STELLA MARIS COLLEGE (AUTONOMOUS), CHENNAI - 600 086
(For candidates admitted from the academic year 2019 & thereafter)
SUBJECT CODE: 19CH/MC/SP 64
B.Sc. DEGREE EXAMINATION, APRIL 2022
BRANCH IV – CHEMISTRY
SIXTH SEMESTER

COURSE : MAJOR CORE
TITLE OF PAPER : SPECTROSCOPY
TIME : 30 MINUTES   **Maximum Marks** : 30 Marks

SECTION –A
Answer all the questions on the question itself   (30 x 1 =30 Marks)
  I.   **Choose the correct answers:**

1. The correct order of different types of energies is _____
   a) $E_{transl} \gg E_{elec} \gg E_{rot} \gg E_{vib}$ b) $E_{vib} \gg E_{elec} \gg E_{rot} \gg E_{transl}$
   c) $E_{elec} \gg E_{vib} \gg E_{rot} \gg E_{transl}$ d) $E_{rot} \gg E_{elec} \gg E_{vib} \gg E_{transl}$

2. A magic acid is a mixture of _____
   a) SbF_3 and fluoro sulphonic acid   b) sulphonic acid and SbF_3
   c) SbF_3 and H_2SO_4 d) fluoro sulphonic acid and $SbCl_3$

3. Which spectroscopic technique is used in deducing the correct structure of O_3 ?
   a) NMR   b) UV-visible   c) microwave   d) IR

4. The order of decreasing vibrational frequency for C-O, C-Cl, C-H, C-Br and C-C is _____
   a) C-C > C-O > C-Br > C-Cl > C-H   b) C-H > C-C > C-O > C-Cl > C-Br
   c) C-Br > C-Cl > C-O > C-C > C-H   d) C-O > C-Br > C-Cl > C-H > C-C

5. The most used laser for Raman spectroscopy is _____
   a) semiconductor laser   b) ND: YAG   c) Ruby laser   d) He-Ne laser

6. In UV-visible spectrometer the narrow spectral band can be isolated by coupling _____ filter with a second filter
   a) glass   b) interference   c) cut off   d) adsorption

7. The lanthanide shift reagents are β- diketonato complexes of _____
   a) Pr & Eu   b) Dy & Ce   c) La & Pr   d) Pr & Ce

8. Which type of ionic species are allowed to pass through the slit and reach the collecting slit in Mass spectrometer?
   a) positive ions of all masses   b) negative ions of all masses
   c) negative ions of the specific mass   d) positive ions of the specific mass

9. The frequency of vibration of a bond is a function of _____
   a) force constant of the bond   b) masses of the atom involved in bonding
   c) force constant of the bond and masses of the atom   d) bond order

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10. What is the correct order of λ_{max} for n $\longrightarrow$ σ^* transition ?
   a) R-OH > R-NH$_2$ > R-SH   b) R-OH < R-NH$_2$ < R-SH
   c) R-OH < R-SH < R-NH$_2$ d) R-OH > R-SH > R-NH$_2$

II.   Fill in the blanks :

11. The mass spectrum of bromomethane shows a characteristic isotopic molecular ion peak at _____

12. The number of bending mode of vibration in CH$_3$CHO is _____

13. The wavelength (λ) of a light is 420 nm, then its frequency is found to be _____

14. The number of signals in ^{13}C NMR for 2-propanol is _____

15. % Transmittance of the solution in UV- Visible spectroscopy will range between _____

16. For symmetric top rotors the moment of inertia is _____

17. The fingerprint region in IR is _____

18. The resonating frequency at which the chemical shift of CHCl$_3$ (δ = 7.28 ppm) occurs relative to TMS on a spectrum recorded on a 300 MHz spectrometer is found to be _____

19. The selection rule for microwave spectroscopy is _____ .

20. In UV absorption band the $\pi \rightarrow \pi^*$ transition is designated as _____ band

III.   Match the following:

21. Mass   - A. lanthanide shift reagents
22. Raman   - B. electronic transition
23. UV- Visible   - C. Polarizability
24. Microwave   - D. MALDI
25. NMR   - E. dipole moment

IV.   Answer in one / two lines :

26. What is fermi resonance ?
27. What is hypsochromic shift ?
28. What is Nitrogen rule ?
29. State Beer Lambart's law
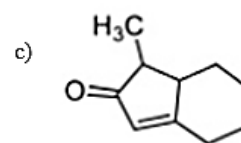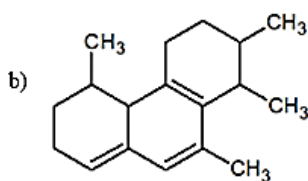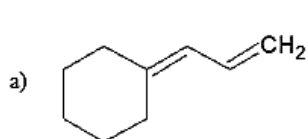30. What does resonance mean in NMR?
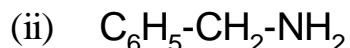
SECTION – B

V.   Answer any FIVE of the following: (5 x 6 = 30 Marks)
   1. Calculate λ_{max} for the given compounds: (3 x 2 = 6 Marks)

2. Explain the (2 x 3 = 6 Marks)

    (i)   Mc Lafferty rearrangement for 2-pentanone

    (ii)   Retro Diel's Alder fragmentation for 4,5- dimethyl cyclohex-1-ene

3. Distinguish between the given pairs using IR spectroscopy: (3 x 2 = 6 Marks)

    (i) $CH_3- NH_2$ and CH_3CN

    (ii)   PhOH and $CH_3-O-C_2H_5$

    (iii) CH_3CHO and CH_3COOH

4. Define Franck Condon principle. Explain how it is related to study the intensity of peaks.

5. a) From the rotational microwave spectrum of $^1H^{35}Cl$, it has been found that B = 10.59342 cm^{-1} . Given that the masses of ^1H and ^{35}Cl are 1.0078250 and 34.9688527 amu, respectively, determine the bond length of the $^1H^{35}Cl$ molecule. (3 Marks)

    b) Identify the number of signals for the following compounds in ^1H NMR spectrum :

                                                     (3 x 1 = 3 Marks)

    (i) $H_3C—COOMe$ (ii) $C_6H_5-CH_2-NH_2$ (iii)
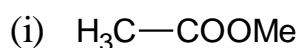
6. Discuss the principle and instrumentation of Single beam UV-Visible spectrometer with a schematic diagram.

7. What are the factors affecting the $^3J_{HH}$ in vicinal protons with examples?

SECTION-C

VI.   **Answer any TWO of the following :**   **(2 x 20 = 40 Marks)**

8. a) An organic compound with the molecular formula C_7H_8 gives the following spectral data:

    UV: λ_{max} 267nm & 269 nm

    IR : ν_{max} (cm^{-1}) 3500 (s); 2940 (s) ; 1440 to 1625 (s) ; 700

    ^1HNMR : δ(ppm) 7.0 – 7.38 [5H,s] and 2.34 [3H,s]

    Mass : M+ m/z 92, the other fragment ions show m/z 91(prominent peak), m/z 77, 65, 51 & 39

    Deduce the structure of the compound and give the fragmentation pattern of the compound

                                        (1+2+2+2+ 3+2 = 12 Marks)

b) What will be the force constant (k) for the bond in HCl if the fundamental vibrational

frequency is 8.667×10^{13} s^{-1} ?   (4 Marks)

c) What are stokes and anti-stokes lines ?   (4 Marks)

9. a) Account for the following: (4 x 2 = 8 Marks)

(i)   Ethylacetoacetate exhibits two bands in UV-Visible spectrum one at 275 nm (ε_{max} ~20) and 245 nm (ε_{max} ~18000)

(ii)   The C-I stretching frequency is very less (500 cm^{-1}) than C-H (2960 cm^{-1}) in IR spectrum.

(iii)   In mass spectrum the molecular ion peaks of aromatic hydrocarbons are more intense than aliphatic hydrocarbons.

(iv) ^{13}C NMR shows an increasing order of chemical shift value :

methane < acetylene < ethylene

b) Describe the principle and instrumentation of Mass spectrometry   (12 marks)

10. a) Explain the factors affecting UV- visible absorption bands   (8 marks)

b) Differentiate between IR and Raman spectroscopy   (5 Marks)

c) What is relaxation process in NMR? Explain   (7 Marks)

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