

- (c) Predict and draw the intensity distribution in hyper fine lines of ESR spectrum of methyl radical ($\cdot\text{CH}_3$). (5,5,5)

(1500)

[This question paper contains 8 printed pages.]

Your Roll No.....

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Name of the Paper : DSC-PHOTOCHEMISTRY
AND SPECTROSCOPY

Name of the Course : B.Sc. (Hons) Chemistry

Semester : VI

Duration : 2 Hours

Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **FOUR** questions in all. Question No. 1 is compulsory.
3. The questions should be numbered in accordance to the number in the question paper.
4. Use of Scientific Calculator is permitted.

Planck's Constant: 6.626×10^{-34} Js : Mass of Electron:
 9.1×10^{-31} Kg

P.T.O.

1. Answer **any 5** of the following :

- (a) Zero-point energy in vibrational spectra is never zero. Comment.
- (b) Why electronic transitions are said to be vertical transitions.
- (c) Why the symmetric stretching mode of vibration of CO_2 molecule is Raman active and asymmetric mode of vibration is Raman inactive?
- (d) What are the laws of photochemistry?
- (e) Explain the terms chromophore and auxochrome. Give one example of each.
- (f) As the number of conjugated atoms in a molecule increases, red shift is observed. Explain with help of one example. (5×3=15)

- (b) Explain the Phosphorescence phenomenon with the help of a suitable energy diagram. Why is it a delayed phenomenon?
 - (c) The first UV peak of 1,3-butadiene is observed at 210 nm, corresponding to a transition from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital). Based on free electron model, calculate the length of the box to which this transition corresponds. (5,5,5)
6. (a) Explain the term chemical shift. What is TMS? Why is it used as a reference standard in NMR?
- (b) What is spin-spin coupling? Explain and sketch the NMR spectrum of methanol with and without spin-spin coupling.

- (ii) Triple bond has higher stretching frequency than corresponding double bond, which in turn has higher frequency than single bond. Explain.

- (c) A molecule XY_2 has the following IR and vibrational Raman spectral data :

Wavenumber (cm^{-1})	IR	Raman
1243	Inactive	Active
2920	Active (PR)	Inactive
786	Active (PQR)	Inactive

Predict the geometry of XY_2 molecule. (5,5,5)

5. (a) Define Lambert-Beer's Law. What are its limitations? Give one application of this law.

2. (a) What is the essential condition for a molecule to be microwave active? Which of the following molecules are expected to be microwave active: SF_6 , H_2O , N_2 , HCN , NO , and CO_2 . Give reason.
- (b) The HCl molecule shows pure rotational lines at the following frequencies (cm^{-1})

20.7, 41.4, 62.1, 82.8

Assign these lines to the corresponding $J \rightarrow J+1$ rotational transitions. Calculate the bond distance of HCl .

The atomic masses are : $H = 1.673 \times 10^{-27} \text{ kg}$;
 $Cl = 58.06 \times 10^{-27} \text{ kg}$.

- (c) (i) Explain, why many of the lower rotational levels are thickly populated.

- (ii) Show that the rotational level whose quantum number is given by the expression has a maximum population :

$$J = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad (5,5,5)$$

3. (a) Discuss how a simple harmonic oscillator system differs from a homonuclear diatomic molecule undergoing anharmonic oscillations in terms of energy relation and energy vs displacement curve from mean position.
- (b) (i) How the presence of Hydrogen bonding can be predicted in IR spectra? Explain with an example.
- (ii) An intense band and the first overtone transition of HBr (bond length 0.142 nm) are centered at 2560 cm^{-1} and 5028 cm^{-1} .

Calculate the anharmonicity constant and force constant for H-Br bond. Mass of hydrogen: 1.0 g/mol and Mass of Br: 80.0 g/mol.

- (c) (i) How will you distinguish between the overtones and hot bands of a spectrum?
- (ii) Calculate the number of fundamental vibrational modes for NH_3 , H_2O and HCN .
- (5,5,5)

4. (a) What are Rayleigh, Stokes and anti-Stokes lines? How is the intensity of stokes lines different from that of anti-stokes lines in pure Raman spectrum? Explain giving reasons.
- (b) (i) Explain the factors that control intensity of spectral lines/band.