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Ex/M.Sc/CH/3/A-3121/12/2019

M. Sc. CHEMISTRY EXAMINATION, 2019

(3rd Semester)

ANALYTICAL CHEMISTRY SPECIAL

PAPER - XII - A

Time : Two hours

Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - A - 3121

UNIT - A - 3121a

- e) Taking ν_{CO} as a probe, how will you monitor the oxidative addition reaction in Vaska compound? $1\frac{1}{2}$
- f) Justify the trend of infrared stretching frequencies observed for the following compounds :
- | | | | |
|---|---|-----------------------|---|
| CO | : | 2143 cm^{-1} | |
| [Mo(CO) ₆] | : | 2004 cm^{-1} | |
| [Mo(CO) ₃ (PPh ₃) ₃] | : | 1950 cm^{-1} | |
| [Mo(CO) ₃ (NH ₃) ₃] | : | 1855 cm^{-1} | 2 |
11. a) Discuss the secondary and tertiary structures of proteins. Using one suitable example, mention its CD or ORD patterns upon changing its secondary and tertiary structures. 3
- b) Prove that $[\psi]_{\lambda}^T$ (in degree) $\approx 3300 \Delta\epsilon$. 2
- c) What will be the nature of cotton effect in case of diastereomers and enantiomers? 2
- d) Define circular birefringence. 1
- e) IR and Raman spectroscopic techniques are complementary – comment on. 2
- f) What is LASER Raman spectroscopy? What are its advantages over classical Raman spectroscopy? $2\frac{1}{2}$

1. How could you identify all possible isomers of the compound [SnF₄(pyridine)₂] from their NMR spectra?
[For ^{119}Sn ; $I = \frac{1}{2}$] 2
2. $A+B \rightleftharpoons AB$ is a rapid exchanging system.
How can the equilibrium constant (K) of the above reaction be determined from NMR measurement?
[A, B & AB are all NMR active species] 4
3. Availing suitable Bloch equation establish the required relation between free induction decay signal and T_1 , which can be employed in measuring the spin-lattice relaxation time. 3
4. Comment on any one of the followings :
i) ^{31}P NMR of P_4S_3

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ii) Geometrical isomerism of $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}_3]$

[For ^{103}Rh ; $I = \frac{1}{2}$] 1 $\frac{1}{2}$

5. “ $J_{^{13}\text{C-H}}$ largely depends on the S-character of C-H bond.”
Elaborate. 2

OR

Explain why $J_{^{13}\text{C-H}}$ coupling constant of $-\text{CH}_2-$ moiety in $(\text{C}_6\text{H}_5)_2\text{CH}_2$ and $(\text{CH}_3)_2\text{CH}_2$ differ from their corresponding carbonium ions. 2

UNIT - A - 3121b

6. Giving reason(s), predict the number of possible resonance line(s) be observed in NQR spectrum of CH_3Br molecule. Calculate the energy of each level generated due to quadrupole interaction in the molecule as function of eQq

[For ^{79}Br ; $I = \frac{3}{2}$] 2+2

7. “ PFCl_4 retains its molecular symmetry in crystalline state whereas PPhCl_4 does not.” Explain the statement on the basis of NQR spectral study. 2

OR

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Describe how NQR spectroscopic technique can be employed to detect explosive or narcotic substances. 2

8. Enumerate the reasons for appearance of multiline Mössbauer spectrum. Why Mössbauer spectra can only be measured in the solid state? 3+1 $\frac{1}{2}$
9. “Oxidation state of Sn is easier to understand than that of Fe with the help of Mössbauer spectroscopy”. Justify or contradict the statement with proper argument. 2

UNIT - A - 3122

10. a) What makes a molecule Raman active? Using classical theory, explain the occurrence of Stokes and anti-stokes Raman scattering. 3
- b) The equilibrium vibration frequency of I_2 is 215 cm^{-1} and the anharmonicity constant is 0.003. Calculate the intensity of the ‘hot band’ relative to that of the fundamental at 300 K. 2
- c) How will you prove the occurrence of linkage isomerism in $[\text{Ru}(\text{dmsO})_6]^{2+}$ (dmsO = dimethylsulfoxide) with the help of IR spectroscopy? 2
- d) The symmetrical stretching mode of CO_2 is infrared inactive but Raman active. Explain. 2

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