2014

CHEMISTRY

(Major)

Paper : 6.1

(Spectroscopy)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer/Choose the correct answer of the following : 1×7=7

(a) A molecule undergoes transition from ground state to an excited state. If the uncertainty in excited state energy level is 10^{-30} J, calculate the lifetime of the molecule in the excited state.

(b) What is the lowest vibrational energy in terms of oscillation frequency for a diatomic molecule undergoing simple harmonic motion?

(c) Show pictorially the symmetric stretching and symmetric bending vibrations of water molecule.

(d) The term symbol for a particular atomic state is $^3S_1$. What are the values of L and J for this state?

(e) The photoelectron ejected from a diatomic molecule with an energy of radiation $3{\cdot}4\times10^{-18}$ J has the kinetic energy of $1{\cdot}0\times10^{-8}$ J. Calculate the ionization energy per mole for this ejection.

(f) Which of the following statements is true?

(i) Nuclei with odd mass cannot have half integral spins

(ii) Nuclei with both p and n even have non-zero spin

(iii) Nuclei with both p and n odd have integral spin

(g) How many normal modes of vibration does CCl_4 possess?

2. Answer the following briefly : 2×4=8

(a) Indicate whether C—C stretching vibration in CH_3CCl_3 and symmetric stretching vibration in SO_2 are IR active or not.

(b) Prove that the mass to charge ratio of an ion in a mass analyzer following a circular path is inversely proportional to the accelerating potential applied.

(c) How many normal vibration modes are possible for linear ethyne and non-linear benzene molecules?

(d) Predict the appearance of the high-resolution NMR spectrum of acetaldehyde.

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

(a) What are the factors which determine intensities of spectral lines? Discuss. 5

(b) Discuss the principle of obtaining Raman spectra of molecules clearly defining Stokes' and anti-Stokes' radiations and Rayleigh scattering. Why are Stokes' lines more intense than anti-Stokes' lines? 4+1=5

(c) Calculate the moment of inertia of a H_2O molecule around its two-fold axis. The HOH bond angle is 104·5° and the bond length is 95·7 p.m. 5

(d) Draw the proton NMR spectra of CH_3CH_2Br and $CH_3CHBrCH_3$. Indicate the approximate chemical shift, fine structure due to spin-spin coupling and the relative intensities of the lines. 5

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

(a) *(i)* Describe how z-components summation method is used to deduce various allowed values of j for $^2P_{3/2}$ and $^2P_{1/2}$. 3

(ii) Discuss Franck-Condon principle to explain intensities of vibronic transitions due to absorption or emission of a photon of appropriate energy. 5

(iii) How does isotopic effect change the position of microwave band? 2

(b) *(i)* Write the difference between fluorescence and phosphorescence. 5

(ii) Which of the following systems will show ESR spectrum? Give reasons : 5

H, Na^+, $^{\bullet}CH_3$, NO_2, H_2

(c) *(i)* Discuss the vibration-rotation spectrum of CO. 5

(ii) Describe what is chemical shift taking the example of an alkane. 5

(d) *(i)* Give a highly schematic diagram of a mass spectrometer. 3

(ii) Mention four methods of ionizing sample molecules entering the ion source unit in a mass spectrometer. Discuss one method in detail. 5

(iii) Explain, with two examples, what is nitrogen rule in mass spectrometry. 2

(e) *(i)* Explain the fine structure of electronic spectrum of atomic hydrogen. 5

(ii) The wavelength of a radiation absorbed is found to be 500 nm. Express this in terms of wave number, frequency and energy. 3

(iii) A compound with molecular formula C_7H_5N shows the following prominent IR bands :

3050, 2240, 1600, 1500, 750, 700 (all in cm^{-1})

Predict the structure of the molecule. 2

(f) *(i)* What are spherical and symmetric rotors? 5

(ii) The ratio of I_0/I is 1·98 for the absorption by a compound at a specific wavelength. If the concentration of the sample is 0·9 *M* and path length is 0·01 m, find the molar extinction coefficient. 2

(iii) Using IR spectra, how will you distinguish between ethanol and ethanal? 3

★★★