STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI – 600086
(For candidates admitted from the academic year 2019-20 & thereafter)

SUBJECT CODE: 19CH/PC/MS34

M.Sc. DEGREE EXAMINATION, NOVEMBER 2020
BRANCH IV- CHEMISTRY
THIRD SEMESTER

COURSE: MAJOR CORE
PAPER: MOLECULAR SPECTROSCOPY **MAXIMUM MARKS: 50**
TIME: 90 MINUTES

PART A

ANSWER ALL THE QUESTIONS **(11 x 1 = 11 marks)**

I. Choose the correct answer

1. The number of signals in the C-13 NMR is less than the number of carbons in the compound. We can predict
   a) Symmetry in the compound b) Presence of a diastereomer
   c) Presence of an aromatic ring d) Presence of more than one tertiary carbons

2. The presence of a 'doublet' and a 'septet' in the proton NMR spectrum of a compound indicates the presence of a
   a) ethyl group b) isopropyl group c) sec- butyl group d) ethyl or methyl group

3. Consider the fragmentation in the mass spectra of an organic compound
   A^+ (m/z = 148) → B^+ + CO.
   If B^+ is a metastable ion its m/z value will be
   a) 120 b) 97.3 c) 134 d) 28

4. The selection rule for a rovibrational transition is
   $a)\ \Delta v = \pm 1,\ \pm 2,\ \pm 3,$ ... and $\Delta J = \pm 1$ b) $\Delta v = \pm 1,\ \pm 2$ and $\Delta J = 0$
   c) $\Delta v = 0$ and $\Delta J = \pm 1$ d) $\Delta v = \pm 1$ and $\Delta J = \pm 1, \pm 2,\ \pm 3,$ ...

5. Extended conjugated leads to a _____ in a uv-visible spectrum.
   a) Bathochromic shift b) Hypsochromic shift and hyperchromic shifts
   c) Bathochromic and hyperchromic shifts d) Hypsochromic shift

6. Which of the following transitions are responsible for the ammonia doublet?
   a) 0g → 1g, 0g → 1u b) 0u → 1g and 0u → 1u
   c) 0u → 1u and 0g → 1g d) 0g → 1u, 0u → 1g

II. Answer in a line or two

7. State Stevenson's rule.
8. Give the products of Retro Diels-Alder Cleavage of 1,4 dimethyl cyclohexene.
9. Differentiate between overtones and hot bands.
10. Calculate the number of modes of vibrations for cyclohexane.
11. What is the term symbol of the hydrogen molecule in the excited state σ_{2p_g}?

SECTION B

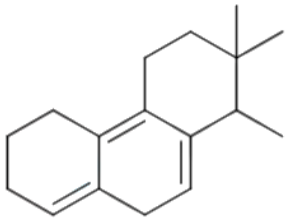
ANSWER ANY THREE QUESTIONS (3 x 8 = 24 marks)

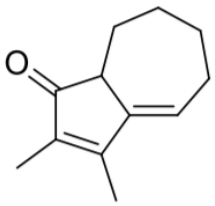
12. Discuss Solid State NMR and explain the significance of Magic angle. (5 + 3 marks)
13. a) Explain Nuclear Overhauser enhancement with an example. (4 marks)
    b) Show that the ratio of the M, M+2, M+4 peak in the molecule CH_2Cl_2 is in the ratio 9:6:1. Given that the isotopic abundance of ^{35}Cl and ^{37}Cl are 75% and 25% respectively. (4 marks)
14. a) Classify molecules based on their moment of inertia. (4 marks)
    b) Explain the quantum theory of Raman effect. (4 marks)
15. a) State the Franck-Condon principle. Explain the intensity distribution when $r_e' \approx r_e''$, $r_e' < r_e''$ and $r_e' \gg r_e''$. (5 marks)
    b) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the rotational constant B and hence the moment of inertia and bond length of the molecule. (The reduced mass of BrF is 25.4312 x 10^{-27} kg) (3 marks)

SECTION C

ANSWER ANY ONE QUESTION (1 x 15 = 15 marks)

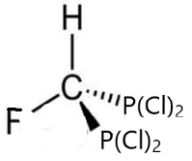
16. a) An organic compound with molecular formula C_8H_7OBr showed abundant mass spectral peaks at M+(m/z 198), base peak (m/z 183) and fragment ion (m/z 155). All three peaks showed a M+2 peak. Other spectral data are
    UV: λ_{max} = 258 nm ($\log_{10} \varepsilon$ = 4.2) Solvent: ethanol
    IR: 1693 cm^{-1} CCl_4 Solution
    ^{1}HNMR: δ7.4 (2H, d), δ7.6 (2H, d) and δ2.4 (3H, s).
    ^{13}C NMR (decoupled): 198, 125, 129, 131, 139, 25
    Deduce the structure of the compound and predict the principal ions in its mass spectrum. (8 marks)
    b) Calculate the λ_{max} values of the following compounds based on the Woodward-Fieser's rules. (4 marks)





    c) Give the energy expression of an anharmonic oscillator and calculate the zero point energy from it. (3 marks)

17. a) Explain McLafferty rearrangement using hexanone as example. (4 marks)
    b) Give number of signals and splitting pattern obtained in the ^{1}H NMR and ^{31}P NMR of (1 + 2 marks)



c) Discuss the polarizability ellipsoids of the water molecule and deduce which modes are Raman active. (5 marks)

d) The fundamental band for HCl is centered at 2886 cm^{-1}. If the rotational constant is 10.61 cm^{-1}, calculate the wavenumber of the first two lines of the P and R branches of HCl. (3 marks)

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