Total No. of printed pages = 6

3 (Sem 6) CHM M1

2015

CHEMISTRY

(Major)

Theory Paper : M-6.1

(Spectroscopy)

Full Marks – 60

Time – Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : 1×7=7

   (a) What is the energy (in kJ mol^{-1}) of visible rays with λ = 400 nm ?

   (b) Explain "H_2, N_2, O_2 etc molecules do not show pure rotational or vibrational spectra".

   (c) Which is not correct ?

      (i) Spherical top molecules have all three moments of inertia equal.

[Turn over

(ii) Linear molecules have two moments of inertia equal and one is negligibly small.

(iii) Asymmetric top molecules have two moments of inertia equal, but the other is not small.

(d) What is a fundamental band in pure vibrational spectra ?

(e) What are Raman lines ?

(f) The absorbance of 5.4×10^{-4} M Fe^{3+} solution at 530 nm was 0.54. Calculate molar absorption coefficient, if the path length was 1 cm.

(g) What is spin-spin relaxation in NMR spectroscopy ?

2. Answer in short : 2×4=8

(a) The order of electronegativity in halogens is I < Br < Cl < F and proton NMR signals in CH_3X(X = I, Cl, Br, F) are

CH_3F	CH_3Cl	CH_3Br	CH_3I
4.26δ	3.0δ	2.82δ	2.16δ

Explain the trend in NMR signals.

(b) What are α–cleavage and induce cleavage in mass spectroscopy ?

(c) The moment of inertia of $HC^{12}N^{14}$ molecules is 1.89×10^{-46} kgm^2. Calculate the rotational constant.

(d) On what factors the relative intensities of spectral lines in rotational spectra are expected to depend on ?

3. Answer any *three* questions of the following : 3×5=15

(a) Distinguish between emission and absorption spectra. State spectroscopic displacement law. Why the magnitude of energy of the electron in all the energy levels of an atom should decrease by a factor of 0.99945 ? 3+2=5

(b) What is rotational spectroscopy ? How it differs from infrared spectroscopy ? 4+1=5

(c) What is oscillator strength or f-number ? Why it is necessary to introduce this number in electronic spectroscopy ? How allowed and forbidden transitions are related to f-number ? 3+1+1=5

(d) From the concept of quantum theory, prove that the frequency absorbed or emitted by a nucleus in moving from one energy level to another is directly proportional to the applied magnetic field. 5

4. Answer any *three* questions : 10×3=30

(a) (i) Explain with examples what are the types of ions produced in a mass spectrometer ? 7

(ii) What is the use of 'Ring rule' in interpretation of mass spectra ? 3

(b) (i) Discuss the theory of electron spin resonance spectroscopy. 7

(ii) Taking example of hydrogen atoms, explain what is meant by hyperfine splitting in electron spin resonance spectroscopy. 3

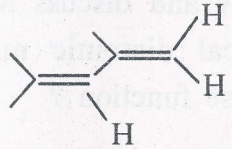
(c) (i) Define and explain what do you mean by equivalent hydrogens, coupling constant and up field and down field in NMR spectroscopy. 2+2+3=7

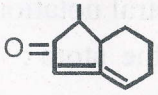
(ii) Predict how the high resolution ^{1}HNMR spectrum of each of following compounds will appear 3

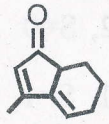
2-iodopropane and ethanol.

(d) (i) "The absorption at longer wavelength in electronic spectroscopy is due to the combination of a chromophore and an auxochrome group." Describe what do you mean by chromophore and auxochrome. Also explain briefly red shift and blue shift. 4+3=7

(ii) Predict λ_{max} of $\pi \rightarrow \pi^*$ transition for the following three molecules using Woodward's rule. 3

(a) 

(b) 

(c) 

(e) (i) Explain how a non-linear N-atomic molecule and a linear N-atomic molecule can have 3N-6 and 3N-5 different internal vibrations respectively. Sketch the fundamental vibrations of water molecule, also show change in electric dipole moment produced by bending and symmetric vibrations of the molecule. 2+3+2=7

(ii) The infrared spectrum of CO shows a vibrational absorption peak at 2170 cm^{-1}. What is the force constant for the CO bond. ? 3

(f) (i) Discuss the effect of isotopic substitution in rotational spectroscopy with respect to ^{12}C ^{16}O and ^{13}C ^{16}O molecules.

Draw and discuss Morse curve for a typical diatomic molecule. What is Morse function ? 4+2+1=7

(ii) Give spectral notation for the following states of the atom : 3

(a) n=4, L=2, S=0

(b) n=4, L=1, S=1, J=0

(c) n=3, L=2 and multiplicity 2.