

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 $\lambda = 400 \text{ nm}$?
 - (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 $\text{I} < \text{Br} < \text{Cl} < \text{F}$ and proton NMR signals in CH_3X ($\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{F}$) are

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

Explain the trend in NMR signals.

- (b) What are α -cleavage and induced cleavage in mass spectroscopy ?
- (c) The moment of inertia of $\text{HC}^{12}\text{N}^{14}$ molecules is $1.89 \times 10^{-46} \text{ kgm}^2$. 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

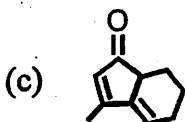
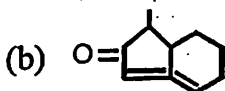
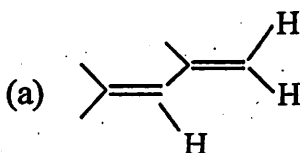
- (c) (i) Define and explain what do you mean by equivalent hydrogens, coupling constant and up field and down field in NMR spectroscopy. 2+2+3=7

- (ii) Predict how the high resolution ¹H NMR 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



(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 $^{12}\text{C } ^{16}\text{O}$ and $^{13}\text{C } ^{16}\text{O}$ 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.