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3 (Sem-6) CHM M1

2020

CHEMISTRY

(Major)

Paper : 6·1

(**Spectroscopy**)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

The symbols, used here, signify their usual meaning.

1. Answer in brief: **(any seven)** $1 \times 7 = 7$

(a) Why cannot IR radiation induce electronic transition ?

Contd.

- (b) Consider the following relationships among the components of moment of inertia :

$$I_A = I_B = I_C; \quad I_A \neq I_B \neq I_C;$$

$$I_A = 0, I_B = I_C; \quad I_A \neq 0, I_B = I_C$$

Which of these combinations represent CO_2 molecule ?

- (c) Which of the following molecules will be simultaneously IR and microwave active ?



- (d) State True **or** False :

As the vibrational quantum number increases, the spacing between two adjacent vibrational levels of a diatomic molecule decreases.

- (e) In the Raman effect, the transfer of energy between the photon and the molecule lies in the range 3 to 3000 cm^{-1} . What types of transitions the molecule may undergo due to this energy transfer ?

- (f) State the rule of mutual exclusion in connection with Raman spectroscopy.

- (g) State in which of the following compounds will the protons show resonance at the highest downfield : CH_2Cl_2 , CH_3F , CH_3I

- (h) Name the transitions which are responsible for the coarse and the fine structures of the electronic spectrum.

2. Answer the following questions : $2 \times 4 = 8$

- (a) For the transition from the energy level A to the energy level C of a quantum mechanical system a radiation with wavelength 450 nm is absorbed. Again transition from level B to level C of the same system requires a radiation of wavelength 850 nm . Find the wavelength of the radiation required for the transition from the level A to the level B.

- (b) Considering a diatomic molecule to be rigid rotator, write in brief how the presence of heavier isotope affects the rotational spectrum.

- (c) The Stokes' lines are more intense than the anti-Stokes' lines. Explain.

(d) The IR spectra of ethanol are taken under the following two conditions :

(i) 10% (V/V) in CCl_4 and

(ii) 1% (V/V) in CCl_4 .

Discuss what difference you may observe in the two spectra.

Or

What do you mean by characteristic group frequencies in IR spectroscopy? Explain with example.

3. (a) Answer **either** [(i) and (ii)]

or [(iii) and (iv)] :

(i) Define transition moment. What do you mean by allowed and forbidden transitions in the context of transition moment? 3

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

Or

(iii) Discuss how the component of dipole moment along a particular direction varies with time in anti-symmetric stretching vibration of CO_2 . 3

(iv) A monochromatic radiation is allowed to pass through a solution of a compound with concentration 10 mol m^{-3} when the intensity of the radiation reduces to $\frac{1}{10}$ th of the initial value. Calculate molar extinction coefficient. 2

(b) Considering diatomic molecule to be anharmonic oscillator, deduce expressions for energy needed for the allowed vibrational transitions. Explain fundamental absorption and overtones. 5

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

(i) What do you mean by symmetric and antisymmetric vibrations? What are perpendicular and parallel vibrations? Discuss taking the example of H_2O . 3

- (ii) Using a monochromatic radiation of wavelength 435.8 nm the Raman spectrum of $C_2H_2(g)$ is observed. The spectrum shows one of the lines at 511 nm . Determine the wavenumber of the vibrational band corresponding to this observation. 2

Or

- (iii) The spacing between the consecutive S-branch lines in the pure rotational Raman spectrum of H_2 is 243.2 cm^{-1} . Calculate bond length of H_2 . 5

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

- (a) Write the selection rules associated with the electronic transitions in atom. Hence, explain the fine structure of the spectra of H-atom. 5

- (b) A radiation of frequency $5.14 \times 10^{15} \text{ Hz}$ ejects a photoelectron from Ar. The kinetic energy of the photoelectron is 5.4 eV . Calculate binding energy. 3

- (c) The $\pi \rightarrow \pi^*$ transition in ethene is observed at 170 nm with molar extinction coefficient of $1000 \text{ m}^2 \text{ mol}^{-1}$. Will these values vary markedly in (i) 1,3-butadiene, and (ii) 1,5-hexadiene? Explain with reason. 2

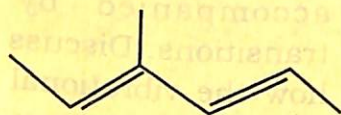
Or

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

- (i) the internuclear distance in the ground and the excited electronic stages is same, and
(ii) internuclear distance in the excited state is considerably greater than that in the ground state which may lead to dissociation of the molecule. 5

- (e) Define chromophore and auxochrome. What do you mean by blue shift of λ_{max} value? The $\pi \rightarrow \pi^*$ transition in aniline is observed at 230 nm. State how this value will change in anilinium ion. 3

- (f) Using Woodward-Fieser rules predict the λ_{max} value of $\pi \rightarrow \pi^*$ transition in — 2



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

- (a) The two spin states of a proton are degenerated in absence of magnetic field. In presence of magnetic field, B_z , in the z-direction this degeneracy is lifted. Deduce an expression for the energy difference between the two spin stages. Write how transition from the lower to the higher spin state may be induced. 3+2=5

- (b) Why is tetramethylsilane used as reference in NMR spectroscopy? 3

- (c) Calculate the frequency of the radiation required by an electron to undergo transition from the lower spin state to the higher spin state when a magnetic field of strength 0.34 T is used.

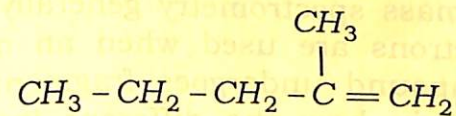
Given $\beta = 9.273 \times 10^{-24} \text{ JT}^{-1}$ and $g = 2$. 2

Or

- (d) What do you mean by hyperfine structure of ESR signals? Discuss about the hyperfine structure of the ESR spectrum of deuterium. 1+3=4

- (e) Write in brief about diamagnetic shielding in ^1H NMR spectroscopy. 2

- (f) State how many ^1H NMR signals will be shown by



Identify the protons which will show resonance at the highest downfield. Predict the splitting of signals due to spin-spin coupling. 4

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

(a) Draw a schematic labelled diagram of the mass spectrometer. What do you mean by electron ionization process? Discuss the fragmentation pattern of methanol. Identify the species responsible for the base peak.

1+3+1=5

(b) What do you mean by McLafferty rearrangement? Explain taking the example of pentanal.

3

(c) Write how the molecular mass of an organic compound can be determined by varying the energy of the bombarding electron in mass spectrometry.

2

Or

(d) In mass spectrometry generally 70 eV electrons are used when an organic compound undergoes fragmentation. Explain how the different ions are detected according to their $\frac{m}{z}$ values by varying the accelerating potential.

4

(e) Show the fragmentation of 2-methylbutane in electron ionization process. Identify the peaks with higher intensities.

3+1=4

(f) Write how a mass spectrum is presented. Distinguish between molecular ion peak and base peak.

2