LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – APRIL 2010

CH 3810 - MOLECULAR SPECTROSCOPY

Date & Time: 26/04/2010 / 9:00 - 12:00   Dept. No.   Max. : 100 Marks

PART A
Answer ALL the questions.   (10 x 2 = 20 Marks)

1. What is 'resolving power' of a spectrometer? Mention any one method of improving it.
2. The rotational constant for $H^{35}Cl$ is observed to be 10.5909 cm^{-1}. Calculte the bond length.
3. What is centrifugal distortion constant and its significance?
4. Explain the principle of mutual exclusion with an example.
5. Mention three important characteristics of lasers which differ from ordinary light.
6. What is the chemical shift in terms of δ, if the observed chemical shift of proton is 200Hz from TMS and the instrument frequency is 60MHz ?
7. Which of the following will show esr spectrum? Give reasons. i) Cu^{2+} ii) CO_2 iii) NO_2 iv) Cl^-
8. Predict the number of lines in the ESR spectrum of free radical of $[^{13}CF_2H]^.$.
9. What are the most mass spectroscopic ionization methods?
10. Define i) base peak ii) metastable peak.

PART – B
Answer ANY EIGHT questions   (8 x 5 = 40 Marks)

11. What are the factors governing the intensity of the spectral lines? Explain any two of them.
12. Explain in detail the principle and application of Fourier Transform Technique and its impact on modern spectroscopy.
13. The Bond length of $^1H^{19}F$ is 92.7 pm. Bond force constant is 966 Nm^{-1}. Calculate the zero-point energy, the energy of the fundamental vibration ν_0, the rotational constant B and the wave numbers of the lines P_1, P_2, R_0 and R_1
14. Differentiate the origin and nature of Stokes' lines, Anti-Stokes' lines and Rayleigh scattering with respect to their position in spectrum and the intensity of the spectral lines.
15. With an example explain the three most important components of a laser?
16. (a) State the principle of PES. What is the essential difference between XPES and UV-PES?
    (b) With an example explain how PES can be applied to molecular structure.

    (2+3)
17. How does the coupling constant, J become arbitrarily negative or positive ?

18. Draw all possible orientations of magnetic moment of K^{39} ($I= 3/2$) in a magnetic field of 0.1T. Calulate the transition frequency from one of these transitions to an adjacent transition.

19. Indicate the resonance lines expected for the nuclei i) I^{127}($I= 5/2$), $\eta =0$, Ho=0 ii) N^{14}($I=1$), $\eta =0$, Ho=0

20. What are the ions formed corresponding to the peaks of 2-pentene at m/z = 70,55, 41, 39 29 and27?

21. What are chemical shift reagents and explain their role in the characterization of NMR spectrum of the compounds.

22. What is zero field splitting in EPR? How does it explain the hyperfinr splitting of Mn(II) system?

PART – C
Answer <u>ANY FOUR</u> questions (4 x 10 = 40 Marks)

23. (a) Discuss the factors contributing to the broadening of the spectral lines.
    (b) The fundamental and first overtone transitions of CO are centered at 2143.26 $cm^{-1}$and 4260.04 cm^{-1} respectively. Evaluate the equilibrium vibration frequency, anharmonicity constant, and the exact zero point energy.   (6+4)

24. a) Explain the origin of P, Q, R branches of the rotation-vibration spectra with a diagram.
    b) State and explain the Franck-Condon Principle. How are the intensity variations of electronic spectra explained by this principle?   (5+5)

25. a) What is population inversion? Show that a population inversion cannot be achieved in a 2- level system and it requires a minimum of 3 energy levels.
    b) The ionization energy for 3s electron is 30 eV. The kinetic energy of electrons ejected is 5416.07 eV. Find the wavelength of X-rays used for this PES experiment. (1eV = 1.602×10^{-19}J)   (6+4)

26. What are the factors influencing chemical shift of NMR spectrum?

27. Explain the principles involved in the Mossbauer spectral analysis and how this technique differentiates the structure of $[K_3(Fe(CN)_6]$ and $[K_4(Fe(CN)_6]$

28. What would be the EPR spectrum expected for $[Cu(salen)_2]^{2-}$?

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