(7 pages) **Reg. No. :** .....

Code No. : 9403 **Sub. Code : HCHM 43**

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2015.

Fourth Semester

Chemistry

PHYSICAL CHEMISTRY

(For those who joined in July 2012 onwards)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. The rotational constant B of rotational spectra of diatomic molecule is defined as

   (a) $B = h/8\pi^2 Ic\ cm^{-1}$ (b) $B = 8\pi^2/Ic\ cm^{-1}$

   (c) $B = 8\pi^2 Ic/h\ cm^{-1}$ (d) $B = hIc/8\pi^2\ cm^{-1}$

2. The rotational transitions for a rigid diatomic molecule are governed by the selection rule

   (a) $\Delta J = \pm 2$ (b) $\Delta h = \pm 2$

   (c) $\Delta J = \pm 1$ (d) $\Delta h = \pm 1$

3. The mean region of IR spectra for CO_2 is

   (a) 1560 cm^{-1} (b) 1330 cm^{-1}

   (c) 1460 cm^{-1} (d) 1530 cm^{-1}

4. The Raman shifts fall in the range ———— for vibrational energy changes

   (a) 400-4000 cm^{-1} (b) 100-400 cm^{-1}

   (c) 100-4000 cm^{-1} (d) 400-800 cm^{-1}

5. Functional groups C = C, –N = N– which absorb at wave lengths longer than 180 nm are called

   (a) Fluorescence

   (b) Phosphorescence

   (c) Chromophores

   (d) Finger print region

6. Electron binding energy of each emitted electrons can be determined by

   (a) Photo electron spectroscopy

   (b) Auger electron spectroscopy

   (c) ESCA

   (d) X-ray analyzer

7. The magnitude of the nuclear magnetic moment is given by

(a) $\mu = g_N \mu_N [I(I+1)]^{1/2}$

(b) $\mu = g_N \mu_N [I(I+1)]^{3/2}$

(c) $\mu = g_N \mu_N [I(I+1)]^{2}$

(d) $\mu = g_N \mu_N [I(I-1)]^{1/2}$

8. In ESR spectra, hyperfine coupling constant (a) is expressed in units of

(a) centimeter (b) nanometer

(c) tesla (d) no-unit

9. An ionic character of NQR spectroscopy is determined by

(a) I.C. = $1 + (e^2Qq/h)o/(e^2Qq/h)$

(b) I.C. = $1 - (e^2Qq/h)o/(e^2Qq/h)$

(c) I.C. = $(e^2Qq/h)o/(e^2Qq/h)$

(d) I.C. = $1 + (e^2Qq/h)/(e^2Qq/h)o$

10. Zeeman splitting in Mossbauer spectroscopy of ^{57}Fe gives ———— lines.

(a) 1 (b) 7

(c) 9 (d) 6

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Discuss the kinetic energy of rotation in rigid rotator model.

Or

(b) Differentiate between collision broadening and Doppler broadening.

12. (a) What are the advantages of Raman spectroscopy over IR?

Or

(b) (i) State the selection rules for vibrational and transition spectra. (2)

(ii) Explain : Hot bands.

13. (a) Explain – Frank-Condon principle.

Or

(b) Explain Reuner-teller effect for linear molecules and John-Teller effect for non-linear molecules.

14. (a) Discuss the ESR spectra of transitional metal complexes.

Or

(b) State the principle and applications of FT-NMR.

15. (a) (i) Discuss the basic principle of Mossbauer spectroscopy. (2)

(ii) Write short notes on :

(1) Doppler effect

(2) Magnetic hyperfine interaction.

Or

(b) The NQR frequency for a nucleus with I = 3/2 in an axially symmetric EFG (n = 0) is 100 MHz. calculate e2Qq/h.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) The first rotational spectra lines correspond to the transition from J = 0 to J = I and appears as $\gamma\, rot = 3.84235\,cm^{-1}$.

(i) Calculate the moment of inertia and reduced mass of CO.

(ii) Calculate the bond length of CO molecule.

Or

(b) Describe the non-linear molecule of polyatomic molecules with suitable examples.

17. (a) Explain in detail about the anharmonic oscillator model in vibrational spectroscopy.

Or

(b) Explain the quantum theory of Raman spectroscopy.

18. (a) (i) State : Birije extraploation.

(ii) Discuss Born-oppenheimer approximation.

Or

(b) Discuss the principle, instrumentation and applications of Auger electron spectroscopy.

19. (a) (i) Explain the principle of ^{13}C and ^{19}F spectroscopy.

(ii) Give the applications of ^{31}P NMR spectroscopy.

Or

(b) Explain the g-factor and hyperfine splitting in ESR spectroscopy.

20. (a) (i) Explain the basic principle of NQR. (4)

(ii) Differentiate NMR from NQR. (4)

Or

(b) (i) Explain in detail about the oxidation states of metal ion in compounds by Mössbauer spectroscopy.

(ii) Define : Zeeman splitting.
