2016

CHEMISTRY

(Major)

Paper : 6.1

(Spectroscopy)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

(Symbols signify their usual meaning)

1. Answer in brief : 1×7=7

(a) State the basic difference between line spectrum and continuous spectrum.

(b) State why microwave radiation cannot induce vibrational transitions.

(c) Write the value of the component of moment of inertia of a linear molecule along the internuclear axis.

(d) State why electronic spectrum is generally broad.

(e) State true or false for the following and if false correct :

Forbidden transitions do not take place at all.

(f) State which of the normal vibrations of CO_2 is Raman active.

(g) In Raman effect, the energy transfer between the photon and the molecule is in the range 3–3000 cm^{-1}. State what types of transitions the molecule may undergo due to this energy transfer.

2. Answer any *four* : 2×4=8

(a) Calculate the energy difference between the two rotational levels in joule of a molecule if it absorbs a photon of wavelength 10 cm.

(b) Write how will you distinguish between ethanol and ethanal by using IR spectra.

(c) In the IR spectrum of pure butan-1-ol, a broadband is observed within the range 3500–3200 cm^{-1} but a dilute solution of the compound in carbon tetrachloride shows an additional band at 3650 cm^{-1}. Explain the observation.

(d) Taking the example of HCl and DCl, discuss the effect of isotopes in the vibrational spectrum. Treat the molecules as harmonic oscillators.

(e) Ethyne shows two IR bands and three Raman bands but none of these bands occur at the same wave number. Explain what information you can draw from this observation regarding the structure of the molecule.

3. Considering a polar diatomic molecule to be a non-rigid rotator, deduce an expression for the energy absorbed in the allowed rotational transitions. Draw schematic diagram to show the difference in the spectrum from that of a rigid rotator. 4+1=5

Or

Using the anharmonic oscillator concept, deduce expressions for the energy required for allowed vibrational transitions. Indicate fundamental absorption and overtones. 5

4. Answer *either (a)* and *(b) or (c)* and *(d)* :

(a) Discuss the factors on which the intensity of spectral line depends. 3

(b) The lifetime of an excited electronic state is 10^{-8} s. Calculate the width of the spectral line in Hz. 2

(c) A hypothetical quantum mechanical system has energy given by the expression $bn(n+2)$, where b is a constant and $n = 1, 2, 3, \cdots$. The selection rule is $\Delta n = \pm 2$. Find how much energy will be required for any allowed transition. What is the value of the lowest energy needed? 2+1=3

(d) A beam of monochromatic radiation is allowed to pass through a solution of a compound with concentration 50 mol m^{-3}, when the intensity of the radiation reduces to one-fifth of the initial value. Find molar extinction coefficient, if the path length is 1 cm. 2

5. Write the quantum mechanical theory of Raman effect. What do you mean by Raman shift? Explain the conditions under which Stokes and anti-Stokes lines are observed. 2+1+2=5

Or

The first line in the pure rotational spectrum of $^{12}C^{16}O$ is observed at $3 \cdot 8424\ cm^{-1}$. Calculate bond length considering the molecule as rigid rotator. Does the bond length of a real molecule change as rotational energy increases? If yes, how? 4+1=5

6. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Using the coupling between orbital and spin momenta, explain the fine structure of the atomic spectra of hydrogen. Write clearly the selection rules involved. 4

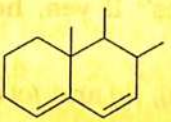
(b) Discuss how a polar solvent affects the λ_{max} values of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. 2+2=4

(c) Define auxochrome. What do you mean by red shift and blue shift of absorption maximum? 1+1=2

(d) Using the Franck-Condon principle, explain why the intensities of the vibrational lines associated with electronic transitions differ. 4

(e) Write the basic principle of the photoelectron spectroscopy. Name the radiation used in electron spectroscopy for chemical analysis (ESCA). 3+1=4

(f) Using Woodward rules, predict the λ_{max} value of $\pi \rightarrow \pi^*$ transition in



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7. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Show schematically the splitting of the spin states of the protons of CH_3OH in continuously increasing magnetic field. If a radiation with a definite frequency in applied, explain which will show resonance at down field compared to the other protons. 1+3=4

(b) A proton NMR spectrometer operates with a radiation of frequency 100 MHz. Find at what magnetic field, a free proton will show resonance given that the values of nuclear magneton and nuclear g factor are $5 \cdot 05 \times 10^{-27}$ JT^{-1} and $5 \cdot 585$ respectively. 3

(c) How many proton NMR signals will be shown by 2-chloropropane? Discuss the effect of spin-spin coupling on the signals. 3

(d) Show schematically, how the spin states of an electron splits up in an applied magnetic field. Find the energy difference between the two spin states. 1+3=4

(e) Discuss the hyperfine structure of the e.s.r. spectrum of H-atom. 3

(f) Explain why tetramethylsilane is used as reference in ^{1}H-NMR spectroscopy. 3

8. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) In mass spectrometry, ions are detected according to their mass-to-charge ratio. Discuss the principle of mass spectrometry to explain how the ions are detected. 4

(b) The electron ionization mass spectrum of 2-methyl-pentane shows some prominent peaks at m/z values of 86, 71, 57 and 43. Identify each species showing adequate fragmentation. 4

(c) Write how a mass spectrum is presented. Distinguish between molecular ion peak and base peak. 1+1=2

(d) Mention different components of mass spectrometer. Discuss with example about the electron ionization process. 1+3=4

(e) What do you mean by McLafferty rearrangement? State why this rearrangement was proposed. Explain this rearrangement taking the example of pentan-2-one. 1+1+2=4

(f) Indicate the species responsible for the molecular ion peak and base peak of ethanol. Indicate their m/z values. 2

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