LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2009

CH 3810 - MOLECULAR SPECTROSCOPY

Date & Time: 07/11/2009 / 9:00 - 12:00   Dept. No.   Max. : 100 Marks

PART A

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

1. What is an S/N ratio? How can it be enhanced?
2. What is Fourier Transform spectroscopy? What is its advantage?
3. CO_2 gives two IR absorptions although the molecule has no dipole moment. Why?
4. Differentiate between a hot band and an overtone in the nature of their transitions
5. With a neat diagram indicate the three important parts of a laser?
6. What will be the chemical shift (in Hz) if a compound exhibiting NMR signal at $\delta = 2.5$, using 60 MHz spectrometer?
7. What are the sources of radiation needed for NMR and EPR spectrometer? Give reasons.
8. Predict the number of lines in the EPR spectrum of the free radical $[CF_3D]^{.}$
9. What is FTICR spectrometry? Mention any one advantages of this method.
10. What are the most probable species responsible for peaks at m/z = 46, 45, 31 and 29 in the mass spectrum of ethanol?

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

11. Outline the causes for broadening of the spectral lines.
12. The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1}. Calculate the rotational constant, B, and hence the moment of inertia and the bond length of the molecule. Find which transition gives rise to the most intense spectral line at room temperature (300K).
13. Sketch the energy transition processes to differentiate the origin of Stokes' lines, Anti-Stokes' lines and Rayleigh scattering with respect to their position in spectrum and the intensity of the spectral lines.
14. What is population inversion? Prove that a population inversion can be easily achieved in a three level system.
15. Draw Jablonski energy level diagram and explain the various absorption and emission processes.
16. State and explain the Franck-Condon Principle. How are the intensity variations of electronic spectra explained by this principle?
17. What are the factors influencing the coupling constant, J? How do they affect?

1

18. What are the possible ways to simplify the complexity of NMR spectrum?

19. What would be the EPR pattern of benzene anion radical?

20. Discuss the principles involved in the characterization of compounds by NQR spectroscopy.

21. Indicate the resonance lines expected for a) $N^{14}(I=1)$, $\eta=1$, $H_0=0$ b) $N^{14}(I=1)$, $\eta=1$, $H_0 \neq 0$

22. How will you distinguish 3-methyl cyclohexene and 4-methyl cyclohexene using mass spectroscopy?

PART – C

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

23. (a) Explain the factors affecting the intensity of spectral lines.
    (b) The successive rotational Raman lines are separated by 243.3 cm^{-1} in H_2 molecule. Obtain the moment of inertia and the bond length of H_2.   (6+4)

24. a) Explain the origin of P, Q, R branches of the rotation-vibration spectra.
    b) The Bond length of NO is 1.151 Å. Bond force constant is 1595 Nm^{-1}. Calculate
       (a) Zero-point energy and the energy of the fundamental vibration ν_0.
       (b) Calculate the rotational constant B.
       (c) Calculate the wave numbers of the lines P_1, P_2, R_0 and R_1 (5+5)

.25. a) State and explain the principle of PES. What is the essential difference between XPES and UV-PES? With an example explain how PES can be used in structural elucidation.
    b) When a radiation of 304 Å is used to obtain the PES of benzene, the ionization potential for the electron is 9.3 eV. Find the kinetic energy and velocity of the electrons. [1 eV = 1.602 x 10^{-19} J]   (6+4)

26. a) Predict the multiplicities of the signals in the NMR spectra of 1,3-dichloropropane.
    b) How is Mossbauer spectroscopy useful in differentiating the complexes, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$

27. Explain the factors influencing the EPR spectral lines if the system possesses more than one unpaired electron with examples.

28. How is molecular ion (parent) peak recognized and confirmed?

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