2017

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 which of the following will be microwave active :

CH_4, CH_3Cl, SF_6, OCS

(b) Which of the following radiations is associated with e.s.r. spectroscopy?

Radiowave, Microwave, Infrared, X-ray

(c) For a spherical top molecule, write the relationship among the three components of moment of inertia.

(d) If the spacings between the consecutive translational, rotational and vibrational levels are $\Delta\varepsilon_{tr}$, $\Delta\varepsilon_{rot}$ and $\Delta\varepsilon_{vib}$ respectively, arrange these values in the increasing order.

(e) Find how many stretching vibrations CH_4 possesses.

(f) State which of the following nuclei possesses integral spin and which possesses half-integral spin :

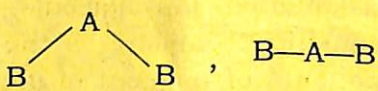
^{12}C, ^{2}H, ^{16}O, ^{13}C, ^{14}N

(g) In order to be infrared active, the dipole moment of the molecule must fluctuate with vibration. State the condition under which a molecule becomes Raman active.

2. Answer any *four* : 2×4=8

(a) Considering a diatomic molecule to be rigid rotator, find an expression in wave number for the energy required for rotational transitions to take place.

(b) Write how you can distinguish between the following two structures of the molecule B_2A using infrared and Raman spectra :



(c) Explain why Stokes lines are more intense than anti-Stokes lines.

(d) The infrared spectrum of ethanol (10% v/v solution in CCl_4) shows one sharp band at 3640 cm^{-1} and a strong broad band at 3340 cm^{-1}. But when the concentration is 1% (v/v in CCl_4), the band at 3640 cm^{-1} appears with increased intensity with simultaneous decrease in intensity of the later band. Explain this observation.

(e) Write in brief how the presence of heavier isotope affects the rotational spectrum of a diatomic molecule. Use rigid rotator concept.

3. (a) Answer *either (i)* and *(ii) or (iii)* and *(iv)* :

(i) For a certain quantum mechanical system, the transition from level m to level n involves absorption of radiation with wavelength 480 nm. Again a radiation with wavelength 880 nm is absorbed in the transition from level p to level n of the same system. Find the wavelength of the radiation needed for the transition from level m to the level p. 3

(ii) Explain how the path length of sample affects the intensity of spectral line. 2

Or

(iii) Write the expression for transition moment. Using this, explain what you mean by forbidden transition and selection rule. 3

(iv) A particular molecule undergoes spectroscopic transitions from the ground state to the excited state where its lifetime is about 0·1 s. Calculate the width of the spectral line in Hz. 2

(b) Explain with diagram the appearance of *P*- and *R*-branches in the rotation-vibration spectrum of a diatomic molecule. 5

(c) Answer *either (i) or (ii)* and *(iii)* :

(i) For H_2, the spacing between the consecutive *S*-branch lines in the pure rotational Raman spectrum is 243·2 cm^{-1}. Calculate bond length of H_2. 5

Or

(ii) The infrared spectrum of thioacetic acid shows the prominent bands 2960 cm^{-1}, 2500 cm^{-1}, 1700 cm^{-1}, 1450 cm^{-1} and 1380 cm^{-1}. Indicate the groups responsible for these bands. Write what the structure of the molecule should be. 3

(iii) Write how you can distinguish between acetone and acetic acid using infrared spectra. 2

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

(a) Name the transitions that may take place along with electronic transitions in a diatomic molecule. Write how the difference in intensities of the vibrational lines associated with electronic transitions can be explained. 1+4=5

(b) The $\pi \rightarrow \pi^*$ transition in ethene is observed at 170 nm. Write in which of the following this should vary—

(i) Buta-1, 3-diene;

(ii) Hexa-1,5-diene. 2

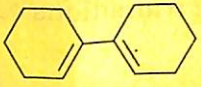
(c) The photoelectron ejected from N_2 with a radiation of wavelength 58·4 nm has kinetic energy of 5·6 eV. Calculate the ionization energy of N_2. 3

Or

(d) Name the main electronic transitions observed in organic molecules. Indicate the regions of wavelengths where these transitions may take place. What types of electronic transitions are observed in carbonyl chromophore? Mention the effect of conjugation on these transitions. 3+1+1=5

(e) Define chromophore and auxochrome. The λ_{max} value of benzene is 204 nm. State how this is affected in aniline. 2+1=3

(f) Using Woodward-Fieser rules, predict the λ_{max} value of 2



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

(a) Draw schematic diagram to show the effect of applied magnetic field (B_z) on the spin states of a proton. Find an expression for the energy difference between the spin states in presence of the applied field. 1+3=4

(b) State how many ^{1}H-NMR signals will be shown by 1-chloropropane. Discuss the effect of spin-spin coupling. 1+3=4

(c) Of CH_3F and CH_3Br state protons of which compound will show resonance at more downfield compared to the protons of the other compound. Write the reason behind your answer. 2

Or

(d) Why do the protons in different chemical environments show resonance at different magnetic fields? Explain taking the example of chloroethane. Discuss what you mean by chemical shift. 2+3=5

(e) Calculate the frequency of the radiation needed for ^{1}H magnetic resonance to take place for a proton if the applied magnetic field strength is 7·05 T.

Given : $g_N = 5 \cdot 585$, $\beta_N = 5 \cdot 05 \times 10^{-27}$ JT^{-1} 2

(f) Discuss the hyperfine structure of the e.s.r. spectrum of deuterium. 3

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

(a) In the mass spectrometry experiment, the ions with different m / z values can be detected by changing the accelerating potential. Explain how this is possible. 5

(b) The mass spectrum of hexanoic acid shows a peak at $m/z = 60$ involving McLafferty rearrangement. Identify the species. Write the structures of the molecular radical ion and the fragments formed. 3

(c) State what type of cleavage you may expect in the EI mass spectrometry of acetone. Write the structures of the fragments formed. 2

Or

(d) In normal EI mass spectrometry, generally 70 eV electrons are used. What happens to an organic molecule under this condition? Explain taking the example of butane. Write how the molecular mass of a compound can be determined using EI mass spectrometry. 3+2=5

(e) The mass spectrum of bromomethane shows two strong peaks at m/z values of 94 and 96 having almost equal intensity. Identify the two species involved with proper justification. 2

(f) State nitrogen rule and write the logic behind it. 1+2=3

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