M.Sc. CHEMISTRY
FOURTH SEMESTER
SPECTROSCOPY-III
MSC-401

(Use separate answer scripts for Objective & Descriptive)

Duration : 3 hrs. Full Marks : 70

[PART-A : Objective]

Time : 20 min. Marks : 20

Choose the correct answer from the following: *1x20=20*

1. The asymmetric stretching of CO_2 molecule is:
   a. IR active but Raman inactive
   b. IR inactive and Raman active
   c. both IR and Raman active
   d. both IR and Raman inactive

2. The intensity of NMR splitting pattern of a single magnetic nucleus with two near by equivalent protons is:
   a. 1:2:1 b. 2:1:2 c. 1:1:1 d. 1:4:1

3. As per Beer-Lambert Law, relation among absorbance(A), the molar absorption coefficient(ε) and transmittance(T) is:
   a. $A = \varepsilon Cl = -\log T$
   b. $A = \varepsilon Cl = T$
   c. $A = \varepsilon C/l = 1/T$
   d. $A = \varepsilon l = c \log T$
   l = thickness of the sample

4. UF_6 molecule is a/an:
   a. spherical top molecule
   b. asymmetric top molecule
   c. prolate top molecule
   d. oblate top molecule

5. Radiation of frequency 10^{14}Hz is a/an:
   a. visible radiation
   b. microwave radiation
   c. x-ray radiation
   d. radio frequency radiation

6. The spectroscopic technique by which the ground state dissociation energies of a diatomic molecule can be estimated is:
   a. infra red spectroscopy
   b. microwave spectroscopy
   c. UV-visible absorption spectroscopy
   d. X-ray spectroscopy

7. Which of the following molecule exhibit rotational spectra?
   a. H_2 b. CO c. N_2 d. CO_2

8. The microwave spectrum of a molecule yields three rotational constants. The molecule is a/an:
   a. prolate symmetric top
   b. asymmetrical top
   c. spherical top
   d. oblate symmetric top

9. The number of vibrational spectral lines common in both IR and Raman spectra for CO_2 is:
   a. 1 b. Zero c. 2 d. 3

10. What is the x axis of a mass spectrum?
    a. mass
    b. mass/charge
    c. charge
    d. mass/energy

11. Which of the following is the definition of a base peak of the mass spectrometer?
    a. Ion with lowest m/e.
    b. Molecular ion peak.
    c. Most abundant ion.
    d. Ion arising from loss of proton from the molecule.

12. Ring strain in lactone:
    a. decreases c = c stretching frequency
    b. increases c = c stretching frequency
    c. increases c = 0 stretching frequency
    d. decreases c = 0 stretching frequency

13. C-H stretching frequency of an alkane is 2900 cm^{-1}. The corresponding frequency for C-D stretching is:
    a. 3952.6 cm^{-1}
    b. 2860 cm^{-1}
    c. 2128 cm^{-1}
    d. 1561 cm^{-1}

14. Nuclear Overhauser effect helps in predicting the:
    a. two different protons in close proximity
    b. protons on adjacent carbon atoms
    c. the geometry of the molecule
    d. olefinic protons

15. The complexes of metal Europium(EU) and Neodymium(Nd) are respectively known to cause shift of NMR signal:
    a. both down field
    b. both up field
    c. down field and up field
    d. up field and down field

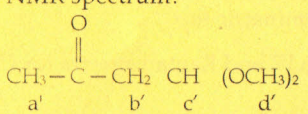
16. The separation between the first stoke's line and first anti stoke's line in the rotational Raman spectra of oxygen molecule is:
    a. 4B b. 8B c. 12B d. 20B

17. The product of nuclear g factor (g_N), the nuclear magneton (β_N) and the magnetic field gives:
    a. spin-spin coupling constant
    b. magnetogyric ratio
    c. chemical shift
    d. energy of transition from α to β state

18. Rotational constant of $^{14}N_2$ is 2 cm^{-1}. The frequency of Rayleigh line is 20487 cm^{-1}. The wave number of first anti-stokes rotational line (in cm^{-1}) is:
    a. 20475 b. 20475 c. 20495 d. 20499

19. Quaternary carbon spectrum:
    a. appear in both ^{13}C NMR and DEPT spectrum.
    b. miss in both ^{13}C NMR and DEPT spectrum.
    c. miss in ^{13}C NMR but appear in DEPT spectrum.
    d. appear in ^{13}C NMR but miss in DEPT spectrum.

20. Which hydrogen a'-d' in the following molecule give a triplet signal in a normal 'H NMR spectrum?



    a. hydrogen a'
    b. hydrogen d'
    c. hydrogen b'
    d. hydrogen c'

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(PART-B : Descriptive)

Time : 2 hrs. 40 min. **Marks : 50**

[Answer question no.1 & any four (4) from the rest]

1. a) Discuss the characteristic vibrational frequencies of alkanes. 5+3+2=10
   b) What will be the characteristic vibrational frequency in wave number unit of C-C bond having force constant 5.0×10^5 dynes per centimeter?
   c) Calculate the total number of modes of vibration in allyl bromide, $CH_2=CHCH_2Br$

2. a) Explain why the frequency of C=0 is higher in γ lactum as compared to δ lactum. 5+5=10
   b) Discuss with examples the different types of bending vibrations.

3. a) Suggest the method to distinguish primary, secondary and tertiary alcohols from their mass spectra. 5+5=10
   b) In the mass spectrum of a compound peaks for m/e values at 88, 70, 55, 42 was found. Identify the compound with proper explanation.

4. a) On the basis of Dirac Vector model explain the phenomenon of spin-spin coupling. 5
   b) What do you mean by first order and non-first order spectrum in NMR spectroscopy? State the conditions. 3+2=5

5. a) Predict and explain the proton NMR and ^{13}C NMR spectra of pentanoic acid. 5+5=10
   b) Discuss the advantages and disadvantages of ^{13}C NMR over proton NMR.

6. a) What do you mean by DEPT technique? Discuss the DEPT spectra of Isopentyl acetate and compare it with the decoupled ^{13}C spectrum. 2+3+2=7
   b) Discuss the effect of deuteration in simplification of complex NMR spectra. 3

7. A compound with molecular weight 116 gives the following spectral information's. 10
   i) UV : 283 mμ ε_{max} 22
   ii) IR : 3000-2500 (b), 1715 (s), 1342 (w) [in cm^{-1}]
   iii) NMR : 7.88γ singlet (3H), 7.40γ triplet (2H)
   7.75γ triplet (2H) and -1.1γ singlet (1H)
   Find the structural formula of the compound.

8. a) What do you mean by shift reagent? Discuss the chemical properties of shift reagent. Mention some applications of it. 2+2+1=5
   b) What is a 90^0 pube? Discuss the working principle of F.T. NMR spectroscopy. What do you mean by FID? 1+3+1=5

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