

M.Sc. 4th Semester Examination, 2021

CHEMISTRY

(Physical Chemistry Special)

Paper: CHEM 402E

Course ID: 41452

Time: 2 Hours

Full Marks: 40

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* of the following questions: 2×5 = 10
- a) The symmetric stretching mode of CO₂ is IR inactive but Raman active. - Explain.
 - b) What are the conditions for a molecule to be microwave active in rotational transition?
 - c) Justify that the ground state vibrational level of a diatomic molecule is more densely populated.
 - d) Define hyperfine splitting in ESR spectra.
 - e) Explain why $n \rightarrow \pi^*$ transition produces weak absorption band.
 - f) Define spin-spin splitting in NMR spectra.
 - g) Write down the relative intensities for (i) $I = 1/2$ and $N = 2$ (ii) $I = 1$ and $N = 2$ in ESR transition.
2. Answer *any four* of the following questions: 5×4 = 20
- a) Explain the different modes of vibration of H₂O. 5
 - b) What is the selection rule for the ESR transition? How many lines are obtained in the ESR spectra of phenyl radical and why? 1+4 = 5
 - c) Briefly explain the NMR spectra of methanol. 5
 - d) Write down the energy expression and selection rule for a rigid rotator. Show that the frequency separations of rotational spectra are equispaced. (1+1)+3 = 5

- e) Derive the expression of frequency of radiation for electronic transition showing P and R branch of the band. 5
- f) Write down the selection rule for anharmonic oscillator. Show that the energy levels are not equispaced for an anharmonic oscillator. 1+4 = 5

3. Answer *any one* of the following questions: 10×1 = 10

- a) i) Show that for the rotational spectrum of a diatomic molecule, the rotational quantum number (to the nearest integral value) for the maximum populated level is given by,

$$J_{\max} = \sqrt{\frac{kT}{2Bh}} - \frac{1}{2}. \text{ The terms have their usual significance.}$$

- ii) What is meant by fundamental, overtone and hot bands in vibrational spectroscopy?
- iii) The vibrational frequency of $^1\text{H}^{79}\text{Br}$ is $\nu_e = 2649.7 \text{ cm}^{-1}$ and $x_e\nu_e = 45.2 \text{ cm}^{-1}$. Find the frequency (in cm^{-1}) of the fundamental and first overtone of $^1\text{H}^{79}\text{Br}$.
- iv) What are chromophores? 3+3+3+1 = 10

- b) i) How will you determine bond length by rotational spectra?
- ii) In the far I.R. spectrum of HBr, there is a series of lines having a separation of 16.94 cm^{-1} . Calculate the moment of inertia and the inter-nuclear distance.
- iii) Write the name of a reference compound which is usually used for H^1 NMR study. What are the reasons behind the selection for such a reference?
- iv) Transitions usually start from the middle of $v = 0$ level of ground electronic state - Explain. 2+4+2+2 = 10