LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

SECOND SEMESTER – **APRIL 2015**

CH 2821 - MOLECULAR SPECTROSCOPY

Date : 21/04/2015 Dept. No. Max. : 100 Marks

Time : 01:00-04:00

Part-A

Answer all questions. Each question carries two marks: ***(10x2=20)***

1. Why is $^{14}N^{16}O$ has higher moment of inertia than $^{15}N^{16}O$?
2. Mention the condition under which a harmonic oscillation becomes anharmonic.
3. Cis-alkenes generally absorb infrared light more strongly than trans-alkenes. Give reason.
4. What is Born-Oppenheimer approximation?
5. What is the crieteriafor a molecule to be Raman active?
6. Cite the allowed orientations of the nuclear magnetic moment vector in an externally applied magnetic field for a magnetic nucleus with spin 3/2.
7. Methyl protons are highly shielded whereas H-bonded protons are deshielded. Explain.
8. What is relaxivity? How is it measured?
9. Differentiate isotropic and anisotropic systems.
10. Mossbauer spectra are recorded by mounting the sample nucleus in solid matrices. Give reason.

Part-B

Answer any eight questions. Each question carries five marks: ***(8x5=40)***

11. Calculate the moment of inertia of CO which shows its first line in therotational spectrum at $3.842cm^{-1}$.
12. Discuss the effect of polar solvents on the electronic transitions of molecules.
13. How are bridging and terminal carbonyls identifiedby IR spectroscopy?
14. Explain Laporte allowed and Laporte forbidden transitions with suitable examples.
15. When *p*-nitrophenol is dissolved in water, the color is yellow, but when NaOH is added,the color deepens and absorbs at longer wavelength. Account for this observation.
16. Explain McLafferty rearrangement with an example.
17. Explain the mechanism of spin-spin splitting in NMR spectroscopy with an illustrative example.
18. Write a note on contrast enhancing agents for MRI.
19. Explain the methods of simplifying complex NMR spectra.
20. The epr spectrum of glycolic acid radical (HOCHCOOH) consists of two sets of doublets. Interpret the spectrum with the hyperfine splitting energy level diagram.
21. Explain the method of studying the oxidation states of metal ions in their compounds by Mossbauer spectroscopy.
22. Explain the Mossbauer spectral features of ferrocyanide and ferricyanide ions.

Part-C

Answer any four questions. Each question carries ten marks: ***(4x10=40)***

23a. Prove that there are almost as many molecules in the J=1 state, at equilibrium, as in the J=0 state for a typical value of B=2 cm^{-1}. **(5)**

b. The fundamental vibrational frequency of $^{12}C^{16}O$ is 2168.9cm^{-1}. Calculate its force constant. **(5)**

24a. How will you identify the different modes of association of SO_4^{2-} group in $[Co(NH_3)_6]_2(SO_4)_3.5H_2O$ and $[Co(NH_3)_5\,SO_4]Br$ by IR spectroscopy? **(6)**

b. Explain mutual exculsion principle with an example. **(4)**

25a. Explain the P- and R-branch lines of the vibration-rotation spectrum.

b. The C-H stretching vibration of an alkane appears at 2960 cm^{-1}. Predict the position of the Raman lines if the alkane is irradiated with light of wavelength 435.8 nm.

26a. Explain the factors which affect the magnitude of vicinal and geminal H-H coupling constants with illustrative examples. **(8)**

b. ^{13}C NMR spectra are recorded as proton decoupled spectra. Explain. **(2)**

27. Explain the epr spectra of naphthalene and triplet naphthalene with suitable hyperfine splitting energy level diagrams.

28a. Explain the principle of Mossbauer spectroscopy. **(6)**

b. Explain the application of Mossbauer spectroscopy to differentiate high- and low-spin compounds with illustrative examples. **(4)**

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