PG Even Semester (CBCS) Exam., May—2017

CHEMISTRY

(2nd Semester)

Course No. : CH–203 (C)

(Molecular Spectroscopy)

Full Marks : 75
Pass Marks : 30

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Show that for a transition between two stationary states, the rate of development of the excited state is an exponential function of time. 11

(b) Discuss Born-Oppenheimer approximation and its limitations. 4

2. *(a)* Assuming the rigid rotor model, show that the rotational energy levels of diatomic molecules are quantized. 9

(b) Write short notes on : 3+3=6

(i) Fluorescence

(ii) Phosphorescence

UNIT—II

3. *(a)* Discuss the principle of the spectrum of diatomic vibrating rotator. Give the selection rule and obtain the final expression for PQR branch. Show the transition diagrammatically. 11

(b) What do you mean by fundamental absorption and overtones absorption in the IR spectra? 4

4. *(a)* Explain why the C = O stretching vibration of an aldehyde gives a strong absorption in the IR spectrum while the C = C vibration in an alkene is normally weak. 4

(b) Explain the symmetry and fundamental vibrations of CO_2 and H_2O molecules observed in the IR-absorption spectra. 3+3=6

(c) Write short notes on the following : 2½+2½=5

(i) Anharmonic oscillator

(ii) Hot bands

UNIT—III

5. *(a)* Explain the principle of Raman spectroscopy based on both classical and quantum theories with schematic diagrams. 10

(b) Discuss briefly about the information that can be derived from vibrational analysis of an electronic vibration spectra. 5

6. *(a)* Explain the Raman activities of vibrations in H_2O and CO_2 in the light of symmetry and polarizability ellipsoid along with a schematic diagram. 6

(b) Show that the shape of BeH_2 changes upon excitation. 4

(c) A molecule A_2B_2 has IR absorption and Raman spectral lines in the following table :

Frequencies (cm ^{1})	*Infrared*	*Raman*
3374	—	strong
3287	very strong	—
1973	—	very strong
729	very strong	—
612	—	weak

Deduce the structure of the molecule and assign the observed vibration to particular molecular modes. 5

UNIT—IV

7. *(a)* Explain and obtain an expression for interaction of nuclear spin with a magnetic field. 10

(b) Draw and explain the ^{1}H-NMR spectrum of pure ethanol and ethanol mixed with water. 5

8. *(a)* Explain how NMR techniques differ from ESR techniques. 5

(b) Discuss the effect of relaxation process on line width of NMR spectral lines. 5

(c) Why is the coupling constant of the organic free radical smaller than H-atom? 5

UNIT—V

9. *(a)* Obtain zero-order and first-order hyperfine energies of spin energy levels of the H-atom. 8

(b) Define and express the spin magnetic moment of an electron spin in terms of the Bohr magneton. Give the principle of electronspin resonance (ESR) exhibiting Zeeman splitting. 7

10. *(a)* "Spin-spin interactions with a group of magnetically equivalent nuclei do not produce multiplet splitting." Justify the statement. 8

(b) How do you account for hyperfine splitting of H-atom in a C—H bond? 4

(c) What are the basis spin functions? 3

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