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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 the following in brief : 1×7=7

   (a) State which of the following radiations is associated with NMR spectroscopy :

   X-ray, infrared, γ-ray, radiowave

   (b) Find the normal modes of vibration in case of C_2H_6.

   (c) State why IR radiation cannot induce electronic transition.

   (d) Some relationships between the components of moment of inertia are given below :

   (i) $I_A = I_B = I_C$

(*Turn Over*)

(ii) $I_A \neq I_B \neq I_C$

(iii) $I_A = 0$, $I_B = I_C$

(iv) $I_A \neq 0$, $I_B = I_C$

State which of these combinations represents CO_2 molecule.

(e) Considering a diatomic molecule as the vibrating rotor, write the selection rule.

(f) Draw a schematic diagram to show different components of a mass spectrometer.

(g) Name the quantities which are used to present the mass spectrum of a compound.

2. Answer any *four* questions : 2×4=8

(a) Taking the example of butane, write in brief about the electron ionization process used in mass spectrometry.

(b) Distinguish between molecular ion peak and base peak in mass spectrometry.

(c) Show how the McLafferty rearrangement takes place in pentanal and identify the species with $m/z = 44$.

(Continued)

(d) Indicate the specie responsible for the molecular ion peak and the base peak observed in the EI mass spectrum of ethanol. Find m/z values corresponding to these two peaks.

(e) In the mass spectrum of 2-methyl pentane, two prominent peaks are observed at m/z values of 71 and 43 respectively. Identify the specie showing fragmentation.

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

(i) The energy of a hypothetical quantum mechanical system is given by $An^2(n+1)$, where A is constant and $n = 1, 2, 3, \dots$. The selection rule for the system is $\Delta n = \pm 1$. Calculate the energy of the radiation required for the transition to take place. 3

(ii) Write how the population of states affects the intensity of spectral line. 2

Or

(iii) Identify with reasons the IR active and microwave active molecule(s) from the following : 3

HCl and CO_2

(Turn Over)

(iv) A particular molecule is considered to undergo spectroscopic transition between the ground state and the excited state. If the lifetime in the excited state is about 0·1 s, calculate the width of the spectral line in Hz. 2

(b) Consider a diatomic molecule to be an anharmonic oscillator and write its energy as wave number. Deduce the expressions for energy needed for allowed vibrational transitions. Indicate fundamental absorption and overtones.

1+3+1=5

(c) In the pure rotational spectra of ^{14}NO and ^{15}NO, the first lines appear at 3·4 cm^{-1} and 3·2815 cm^{-1} respectively. If the atomic masses of ^{14}N and O are 14·004 amu and 15·9994 amu respectively, find the atomic mass of ^{15}N. 5

Or

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

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

(a) Considering the diatomic molecule to be non-rigid rotator, find an expression for the energy required in wave number for rotational transitions to take place. Write what difference in the spectra is expected if the molecule is considered to be a rigid rotator. 3+2=5

(b) What do you mean by fingerprint region in IR spectroscopy? Explain with example. 3

(c) Sulphur dioxide shows three bands around 519 cm^{-1}, 1151 cm^{-1} and 1361 cm^{-1} in both the Raman and the IR spectra. Explain what information you can draw from this observation regarding the structure of the SO_2 molecule. 2

Or

(d) Show that the Raman lines in the pure rotational Raman spectrum of a diatomic molecule appear at wave number

$$\bar{v} = \bar{v}_0 \pm 2B(2J+3)$$

where $\bar{v}_0$ is the wave number of the Rayleigh line. Draw the schematic diagram to show the Stokes lines and the anti-Stokes lines. 4+1=5

(e) Taking the example of H_2O, write how many normal vibrational bands you may expect. Explain why the number of the IR bands of H_2O is much more than that indicated by the normal vibrational modes.   1+2=3

(f) Using a monochromatic radiation of wavelength 435·8 nm, the Raman line of C_2H_2 (g) is observed at the wavelength of 511 nm. Find the wave number of the vibrational band corresponding to this observation.   2

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

(a) Write the selection rules associated with the electronic transition of atom. Hence explain the fine structure of the spectrum of H-atom.   5

(b) Discuss with diagram what you mean by v' progression in connection with vibrational coarse structure of electronic spectra of diatomic molecule.   3

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

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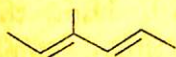
Or

(d) Electronic transition is accompanied by vibrational and rotational transitions. Discuss with diagram how the vibrational bands associated with the electronic spectrum of a diatomic molecule will appear if—

(i) the internuclear distance in the ground and the excited states is the same;

(ii) the internuclear distance in the excited state is considerably greater than that in the ground state, which may lead to dissociation.   5

(e) State what type of electronic transition may be observed in CH_4. Write how the λ_{max} value of this transition varies in CH_3NH_2.   2

(f) A radiation with wavelength 58·4 nm ejects a photoelectron from Ar and the kinetic energy of the photoelectron is 5·4 eV. Calculate binding energy.   3

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

(a) Deduce an expression for the energy difference between the two spin states of an electron in an applied magnetic field in the z-direction. Write how transition from the lower to the upper spin state may be affected. State the selection rule involved.   3+1+1=5

(Turn Over)

(b) State how many ^{1}H NMR signals will be shown by $(CH_3)_2CHCH_2Cl$. Draw schematic diagram to show the signals. Indicate the ratio between the peak areas. Indicate spin-spin coupling citing reasons. 1+1+3=5

Or

(c) Consider the two ^{1}H NMR signals shown by CH_3OH. Explain which protons will show resonance at down field compared to the other if the energy of the radiation is kept constant and the magnetic field is swept. Discuss whether the position of the signals will change or not if the magnetic field is kept constant and the radiation is swept. 3+2=5

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

(e) Write two reasons for using TMS as reference in non-aqueous solvents in ^{1}H NMR spectroscopy. 2

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