15P309 (Pages: 2) Name………………

Reg. No………………

THIRD SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2016
(CUCSS - PG)
(Chemistry)
CC15P CH3 C09 - MOLECULAR SPECTROSCOPY
(2015 Admission)

Time: Three Hours Maximum: 36 Weightage

Part A
(Answer *all* questions. Each question carries **1** weightage)

1. Explain the relevance of Heisenberg's uncertinity principle in predicting the line width of spectrum.
2. Explain the Raman activity of the various modes of vibrations of pyramidal AB_3 molecules
3. Explain why the Stock's lines are more intense than antistock's lines in Raman scattering?
4. What are overtones and combination bands in IR spectroscopy?
5. Comment on the differences between the scales in ^1H and ^{13}C NMR spectroscopy.
6. NO shows a Q branch in the vibration-rotation spectrum why?
7. How many NMR energy levels are possible for nucleus with a spin I=3/2?
8. Predict the EPR spectrum of the following radicals (a) $^{12}CF_2H$, (b) $^{13}CF_2H$.
9. M- nitrophenol in neutral solution absorbs at 330nm while in alkaline solution absorbs at 380nm, in contrast p-nitrophenol has absorption maximum at 320nm in neutral solution and 400 nm in alkaline solution. Explain.
10. How will you confirm the conversion of benzene to cyclohexane with ^1H NMR and ^{13}C NMR spectroscopy?
11. How IR spectroscopy is used in identifying the nitro and cyano groups?
12. Explain Cotton effect.

Part B
(Answer *any eight* questions. Each carries **2** weightage)

13. In a given organic compound two kinds of protons exhibit signals at 50Hz 200Hz using a 60MHz instrument. What will be their relative position using 90MHz instrument? Also convert the position of signals into delta scale.
14. Apply 1H NMR and 13C NMR spectroscopic techniques and explain how will you confirm the following oxidation conversions. Explain all characteristic features of the ^1H NMR and ^{13}C NMR of the substrates and the products.

     a) CH3-CH2-CH2-OH   →   CH3- CH2-CHO

     b) CH3-CH(OH)-CH3   →   CH3-CO-CH3

15. Explain Nuclear Overhauser effect based on cross polarization theory and its application in NMR.
16. The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines separated by 0.71433 cm^{-1}. Calculate the rotational constant, moment of inertia and Br-F bond length.
17. Explain the various factors affecting the intensity of spectral line.
18. Explain McLafferty rearrangement in mass spectrometry.
19. Explain Karplus Equation. How it is used in structure determination?
20. Sketch the approximate ^1H NMR and ^{13}C NMR and mass spectra of 2-butenone. Explain the spectral features.
21. Explain Nitrogen rule and Rule of Thirteen in mass spectrometry.
22. Explain Off- resonance and noise decoupled spectra in NMR
23. Explain the factors contributing to chemical shift in NMR spectroscopy.
24. Explain with energy level diagram, the quadrupolar splitting in Mossbauer spectroscopy.

Part C
(Answer *any two* questions. Each carries **4** weightage)

25. Define and explain quantum mechanically spin-spin coupling to first order approximation. Using tree diagram method explain AX, AX$_2$, AX$_3$, A$_2$X$_3$, and AB type coupling.
26. a) Discuss the use of chemical shift values in obtaining stereochemical information in proton NMR.
    b) Predict the structure of the compound with the following spectral characteristics:
       Molecular formula: C$_8$H$_{10}$O; IR peaks at 3010, 2870, 1605, 1510, 1005 and 805cm-1;
       NMR δ = 2.25 singlet (3H); 3.72 singlet (3H); 6.78 doublet (2H); 7.05 doublet (2H).
27. Explain
       a) Classical and Quantum theory of Raman effect
       b) P,Q and R branches of rotation vibration spectrum.

28. Explain
       a) DEPT and INEPT in NMR
       b) Determination of T1 and T2 (relaxation time) in FT NMR

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