STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2015–2016 & thereafter)

SUBJECT CODE: 15CH/PC/MS34
M.Sc. DEGREE EXAMINATION, NOVEMBER 2019
BRANCH IV- CHEMISTRY
THIRD SEMESTER

COURSE : CORE
PAPER : MOLECULAR SPECTROSCOPY
TIME : 3 HOURS **MAX.MARKS :100**

SECTION – A **(20x1=20)**

Answer all the questions:
Choose the correct answer:

1. 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}

2. The molecule which is IR inactive and Raman active is
   (a) HCl (b) N_2 (c) SO_2 (d) protein

3. In the UV-Visible spectroscopy, the maximum energy required to excite an electron is from
   (a) non-bonded electron (b) π-electron (c) sigma electron (d) none of these

4. If the λmax of a compound shifts to shorter wavelength, the compound is said to exhibit
   (a) bathochromic shift (b) hypsochromic shift
   (c) hyperchromic shift (d) hypochromic shift

5. The sample in NMR absorbs frequency in _____ region.
   (a) microwave (b) X-ray (c) UV (d) radio wave

6. NMR inactive nuclei is _____.
   (a) ^{12}C (b) ^{1}H (c) ^{14}N (d) ^{31}P

7. M+2 peaks are observed in the mass spectrum of the compounds containing one of the following atom
   (a) fluorine (b) iodine (c) bromine (d) nitrogen

8. Which Statement is correct
   (a) Wave number is directly proportional to energy
   (b) Wave length is directly proportional to frequency
   (c) Wave length is directly proportional to energy
   (d) Wave number is directly proportional to wave length

9. Relative to a 2D,3D experiment has a better
   (a) S/N ratio (b) baseline (c) line shape (d) resolution

10. 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

..2

Fill in the blanks:

11. 400-800nm is the wave length region of_____ spectroscope.
12. The number of lines observed in ^{13}C spectrum of p-xylene are_____.
13. In NMR spectra for a triplet, the relative peak areas are in the ratio_____.
14. An organic compound containing an odd number of nitrogen atoms will have a molecular ion with an _____ mass number.
15. The IR spectrum of methanol (CH_3OH) shows sroung absorption at 3340(broad), 2945, 2833 and 1030cm^{-1}. The band assigned to the OH stretching is _____.

Single line answer questions:

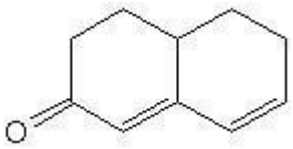
16. What is the selection rule of rotational spectra?
17. What is Born-Oppenheimer approximation?
18. How is the peak intensity arrived in NMR?
19. What is the even electron rule?
20. State Stevenson's rule.

SECTION – B **(5 x 8 = 40)**

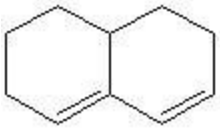
Answer any FIVE questions:

21. Explain the inversion phenomena and Stark effect.
22. Calculate the λ_{max} for the following compounds.

(i)



(ii)



23. Explain the meaning of the terms chemical shift and spin-spin coupling with reference to NMR spectra.
24. Explain the following terms:
    (a) base peak (b) isotope peak (c) molecular ion peak
25. Discuss how acetone and methyl acetate are identified by ^1H NMR and ^{13}C NMR.
26. a) Explain nuclear overhauser effect.
    b) Write briefly on 2D NMR technique. (4+4)
27. a) Determine the term symbol for O_2 molecule.
    b) Explain vicinal and germinal coupling constants (4+4)

SECTION – C (2 x 20 = 40)

Answer any TWO questions:

28. a.Explain the terms overtones and fundamental modes of vibrations ? (5)
    b. Explain Franck Condon principle. (5)
    c. Raman is complementary to IR. Explain with an example. (5)
    d. An organic compound of molecular formula C_8H_8O exhibited characteristic peaks at m/e 120,105,77 and 43. Deduce the structure and explain the fragmentation pattern(5)

29. a. Illustrate with an example "spin decoupling" technique in NMR spectroscopy. (8)
    b. Give an account of the applications of ^{19}F and ^{31}P NMR spectroscopic techniques. (6)
    c. Write short note on: (i) inductive cleavage (ii) Retro Diels-Alder cleavage. (6)

30. a. Assign the structure and justify your answer for the compound,$C_9H_{10}O_2$ with the following data
    UV: λmax:271nm IR: ν=1680cm^{-1}
    1HNMR:δ7.7(d, J=8Hz,2H),6.8(d, J=8Hz,2H),3.9(s,3H), 2.4(s,3H)
    EIMS: m/z 150,135,107 and 43. (10)
    b. Explain Mclafferty rearrangement with suitable example. (5)
    c. Account for the trend in CO stretching frequency values:
    $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$ (5)

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