

6 SEM TDC CHM M 7

2014

(May)

CHEMISTRY

(Major)

Course : 607

(Spectroscopy)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

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

1. Choose the correct option : 1×5=5

(a) The molecule, which is microwave inactive but IR active, is

(i) HCl

(ii) HBr

(iii) CO₂

(iv) None of the above

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(b) ESR spectra are observed in

- (i) UV/VIS region
- (ii) Radio frequency region
- (iii) Microwave region
- (iv) X-ray

(c) The rotational spectrum of a rigid diatomic rotor consists of equally spaced lines with spacing is equal to

- (i) B
- (ii) $2B$
- (iii) $B/2$
- (iv) $4B$

(d) The vibrations without a centre of symmetry are active in

- (i) Raman and IR
- (ii) IR but inactive in Raman
- (iii) Raman but inactive in IR
- (iv) None of the above

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(Continued

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(e) Distance between the centres of peaks of doublet in NMR is called

- (i) harmonic constant
- (ii) spin-spin coupling
- (iii) spin constant
- (iv) coupling constant

2. Answer any five of the following : 2×5=10

(a) Why the nuclei ^1H and ^{13}C are suitable for NMR investigations?

(b) At what magnetic field would the methyl radical come into resonance in a spectrometer operating at 9.523 GHz? Given that $g_e = 2.0027$ and $\beta_e = 9.274 \times 10^{-24} \text{ JT}^{-1}$.

(c) Water is a good solvent for UV and visible spectroscopy but not for IR spectroscopy. Explain.

(d) A molecule must always vibrate and can never be at rest. Give reasons.

(e) Discuss the term 'hot bands' in vibrational spectra.

(f) Define Larmor frequency.

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- (g) Microwave studies are done only in gaseous state. Why?
- (h) Explain bathochromic shift with suitable example.
- (i) Differentiate between Raman scattering and Rayleigh scattering.

UNIT—I

3. (a) Show that the lines in the rotation spectrum of a diatomic molecule are equispaced under rigid rotator approximation.
- (b) Calculate J_{\max} for a rigid diatomic molecule for which the rotational constant $B = 1.567 \text{ cm}^{-1}$ and $T = 300 \text{ K}$.

Or

State and explain the term 'transition probability'.

UNIT—II

4. (a) Calculate the force constant for H—Cl bond in HCl from the fact that the fundamental vibrational frequency is $8.667 \times 10^{13} \text{ s}^{-1}$.

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(Continue)

(5)

Or

- Deduce the expression for the possible transition energies associated with rotation vibration spectra of a diatomic molecule. Hence show that the vibration-rotation spectra will consist of lines with equal spacing on either side of band origin.
- (b) State and explain fundamental and overtone frequencies with mathematical expressions.
- (c) Roughly sketch the fundamental modes of vibrations of CO_2 and show the infrared active vibrations, if there is any.

UNIT—III

5. (a) State and explain the rule of mutual exclusion with an example.
- (b) What are Stokes and anti-Stokes lines? Explain why anti-Stokes lines are weaker than that of Stokes lines.

Or

Explain with mathematical equations, the type of pure rotational Raman spectrum expected for diatomic molecule

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(Turn Over)

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- (c) The exciting line in an experiment is 5650 Å and the Stokes line is at 5810 Å. Calculate the wavelength of the anti-Stokes line.

UNIT—IV

6. (a) State and explain Franck-Condon principle.

- (b) A conjugated diene in hexane absorbs light with $\lambda_{\max} = 219$ nm. Will λ_{\max} increase or decrease if the solvent is changed to ethanol? Explain.

Or

Explain the term chromophore giving two examples.

- (c) Draw the relative energies of molecular orbitals and the type of transition between them.

UNIT—V

7. (a) What is understood by the terms chemical shift and spin-spin coupling?

Or

Discuss the principle of ESR spectroscopy.

(Continued

(7)

- (b) Draw the high resolution NMR spectra of 1-chloropropane and 2-chloropropane.

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- (c) Describe the ESR spectrum of methyl radical.

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