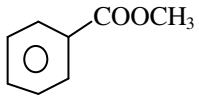
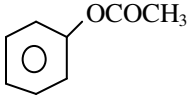
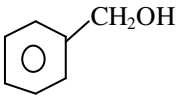
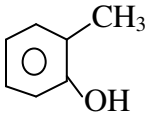
9. Explain the following:
   a) Franc Condon principle
   b) Shift reagents in NMR spectroscopy
   c) Principles of 2D NMR
   d) Types of transition in UV-VIS region

10. a) How will you distinguish between each of the following pairs, using UV-VIS, IR, Raman, NMR or mass spectrometry (any one or combination of methods)

(i)  and 

(ii)  and 

(iii) $(CH_3)_2O$ and $(CH_3)_2CO$ 3x5=15

b) Write a note on meta stable peak in mass spectrometry. 5

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