D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE-1

III Semester

UNIT-I SPECTROSCOPY

Electronic, Vibrational & Rotational Spectroscopy

Section-A (6 marks)

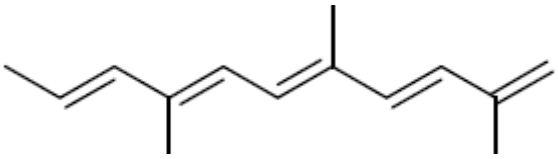
1.Bring out the significance of Finger print region.

2.How is IR spectroscopy useful in distinguishing between intermolecular and intramolecular hydrogen bonding.

3.Explain the principle and applications of microwave spectroscopy.

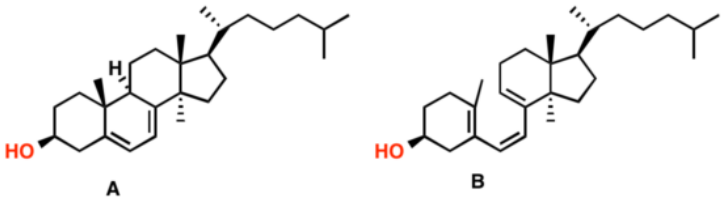
4.Explain the principle, instrumentation and application of IR spectroscopy

5. Estimate the λmax for the compound shown:

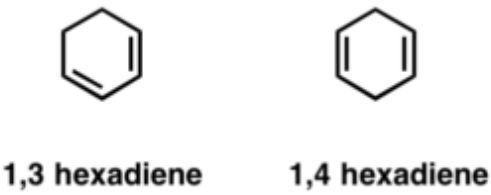


6. Which molecule absorbs at the longest wavelength?

i.



ii.



7. Express the wavenumber value of 3000 cm^{-1} in terms of wavelength (in meter units) frequency (in Hz), and associated energy (in kJ/mol).

8. Explain how you could use the C-C and C-H stretching frequencies in IR spectra to distinguish between four constitutional isomers: 1,2-dimethylcyclohexene, 1,3-octadiene, 3-octyne, and 1-octyne.

9. List actual frequencies for each signal to the nearest cm^{-1} unit

a) 1-methylcyclohexanol

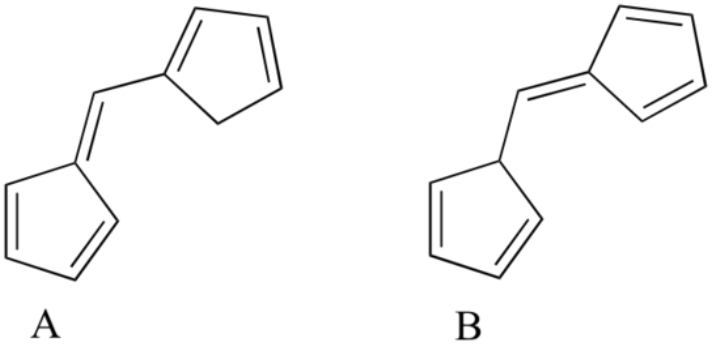
b) 4-methylcyclohexene

c) 1-hexyne

d) 2-hexyne

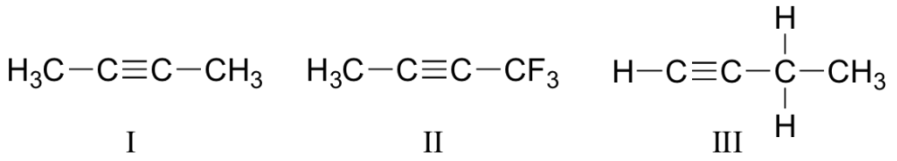
e) 3-hexyne-2,5-diol

10. Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum?

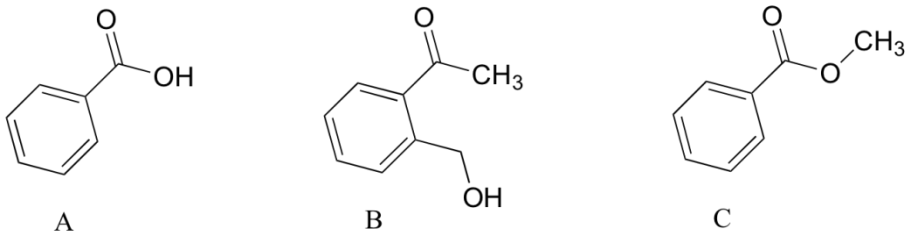


A B

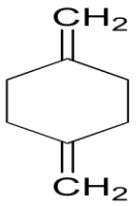
11. Explain how you could use IR spectroscopy to distinguish between compounds I, II, and III.



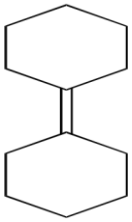
I II III



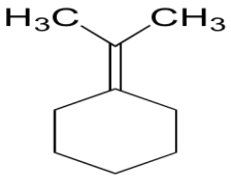
A B C



X

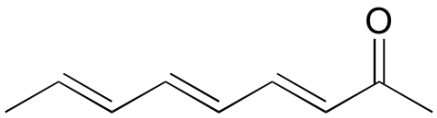


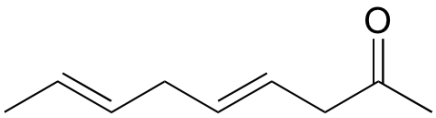
Y



Z

12. Which would be more useful in distinguishing the two compounds shown below: IR or UV spectroscopy? Explain.





13. Explain about solvent effect.

Section-B (15 marks)

1. a) Discuss the various factors of that affect the position and intensity of UV absorption bands.

   b)How are the following distinguish by IR spectrum.

   Nitrophenol and P-nitrophenol.

   Methyl benzoate and phenyl acetate.

   Cyclopentanone and cyclohexanone.

2. a)Explain how Woodward rules are used in the calculation of of dienes.

   b)Define the following terms with examples.

   Chromophore

   Auxochrome

   c)Explain Frank Condon principle.

3. a. Explain the Factors Influencing Vibrational Frequencies.

   b. Given that the C–H stretching vibration for chloroform occurs at 3000 cm−1, calculate the C–D stretching frequency for deuterochloroform. The relevant atomic masses are $^{1}H = 1.674 \times 10^{-27}$ kg, $^{2}H = 3.345 \times 10^{-27}$ kg and $^{12}C = 1.993 \times 10^{-27}$ kg.

4. a. What is Overtone and Combination Bands?

b. Explain about Fermi Resonance and Group Frequencies.

5. Explain about rigid rotor and non-rigid rotor.
6. Explain about simple harmonic oscillator and unharmonic oscillator.
7. Explain about the principle and types of transition present in electronic spectroscopy.
8. a. Calculate the relative populations of rotational and vibrational energy levels.

   b. Distinguish between the energy levels of a rigid and a non rigid rotor.

   c. Outline the selection rules for rotational and vibrational spectra and rationalize the role of the molecular dipole moment in the selection rules.
9. a. Calculate the value of I and r of CO. B = 1.92118 cm-1.

   b. Which of the following molecule exhibit rotational and/or vibrational spectra/(or microwave and infrared active)?

   H2, HF, CO2, OCS, CS2, I2, NH3, CH4, and benzene.
10. a. For HCl, B = 10.593 cm-1 and the centrifugal distortion constant D = 0.00053 cm-1. Calculate the first four rotational levels. Calculate the force constant for HCl from the value of D.

    b. Derive the formula $\Delta E_{rot} = E_{J+1} - E_J = 2B(J+1) - 4D(J+1)^2$ from the formula for E_{J+1} and E_J
11. Explain the microwave spectrum of rigid diatomic molecules. What is non-rigid rotor? How did its spectrum differs when compared to rigid rotor.
12. a. The B rotational constant of a phosphorus pentafluoride, PF_5, molecule is 3.566 Hz. Calculate the lengths of the equatorial P-F bonds.

    b. Which of the following molecules exhibit pure rotational (microwave) spectra?

    HF, NH3, CH4, CH3F, BF3, H2O, C2F2H2, O3, CO2, toluene, Argon---HCl

    c. Classify the following molecules as spherical, symmetric or asymmetric tops, and state which will give pure rotational spectra. For the symmetric tops, sketch the principal axes and indicate the unique axis. SF6, BrF5,

NH3, NO2, CS2, CH2, N2O, CF3I, BH3, BeH2, SO2, C6H6, XeF6, IF7

UNIT-II Raman & ^{1}H- NMR spectra

Section-A (6 marks)

1. A compound is found to have molecular formula $C_9H_{10}O_2$. The IR spectrum shows intense bands at 1740 cm^{-1} and 1220 cm^{-1}. The PMR spectrum shows a five proton singlet at tau-2.8, a three proton singlet at tau-8.04 and a two proton singlet at tau-5.0. Suggest the suitable structure for the compound whose m/z=150.
2. A compound is found to have molecular formula C_3H_8O. The IR spectrum shows intense bands at 3400 cm^{-1}. The PMR spectrum shows a upfield doublet at δ-1.2 (6H) and δ-3.8 (septet, 1H) and δ-4.(S, 1H). What is the structure of the compound?.
3. Explain in detail about the pure rotational raman spectra of diatomic and symmetric top molecules.
4. Enumerate in detail about the vibrational raman spectra of diatomic molecules
5. Discuss in detail about the structural applications of raman spectroscopy
6. What are stokes and antistokes lines ?. Among these two lines which line is more intense. Account for it.

7. (a) State and explain Mutual exclusion principle (2).

   (b)Discuss in detail about the principles of NMR (4).

8. An organic compound of molecular formula C_{10} H_{12} O_2 gives the following proton NMR signals δ-1.0 (t, 3H), 3.4 (s, 2H), 3.8 (q, 2H), 7.0 (s, 5H) and mass spectral peaks at m/z=164, 119, 91, 65.Arrive at the correct structure of the compound and show the mass spectral fragmentation pattern.

9. Explain double resonance in NMR and the applications of the same .

Section-B (15 marks)

10. (a) Discuss in detail about the various factors which affect the chemical shift (7)

    (b)Explain in detail about the advantages of FT-NMR over CWNMR (4)

    (c) Give a brief account on spin-spin coupling (4)

11. Describe in detail about AX and AMX coupling phenomenon (15).

12. Write short note on

    (i) Chemical Exchange

    (ii) Nuclear Overhauser effect

13. Predict the ^1H nmr spectrum of the following compounds

    CH_3CH_2Cl (ii) CH_3CHO (iii) H_3C-CH(OH)-CH_3 (iv) $C_6H_5CH_2OH$ (v) Mesitylene

14. Describe in detail about CWNMR and FTNMR techniques.

15. (a) Explain in detail about the various types of coupling (8)

(b) Explain the origin of chemical shift in nmr spectra. Explain the factors influencing chemical shifts(7).

15. (a) Identify the structure of the organic compound having $C_9H_{11}NO_2$ as the molecular formula and the following spectroscopic data (7)

IR (Nujol) : 1720 cm^{-1}

^{1}H-NMR (CDCl3): 7.9 (d, 2H, J=8Hz), 6.8 (d, 2H, J=8 Hz); 4.3 (q, 2H, J=7.1 Hz); 4.0 (broad, s , 2H, D_2Oexchangeable), 1.2 (t, 3H, J=7.1Hz) ppm

(b) How would you distinguish between 1 chloropropane and 2-chloropropane by proton NMR(8).

16. (a) A compound of the molecular formula $C_9H_{17}Br$ exhibhited the following NMR signals : δ=2.15 (quintet, 2H), 2.75 (t, 2H), 3.38 (t, 2H) and 7.22 (s, 5H). Identify the structure of the compound (5)

(b) Assign the structure and justify your answer for the compound $C_9H_{10}O_2$ with the following spectral data

UV: λ max : 271nm; IR: ν=1680 cm^{-1}

1H NMR: δ-7.7 (d, J=8Hz, 2H), 6.8 (d, J=8Hz, 2H), 3.9 (s, 3H), 2.4 (s, 3H)

EIMS: m/z: 150, 135, 107, 43.

17. (a) Enumerate the applications of chemical shift in NMR.(5)

(b) Illustrate and explain the NMR spectral pattern expected for AX and AMX type molecule (10)

18. (a) Sketch the qualitative proton NMR spectrum expected for $(CH_3CH_2)_2O$ (5).

(b) Explain the principle of Fourier transform resonance spec (5).

(c)How will you distinguish the following pair using proton NMR (2)

(i) cis and trans 1,2 dichloroethene

(d) Three isomeric dimethyl cyclopropanes give respectively 2, 3, 4 signals in their proton NMR spectrum. Identify their structure and explain the origin of the signals 93).

UNIT-III NMR Spectra –^{13}C ^{31}P and ^{19}F and NQR Spectra

SECTION-A (6 marks)

1. Explain spin spin coupling in proton NMR .What do you understand by off reseonance decoupling?
2. Give a brief account on NMR shift reagents
3. Explain in detail about the principle of NQR spectroscopy
4. Discuss in detail about the various factors which affect C^{13} chemical shift.
5. (a) How will you distinguish ortho xylene and para xylene using C^{13} nmr spectroscopy? (2)

   (b) Discuss in detail about the term “off resonanace decoupling” (4)
6. Sketch the P^{31} nmr spectrum of HPF_2 assuming $J_{P-H} > J_{P-F}$ and $J_{P-F} > J_{P-H}$
7. (a) Explain how ^{31}P NMR spectra can distinguish hypophosporous acid from phosphorous acid(3)

   (b)How is the ionic character of the covalent bond estimated from NQR measurements? (3)

8. The ^{19}F NMR spectrum for TiF_4 in donor so;lvents at -30°C showed two triplets of equal intensity. But at 0°C only a single peak is obtained. Explain (6)

9. Illustrate with three different examples the use of ^{31}P NMR in the structural elucidation of some simple phosphorous compounds.

SECTION-B (15 Marks)

10. (a) How does phosphorous acid differ from hypophosphorous acid in its NMR spectrum?(4)

    (b) NF_3 shows a sharp ^{19} F resonance at -205°C while a sharp triplet at room temperature .Account for it.(4)

    (c) How is the spectral width of an NMR signal dependent on the relaxation time?(4)

    (d) ^{11} B NMR spectrum is a nonet And its proton NMR is a decet for B_3H_8 anion. Propose a structure and account for the above observation(3).

11. (a) Explain the NQR spec of BrCN, KI_3, Sn, Pt and Se compounds (7)

    (b) Construct the ^{31}P NMR resonance signals expected for $HP_2O_5^{3-}$ anion if $J_{P-P} > J_{P-H}$ (8).

12. (a) The ^{31}P NMR spectrum of P_4S_3 consists of two peaks with intensity ratio of three to one. The more intense peak is a doublet and the other a quadruplet. Interpret with the structure (5).

    (b) The ^{19}F NMR spectrum of BrF_5 consists of two peaks with intensity ratio of four to one. The more intense peak is a doublet and the other a quadruplet. Interpret with the structure (5).

(c) The ^{19}F NMR spectrum of SF_4 shows two triplets at -98°C whereas at room temperature only a single sharp peak is observed. Explain the observations(5).

13. (a) How many lines are expected in the ^{31}P NMR of $HPO(OH)_2$? (3)

(b) Deduce the ^{19}F NMR spec of triagonal bipyramidal PF_5 molecule (4)

(c) Write short note on applications of ^{19}F and ^{31}P NMR spectroscopy (8)

UNIT-I VESR and Photoelectron Spectroscopy

SECTION-A (6 marks)

1. a).Write a short note on Auger Spectroscopy.
   b). Which of the following systems will show ESR spectrum?
2. a). State and explain Koopmans theorem.
   b.What is kramers degeneracy? Taking Mn(II) case, explain the ESR Spectrum obtained for its complexes.
3. Which of the following systems will show ESR spectrum?

   a)H b)H_2 c)Na

SECTION-B (15 Marks)

4. Write a short note on
   a).hyperfine splitting constant.
   b).g-value
   c).Zeeman equation
   d).Koopmans theorem
5. a).Describe in detail the instrumentation for scanning the ESR spectrum of a compound.
   b.Write a note on g-value and hyperfine splitting constant.
6. a) Describe in detail about the Kramers degeneracy.
   b) Outline the esr spectrum of bis(Salicylaldimine) Copper(II) compex.
7. a).Explain hyperfine splitting.

b).Deduce the PE specta MnF_2 and FeF_2.

c).Deduce the PE spectra of N_2, O_2 and F_2.

UNIT-V Mass and Mossbauer Spectroscopy

SECTION-A (6 marks)

1. What is Nitrogen rule? Explain with suitable examples.
2. Write short note on Mclafferty rearrangement reaction with suitable examples.
3. Explain the basic principle of Mass spectroscopy.
4. Give an account on measurement techniques of FAB & SIMS.
5. What is base peak and metastable peak and briefly explain it.
6. What is quadrapole interaction and explain with suitable examples.
7. What are all the factors which are affecting the Mossbauer spectra.
8. Explain the quadrapole and magnetic interaction of sodium nitropurosside.
9. Explain the cleavage patterns in mass spectra.
10. Calculate the m/e values for catheol and naphthalene and cresols.
11. Calculate the m/e values for decodecane and tertiary butyl amine
12. Explain the application of MB Spectrum of $FeSO_4.7H_2O$, $K_4[FeCN_6].3H_2O$, $K_3[FeCN_6]$, $SnCl_4$.
13. Explain the retro diels alder reaction in mass spectra.

SECTION-B (15 Marks)

14. Explain in detail about the instrumentation of mass spectra.
15. Explain the cleavage patterns for alcohols, ketones and alkanes with suitable examples.
16. Write a note on
    i. Molecular ion peak.
    ii. Metastable ion peak.
    iii. Base peak.
17. i. Explain the quadra pole interaction and magnetic interaction of MB Spectra.(8)

ii . Write a note on nitrogen rule with suitable examples.(7)