STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2019–2020 & thereafter)

SUBJECT CODE: 19CH/PC/MS34
M.Sc. DEGREE EXAMINATION, NOVEMBER 2022
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. Which among the following vibrational transition will appear at lowest frequency?
   a) v =0 to v =1 b) v = 0 to v = 2 c) v = 0 to v = 3 d) v = 1 to v = 2

2. The first excited state of hydrogen molecule is
   a) $^1\Sigma^+_g$ b) $^1\Sigma^-_u$ c) $^3\Sigma^-_g$ d) $^3\Sigma^+_u$

3. Number of signals that appear in the ^{1}H-NMR spectrum of cyclohexane at low temperature is
   a) 1 b) 2 c) 3 d) 6

4. In phenol, the molecular ion is generated by the preferential removal of electron from
   a) σ – bonding molecular orbital b) π – bonding molecular orbital
   c) non-bonding molecular orbital d) any one of σ/π/non-bonding MOs (no restriction)

5. Index of Hydrogen deficiency for the compound $C_{13}H_{26}O$ is
   a) 0 b) 1 c) 2 d) 3

Fill in the blanks:

6. The specific selection rule for the Rotational Raman spectra of a diatomic molecule is ----------.
7. ---------- shift is observed in λ_{max} value of Aniline when it is mixed with HCl.
8. γ-value of ^{13}C-nucleus is roughly ------ times that of γ-value of ^{1}H nucleus.
9. The mass spectrum of a compound shows M^+ (molecular ion) and M+2 peaks in intensity ratio 1:1. This indicates the presence of --------- in the compound.
10. The number of ^{1}H-NMR signals observed for the compound Bicyclo[2,2,2]octane is ----------.

State whether True or False:

11. Rotational constant associated with first excited vibrational level is greater than ground vibrational level of the ground electronic state.
12. n to π* transition is a symmetry allowed electric dipole transition.
13. DEPT is an NMR method used to detect the presence of Chlorine, Bromine and Iodine atom in a molecule.

..2

14. Mass spectrum of a mononuclear metal carbonyls consists of signals with equal spacing of 28units.
15. A sharp signal is observed at 3300cm^{-1} for Aliphatic tertiary amine.

Match the following:

16. v = 2 to v = 3	i) Second overtone transition
17. Low value of transition probability	ii) O-branch lines
18. $\omega_e(1-2x_e)$	iii) S-branch lines
19. $\Delta J = -2$	iv) Second hot transition
20. $\Delta J = +2$	v) Fundamental vibrational transition

SECTION – B **(5 x 8 = 40)**

Answer any FIVE questions:

21. The energy separation of $^{12}C^{16}O$ rotational energy levels between J = 3 and J = 9 is 24 cm^{-1}. Calculate the rotational constant of $^{13}C^{16}O$ in cm^{-1}.
22. Explain the Rovibrational spectra of a Diatomic molecule under invalid Born-Oppenheimer approximation.
23. If high resolution electronic spectrum of a diatomic molecule is given, how will you determine the dissociation energy associated with the excited electronic state.Explain.
24. Explain the following:
    a) H_3PO_2 – ^{1}H-NMR spectra and ^{31}P-NMR spectra
    b) PCl_3F_2 – ^{19}F-NMR spectra and ^{31}P-NMR spectra
25. The g-factor of ^{1}H and ^{13}C are 5.6 and 1.4 respectively. For the same value of the magnetic field strength, if ^{1}H-resonates at 600MHz, calculate at what frequency would ^{13}C resonates.
26. Predict the Fragmentation pattern for the following compounds from their molecular ion.
    a) 1-Hexanol b) 2-Hexanol c) 3-Pentanone and d) Nitrobenzene.
27. A compound ($C_9H_{10}O_2$) displays the following spectral data.
    IR: 1690 cm^{-1}
    ^{1}H-NMR: δ 2.5 (s, 3H), 3.8 (s, 3H), 6.9 (d, J=8 Hz, 2H), 7.8 (d, J=8 Hz, 2H) ppm
    ^{3}C-NMR: δ 197, 165, 130, 129, 114, 56, 26 ppm.
    Predict the structure of the compound.

SECTION – C (2 x 20 = 40)

Answer any TWO questions:

28. a) The rotational Raman spectrum of $^{35}Cl_2$ shows a series of Stokes lines separated by 0.9752 cm^{-1}. Calculate the bond length of the molecule. The spin of ^{35}Cl is 3/2. Does this influence the intensity/spacing in the rotational Raman spectra? (8 marks)

b) How would you distinguish between ortho, para and meta xylenes from proton decoupled ^{13}C spectra? (3 marks)

c) Explain why the ^{13}C chemical shifts span a much larger range than those of protons. (2 marks)

d) Sketch the expected ^{31}P-NMR spectrum of HPF_2 when a) $J_{P-F} > J_{P-H}$ b) $J_{P-H} > J_{P-F}$ (7 marks)

29. Explain:

a) Mc Lafferty Rearrangement (10 marks)

b) Base peak (2 marks)

c) Metastable peak (2 marks)

d) Stevenson's rule (2 marks)

e) Retro Diels-Alder Cleavage (4 marks)

30. a) Derive the energy expression of a a nonrigid diataomic rotor and explain the significance of the centrifugal distortion constant (8 marks)

b) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433cm^{-1} apart. Calculate the rotational constant B and hence the moment of inertia and bond length of the molecule. (6 marks)

c) Alternate lines of the P and R branches in the rotational vibrational spectrum of acetylene are less intense,.Explain (6 marks)

****