



**Indian Association for the Cultivation of Science**  
(Deemed to be University under *de novo* Category)  
**Integrated Bachelor's-Master's Course**  
**End-Semester Examination-Spring 2020**

**Subject: Structure and Spectroscopy**  
**Full Marks: 50**

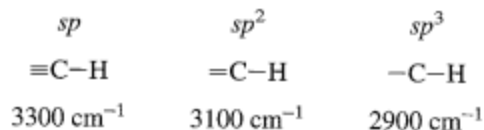
**Subject Code: CHS 1201**  
**Time Allotted: 3 hours**

Part-A

Answer all the questions

5x5

1. A compound of molecular formula  $C_4H_6O_3$  shows only a single band in the proton nmr spectrum at a chemical shift of 2.19, and no splitting of the line occurs due to spin coupling. In the infrared spectrum, the compound displays two closely spaced bands at  $1800\text{ cm}^{-1}$  and  $1760\text{ cm}^{-1}$ . Identify the compound, and explain the origin of the nmr line and the two infrared bands.
2. The C-H stretching vibrational frequency in infrared spectra depends on the state of hybridization of the carbon atom, and generally shows the following sequence.


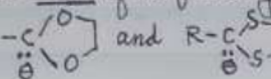
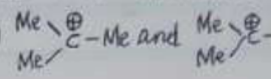
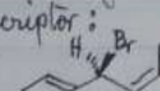
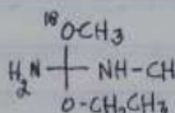
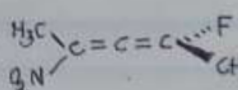


Offer an explanation. (Try to be brief)

3. The chemical shift of the  $CH_3$  protons of diethyl ether is 1.16 and that of the  $CH_2$  protons is 3.36. What is the difference between  $CH_3$  and  $CH_2$  resonance frequencies of the molecule in the presence of an applied field of 1.9 T? [ $\gamma_{\text{proton}} = 26.75\text{ rad T}^{-1}\text{s}^{-1}$ ]
4. The infrared spectrum of  $N_2O$  depicts three vibrational fundamental bands. Assuming that the structure of the molecule is linear, explain how this spectrum allows you to distinguish between  $N-N-O$  and  $N-O-N$ . Sketch the approximate atomic motions of the normal modes.
5. The interatomic vibrational potential of HCl molecule is quite well described by the Morse potential with  $D_e = 42,990\text{ cm}^{-1}$ ,  $\nu_e = 2989.7\text{ cm}^{-1}$ , and  $\nu_e x_e = 52.05\text{ cm}^{-1}$ . Assuming that the potential is unchanged on deuteration, predict the dissociation energies ( $D_0$ ) of HCl.

## Part-B

Answer all the questions

- a) p-Nitrophenol is a stronger acid than p-cyanophenol; but 3,5-dimethyl-4-nitrophenol is a weaker acid than 4-cyano-3,5-dimethyl phenol - justify. 3
- b) Between triethylamine ( $\text{Et}_3\text{N}$ ) and quinuclidine () , which one is a stronger base and why? 2
- c) Between the two species in each of the following pairs, which one is more stable and why? (i)  ; (ii)  . 3
- d) Give one example of each of an electrophilic radical and of a nucleophilic radical. Why are they so called? 2
- e) Justify or criticise the following statements: 3
- Erythro form of a molecule may or may not be optically active.
  - All the stereoisomers of a compound having more than one chiral centre must be optically active.
  - A molecule having only one chiral centre with D-configuration must be dextro.
- f) Draw the following stereoisomers as directed: 2
- (+)-ac conformation of n-butane in Sawhorse representation.
  - Erythro-3-bromo-2-butanol in Newman projection formula.
- g) Assign the stereogenic centre/chiral axis in the following structures as having R/S descriptor: 3
-  ;
  -  ;
  -  .
- h) The conformational energy of propane ( $\text{CH}_3\text{-CH}_2\text{-CH}_3$ ) is about  $0.5 \text{ kcal mol}^{-1}$  higher than that of ethane ( $\text{CH}_3\text{-CH}_3$ ). Give reason. 2
- i) For molecules of type  $\text{CH}_2\text{X-CH}_2\text{X}$ , anti form is stabler than the gauche form when  $\text{X} = \text{Cl}$ ; but the reverse is true when  $\text{X} = \text{F}$ . Justify. 2
- j) Show the  $\text{C}_5$  pathway for the ring inversion of cyclohexane chair conformation showing the corresponding energy diagram. 3