Set. For Deptt.
6.1. 6.2, 6.3, 6.4 only.

3 (Sem–6) CHM M 1

2019

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 meanings

1. Answer in brief : 1×7=7

(a) For the transition of a molecule between the stationary states ψ_m and ψ_n, write the expression for the transition moment.

(b) Which of the following will be Raman active, but not IR or microwave active?

HCl, CO_2, O_2, H_2O

(c) State how the components of moment of inertia of a symmetric top molecule are related.

Or

Write how the components of moment of inertia of the molecule OCS are related.

(d) Let the spacings between the adjacent molecular electronic, vibrational and rotational levels be $\Delta\varepsilon_{elec}$, $\Delta\varepsilon_{vib}$ and $\Delta\varepsilon_{rot}$. Arrange these spacings in increasing order.

(e) State how the spectral line is affected by the lifetime of the excited state of a molecule.

(f) In the mass spectrum of a primary alcohol, a strong peak is observed at $\frac{m}{z} = 31$. Identify the species corresponding to this peak.

Or

The EI mass spectrum of an organic compound containing C, H and N shows the molecular ion peak with even mass. What information can be drawn regarding the number of N atoms in the molecule from this observation?

(g) Write the selection rule for pure rotational Raman spectrum of a diatomic molecule.

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

(a) In the IR spectrum of pure butan-1-ol, a broadband is observed within the range 3500 cm^{-1} – 3200 cm^{-1}. But a dilute solution of the compound in CCl_4 shows an additional band at 3650 cm^{-1}. Explain this observation.

Or

Write how you will distinguish between acetone and acetic acid by using IR spectroscopy.

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

(c) In mass spectrometry, it is generally observed that a molecular ion with even mass cleaves to give fragment ions with odd mass and vice versa. But the EI mass spectrum of pentanal (molecular mass = 86 a.m.u.) shows a strong peak at $\frac{m}{z} = 44$. Explain this observation.

Or

The mass spectrum of an organic compound containing chlorine shows two peaks at $\frac{m}{z}$ values of 64 and 66. The peak at $\frac{m}{z} = 66$ is of one-third intensity as compared to the peak at $\frac{m}{z} = 64$. Which one should be the molecular ion peak? Account for the origin and intensity of the other peak.

(d) Discuss about the fragmentation of acetone to show the formation of the species responsible for the base peak.

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

(i) The energy of a hypothetical quantum mechanical system is given by $an(n+4)$, where a is some positive constant and $n = 1, 2, 3, \cdots$. The selection rule is $\Delta n = \pm 3$. Find a general expression for the energy required for the transition to take place. 3

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

(iii) Taking the example of HCl, explain how the component of dipole moment along a particular direction varies with time due to rotation of the molecule. 3

(iv) A monochromatic radiation of wavelength 400 nm is allowed to pass through a solution with concentration 2 mol m^{-3} taken in a curette of 1 cm width. The solution transmits 20% of the incident radiation. Calculate molar extinction coefficient. 2

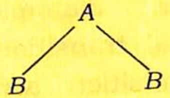
(b) In mass spectrometry, ions are detected according to their mass-to-charge $\frac{m}{z}$ ratios. Deduce the expression for $\frac{m}{z}$ and hence explain how the different ions are detected. 3+2=5

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

(i) The fundamental absorption and the first overtone bands of HCl appear at 2886 cm^{-1} and 5668 cm^{-1} respectively. Calculate the force constant of the bond in HCl. The atomic masses of H and Cl are 1·008 a.m.u. and 35·45 a.m.u. respectively. 5

(ii) The C—H stretching of an alkane appears at 2960 cm^{-1}. If the Raman spectrum of the compound is observed using a monochromatic radiation of 435·8 nm, predict the wavelength of the Stokes line corresponding to this band. 3

(iii) Write how you can differentiate between the following two structures by using IR and Raman spectroscopy : 2



and *B—A—B*

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

(a) Discuss the origin of the *P* and *R* branches in the rotation-vibration spectrum of a diatomic molecule. Show schematically the *P* and *R* branches. 4+1=5

(b) Write the quantum mechanical theory of Raman spectroscopy. Show schematically the Rayleigh lines, Stokes lines and anti-Stokes lines. 4+1=5

(c) Considering the diatomic molecule to be a rigid rotator, deduce an expression in wavenumber unit for the energy required for rotational transition to take place. Explain how the spectrum will differ if the molecule is considered to be a non-rigid rotator. 3+2=5

(d) Find the normal vibrational modes of CO_2. Out of these, how many are stretching and how many are bending vibrations? Explain which vibrations are IR active and which are not. 1+1+3=5

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

(a) Write the selection rules for electronic transition in diatomic molecule. The vibrational transitions along with electronic transition are represented in terms of (v', v'') numbers. Explain how the variation in intensity of (v', v'') transitions can be explained. 1+4=5

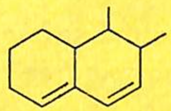
(b) The photoelectron ejected from N_2 with a radiation of wavelength 58·43 nm has kinetic energy of 5·63 eV. Calculate the ionization energy of N_2. 3

(c) Write how a polar solvent affects the $\pi \rightarrow \pi^*$ transition of a compound. 2

(d) Name the main electronic transitions observed in organic molecule and indicate the regions of wavelengths where these transitions may be observed. Name the electronic transitions that may be observed in carbonyl chromophore. Define auxochrome. 3+1+1=5

(e) Explain which of ethene and hexa-1,3,5-triene will have the higher λ_{max} value of $\pi \rightarrow \pi^*$ transition. What do you mean by redshift of λ_{max} value? 2+1=3

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



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

(a) Show schematically how the spin states of an electron split up in an applied magnetic field. Find the energy difference between the two spin states. State what is done in ESR spectroscopy in order to get the spectrum. 1+3+1=5 *(b)* Consider the ^{1}H NMR spectra of the following compounds :

(i) Cl_2CHCH_2Cl

(ii) $ClCH_2CH_2Cl$

How many signals will be shown by each of the compounds? Which protons will show resonance at the highest downfield and why? Explain in which of the compounds spin-spin coupling will be observed and show schematically the splittings of the signals. 1+2+2=5

(c) Explain what you mean by diamagnetic shielding in ^{1}H NMR spectroscopy. Deduce an expression for the chemical shift. State why chemical shift values are independent of the applied magnetic field or frequency. 2+2+1=5

(d) Calculate the strength of magnetic field at which a free proton will show resonance when a radiofrequency of 100 MHz is used. 2

Given g for proton $= 5 \cdot 585$ and $\beta_N = 5 \cdot 047 \times 10^{-27}\ \mathrm{J\,T^{-1}}$.

(e) Discuss about the hyperfine structure of the ESR spectrum of H-atom. 3

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