No. of Printed Pages : 7

MCH–020

M. SC. IN CHEMISTRY

(MSCCHEM)

Term-End Examination

December, 2025

MCH-020 : ATOMIC AND MOLECULAR SPECTROSCOPY

Time : 2 Hours *Maximum Marks : 50*

Note : *Question No.* ***1*** *is compulsory. Attempt any* ***four*** *questions from Question Nos.* ***2*** *to* ***7.*** *Use of simple non-scientific calculator is allowed.*

1. Answer any *five* questions from the following : 2×5=10

   (i) State the Beer-Lambert's law.

   (ii) What is photoelectric effect ? Write the equation of Einstein's photoelectric law.

(iii) Write the selection rule for vibrational transitions.

(iv) State the Franck-Condon's principle.

(v) What is the effect of polar solvent on $n \rightarrow \pi^*$ electronic transitions ?

(vi) How is (Fourier Transform) FT-NMR spectroscopy better than (Continuous Wave) CW-NMR spectroscopy ?

(vii) What causes quadrupole splitting in Mössbauer spectra ?

2. (a) (i) How does the rule of mutual exclusion help in predicting the symmetry in case of H_2O and CO_2 molecules ? 2

(ii) Briefly discuss the basic principle of X-ray Photoelectron Spectroscopy (XPS). 3

(b) (i) Calculate the term symbols for the D state of a hydrogen atom. 2

(ii) Derive an expression for the moment of inertia for a rigid diatomic molecule. 3

3. (a) (i) Which valence state of copper, Cu^{+} or Cu^{2+}, exhibits an ESR spectrum and why ? 2

(ii) The equilibrium vibration frequency for a diatomic molecule is 215 cm^{-1} and the anharmonicity constant x_e = 0.003. Calculate the difference in the frequencies of the fundamental band and the hot band. 3

(b) (i) Give the relationships between the moments of inertia for oblate and symmetrical top molecules. 2

(ii) What is Born-Oppenheimer approximation and how is it important in electronic spectroscopy of diatomic molecules ? 3

4. (a) The lifetime of $^{57}Fe^{*}$ (excited state) is 1.50×10^{7} s. If the excited state is 15.0 keV above the ground state, determine the line width, τ and ratio τ/E. 3

(b) A light source of wavelength, λ illuminates a metal surface and electrons are ejected with a maximum kinetic energy 2 eV. If the same surface is illuminated by a light source of wavelength $\frac{\lambda}{3}$, then calculate the maximum kinetic energy of the ejected electrons. Work function of metal is 1 eV. 3

(c) The Raman line for a substance was observed at 456.8 nm on irradiating with 433.2 nm radiation. Calculate the wave numbers of the Stokes and anti-Stokes lines for the substance if the exciting line is 406.3 nm. 4

5. (a) Give the expression for the nuclear magneton and name the terms involved. 2

(b) The fundamental and first overtone transitions in the vibrational spectrum of NO molecule are observed at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Calculate the equilibrium vibration frequency, anharmonicity constant and the oscillation frequency for the molecule. 4

(c) What is meant by Lyman series of hydrogen ? What will be the wave number of the longest wavelength in the Lyman series ?

[Given R_H = 109, 667.58 cm^{-1}] 4

6. (a) (i) Give any *two* advantages of Raman spectroscopy over IR spectroscopy.

2

(ii) Predict hyperfine structure and transitions in the ESR sperectrum of methyl radical anion. 3

(b) How does spin-spin relaxation help in regaining the population equilibrium in nuclear spin states ? Calculate the ratio of the population of the excited state to that of the ground state for protons in a magnetic field of 1.41 T at room temperature (300 K). 5

7. (a) (i) Calculate the ESR frequency of an unpaired electron in a magnetic field of 0.33 T, given that for a free electron, g_e = 2 and β_e = 9.274 × 10^{-24} JT^{-1}. 2

(ii) Explain why the ^{13}C-^{13}C spin-spin splitting is not observed in ^{13}C-NMR spectrum. 3

(b) In a NMR spectroscopy experiment a proton comes to resonance at a frequency of 100 megahertz. 5

(i) Calculate the energy of the proton corresponding to this radiation.

(ii) Calculate the wavelength of the radiation.

[Given : $h = 6.626 \times 10^{-34}$ Js and 1 megahertz = 10^6 Hz]

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