P.G. Semester-IV Examination, 2023

CHEMISTRY

Course ID : 41452 **Course Code : CHEM-402E**

Course Title : Physical Chemistry Special

Time : 2 Hours Full Marks : 40

The figures in the right-hand margin indicate 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) Write down the Born-Oppenheimer approximation.

   b) Why is N_2 molecule inactive to rotational spectroscopy?

   c) Write down the effect of isotropic substitution on the spectrum of CO.

   d) Define the term 'plane polarised light.'

   e) Mention the selection rules for Raman and IR spectroscopy.

   f) Define the terms 'chemical shift' and 'Larmor frequency.'

   g) What do you mean by the term 'Stark effect' in spectroscopy?

2. Answer any **four** of the following questions: 5×4=20

   a) (i) Discuss the principle of IR spectroscopy in the molecular structure elucidation. 3

   (ii) Write down the rule of mutual exclusion in Raman spectroscopy. 2

   b) Write in short the applications of ESR and Mossbauer spectroscopy. 5

   c) (i) What is Raman scattering?

   (ii) Describe the quantum theory of Raman effect. 1+4=5

   d) (i) Why is the selection rule for pure rotational Raman spectrum $\Delta J = \pm 2$ and $\Delta J = \pm 1$?

   (ii) Explain Stokes and anti-Stokes lines. 3+2=5

   e) (i) What is the significance of zero point energy? Obtain an expression for zero point energy of an anharmonic oscillator.

   (ii) Give selection rules for simple harmonic and anharmonic oscillator. 3+2=5

f) Sketch and explain the polarizability ellipsoids for CO_2 molecule. 5

3. Answer any **one** of the following questions: $10\times1=10$

a) (i) The rotational constant for $^{79}Br^{19}F$ is 0.35717 cm^{-1}. What is the value of J for which the most intense line will be seen at 300K?

(ii) What is the effect of breakdown of Born-Oppenheimer approximation on P and R branches of the IR spectrum of a diatomic molecule?

(iii) The fundamental vibrational frequency of $^{1}H^{35}C1$ molecule is 86.63×10^{12} Hz. Calculate the zero point energy and force constant of HC1.

(iv) Explain the activity of the following molecules with respect to IR and microwave spectrum: H_2, HC1, CO_2, CH_4 and CH_3C1. $3+2+3+2=10$

b) (i) Write down a principle of NMR spectroscopy. 3

(ii) Write in short chemical applications of 'H-NMR'. 2

(iii) Prove that the NMR spectrum of a molecule containing *n* chemically equivalent nuclear spins consists of a single line, even though there are different coupling constants (Explain with NMR Hamiltonian). 5

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