LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – **APRIL 2016**

CH 2821 - MOLECULAR SPECTROSCOPY

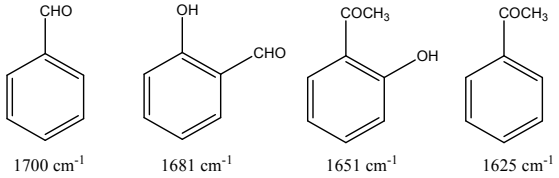
Date: 22-04-2016 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

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

1. The normal modes of vibration of CO_2 molecule are $\bar{\upsilon}_1 = 1330$ cm^{-1}, $\bar{\upsilon}_2 = 667$ cm^{-1} (doubly degenerate) and $\bar{\upsilon}_3 = 2349$ cm^{-1}. Calculate the zero point energy of CO_2 molecule.
2. Why does n→π^* transition undergo blue shift and $\pi \rightarrow \pi^*$ transition red shift with an increase in polarity of the solvents?
3. Differentiate between CH_3CH_2CHO and CH_2=CH-CH_2OH using their IR spectra.
4. What is the reason for the lowering of γ(C=O) absorption in the following compounds?



1700 cm^{-1} 1681 cm^{-1} 1651 cm^{-1} 1625 cm^{-1}

5. Distinguish between o- and m-hydroxybenzoic acids using their IR spectra.
6. Calculate the magnetic field required to flip a ^{1}H nucleus in an NMR spectrometer that operates at 400 MHz. Given $g_n = 5.585$.
7. Sketch the EPR spectrum of a free radical that contains four equivalent protons.
8. What is the significance of asymmetry parameter?
9. Predict the number of Mossbauer transitions possible in ^{119}Sn nucleus.
10. Mention the conditions for a compound to be studied using Mossbauer spectroscopy.

Part-B

Answer any EIGHT questions. **(8 x 5= 40)**

11. Discuss the vibrational energy of a diatomic molecule using Mohr's curve.
12. Why is the absorption characteristics of 2,2'-dimethyl biphenyl similar to o-xylene. Compare its absorption with biphenyl and 2-methyl biphenyl.
13. Explain the fragmentation pattern of pentanoic acid.
14. Rotational and centrifugal distortion constants of HCl molecule is 10.593 cm^{-1} and 5.3 x 10^{-4} cm^{-1} respectively. Estimate the vibrational frequency and force constant of the molecule. Atomic masses of hydrogen and chlorine are 1.673 x 10^{-27} and 58.06 x 10^{-27} kg, respectively.
15. An organic compound A with the molecular formula C_3H_9N shows the following bands in IR spectrum. 3425, 3236 3012 and 1615 cm^{-1}. When compound A is treated with nitrous acid, it forms compound B, which shows a strong broad peak at 3430 cm^{-1} and it also answers positive to Lucas test. Identify the structure of compound A and B.
16. Suggest the structure of the compound with the molecular formula $C_{10}H_{12}O$, whose mass spectrum shows peaks at m/z = 43, 57, 77, 91 (base peak), 105 and 148. It answers positive to iodoform test.
17. Explain the geminal and vicinal coupling with examples.
18. Discuss the NMR of homotopic and enantiotopic protons with examples.

19. Explain the Kramer's degeneracy with a suitable example.
20. Explain the isotropic and anisotropic hyperfine interactions with suitable examples.
21. ^{127}I nuclear quadrupole resonance shows a finite value for asymmetry parameter for the molecule HIO_3. Arrive at its structure.
22. Which of the following exhibits quadrupole splitting? Low spin Fe(II) or Low spin Fe(III) complex- Account for your choice.

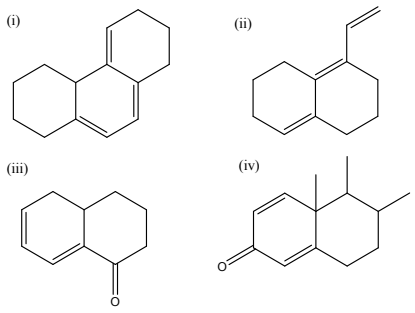
Part-C

Answer any FOUR questions. **(4 x 10= 40)**

23. Explain the Stark effect of linear and symmetric top molecules using rotational spectra.
24. Predict the structure of the compound, which gave the following spectral information.
    UV : λ_{max} = 280 nm, ϵ_{max} = 22
    IR : 3000 - 2500 cm^{-1} (s, b), 1715 cm^{-1} (s), 1342 cm^{-1} (m)
    Mass : 116, 73, 45, 43 (100 % intensity), 28.
    NMR : 7.88 τ (Singlet), 7.40 τ (Triplet), 7.75 τ (Triplet), -1.1 τ (Singlet).

25 a. An yellow acidic compound shows the following spectral data.
    UV : λ_{max} = 285 nm, ϵ_{max} = 6600
    IR : 3035 (m), 3460 (b, s), 1510 (s), 1360 (s) and 740 (s) cm^{-1}
    NMR : unsymmetrical pattern 2.61 – 2.75 τ (4H).
    Identify the structure of the compound and explain its spectral characteristics. **(6)**

b. Calculate the λ_{max} for the following: **(4)**



26. What is the principle of correlation spectroscopy? How will you apply it to 3-bromobutane?

27 a. Discuss the perturbation of energy levels of a molecule with nuclear spin I = 1 in an axially symmetric and asymmetric fields. **(6)**

b. Explain the zero field splitting with an example. **(4)**

28 a. How is Mossbauer spectroscopy useful to distinguish between axial symmetry and rhombic symmetry? **(6)**

b. Mention the conditions that favour resonant absorption. **(4)**

****