2024/06

SET A

M.Sc. CHEMISTRY
SECOND SEMESTER
QUANTUM CHEMISTRY & MOLECULAR SPECTROSCOPY II
MSC – 204 OLD COURSE [REPEAT]

[USE OMR FOR OBJECTIVE PART]

Duration: 3 hrs. **Full Marks: 70**

(Objective)

Time: 30 min. **Marks: 20**

Choose the correct answer from the following: ***1×20=20***

1. The de-Briglie wavelength of the particle of mass 'm' and kinetic energy E_K is
   a. $\frac{h}{\sqrt{2mE_K}}$ b. $\frac{h}{2mE_K}$
   c. $\frac{h}{\sqrt{mE_K}}$ d. $\frac{h}{2\sqrt{E_K}}$

2. According to Born Oppenheimer approximation the change in total energy of a molecule (ΔE_{total}) is sum of change of electronic energy (ΔE_{elec}), change in vibrational energy (ΔE_{vib}) and the change in rotational energy (ΔE_{rot}). The correct order of the change of these energies is
   a. $\Delta E_{elec} > \Delta E_{vib} > \Delta E_{rot}$ b. $\Delta E_{rot} > \Delta E_{elec} > \Delta E_{vib}$
   c. $\Delta E_{vib} > \Delta E_{elec} > \Delta E_{rot}$ d. $\Delta E_{vib} > \Delta E_{rot} > \Delta E_{elec}$

3. The degree of degeneracy of a particle in a 2D box of size 'a' having energy $\frac{9h^2}{4ma^2}$ is
   a. 1 b. 2
   c. 3 d. 4

4. A three level system of atoms has N_1 atom in level E_1, N_2 atom in level E_2, and N_3 atom in level E_3 ($N_2 > N_1 > N_3$ and $E_1 < E_2 < E_3$). Laser emission is possible between levels
   a. $E_3 \rightarrow E_1$ b. $E_2 \rightarrow E_1$
   c. $E_3 \rightarrow E_2$ d. $E_2 \rightarrow E_3$

5. The vibronic spectrum of a diatomic molecule $\bar{w}_e$= 512 cm^{-1}, $\bar{w}_e \chi_e$ = 8 cm^{-1}, where $\bar{w}_e$ is oscillation frequency and χ_e is anharmonicity constant. The dissociation energy of the molecule is
   a. 4096 cm^{-1} b. 6144 cm^{-1}
   c. 8192 cm^{-1} d. 16384 cm^{-1}

6. To record Mössbauerspectrum of iron containing samples, 'X' is used. 'X' after nuclear transformation (Y) gets converted to a species which gives γ radiation that is used in Mössbauer spectroscopic study. 'X' & 'Y' respectively are
   a. ^{57}Fe & β emission
   b. ^{57}Co & β emission
   c. ^{57}Fe & e^- capture
   d. ^{57}Co & e^- capture

7. The solvent residue peak for CD_3CN in ^1H-NMR is due to the presence of
   a. CH_3CN
   b. CHD_2CN
   c. CD_3CN
   d. CH_2DCN

8. The total number of peaks will be seen in ^{13}C NMR of terephthalaldehyde is
   a. 6
   b. 5
   c. 4
   d. 3

9. The first excited electronic state of hydrogen (H_2) molecule is
   a. $^1\sum_g^+$
   b. $^1\sum_u$
   c. $^1\sum_g$
   d. $^1\sum_u^+$

10. The internal standard used in ESR is
   a. TEMPO
   b. DMPO
   c. DPPH
   d. 4-Hydroxy-TEMPO

11. The radical anion formed from naphthalene is expected to show total number of line in its ESR spectrum is
   a. 8
   b. 9
   c. 17
   d. 25

12. For which of the transition Q branch in rotational structure of electronic transition is not found
   a. $^1\Delta \rightarrow {}^1\Delta$
   b. $^1\sum \rightarrow {}^1\sum$
   c. $^2\prod \rightarrow {}^2\prod$
   d. $^3\sum \rightarrow {}^3\prod$

13. Which one is true for the 'g' factor in ESR of most of organic radicals
   a. $g >> 2.0023$
   b. $g << 2.0023$
   c. $g \approx 2.0023$
   d. All

14. The lowest energy is zero for a
   a. Rigid rotator
   b. A particle in cubical box
   c. Linear harmonic oscillator
   d. Hydrogen atom

15. For a diatomic molecule with vibrational quantum number 'n' and rotational quantum number 'J' the vibrational level spacing $\Delta E_n = E_n - E_{n-1}$ and the rotational level spacing $\Delta E_j = E_j - E_{j-1}$ are approximately
   a. ΔE_n = constant, ΔE_j = constant
   b. ΔE_n = constant, $\Delta E_j \propto J$
   c. $\Delta E_n \propto n$, $\Delta E_j \propto J$
   d. ΔE_n = constant, $\Delta E_j \propto J^2$

16. The energy difference of n=2 and n=1 of a particle in one dimensional box is 6 unit of energy. In the same units, what is the difference of energy level of n=3 and n=2 for the above system?

a. 4 b. 5
c. 9 d. 10

17. The intensity distribution of vibrational bands in electronic transition of Iodine molecules (I_2) shows that [r_e'' and r_e' are the equilibrium inter nuclear distances in lower and upper vibrational state respectively]

a. $r_e' >> r_e''$ b. $r_e' < r_e''$
c. $r_e' \approx r_e''$ d. $r_e' << r_e''$

18. The intense violet color of $KMnO_4$ solution is due to

a. d-d transition b. Charge transfer transition
c. Fluorescence d. Scattering of light

19. Which of the following is not ESR active?

a. N_2 b. NO
c. NO_2 d. ClO_2

20. Mössbauer spectrum of $Fe(CO)_5$ in the presence of external magnetic field will show

a. 6 lines b. 5 lines
c. 4 lines d. 3 lines

-- --- --

Descriptive

Time : 2 hrs. 30 mins. **Marks : 50**

[Answer question no.1 & any four (4) from the rest]

1. **a.** Write the expression of ∇^2 in spherical polar coordinate. Define spherical harmonics and give the expression of it. Write the expression of spherical harmonics for l = 0, 1 and m = 0. **6+4=10**

   b. What is meant by degeneracy? Explain with examples. Discuss the degeneracy of the energy of a rigid rotator.

2. **a.** Write down the complete wave function of a two-electron system with normalization requirement and probability density. State Pauli's anti-symmetry principle and express it with the help of exchange operator $\hat{P}_{12}$ **7+3=10**

   b. State Pauli's exclusion principle applied to molecules and show that for a two electron system the Hamiltonian operator commutes with the exchange operator $\hat{P}_{12}$.

3. What are the main types of intensity distribution of vibrational bands in electronic transitions? State the principle behind the explanation of the intensity distribution of the said vibrational bands. Apply this principle to explain the intensity distribution of oxygen and carbon monoxide molecule. Draw the transition diagram with intensity of the transitions in each case. **3+1+2+2+1+1=10**

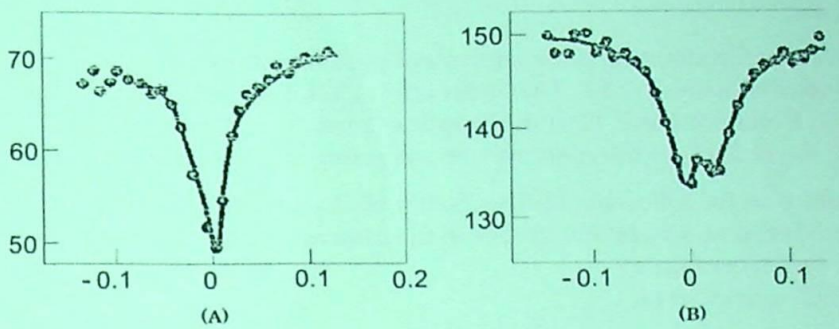
4. **a.** Calculate the g value of a radical showing ESR signal at 0.3292 T in a spectrometer operating at 9,223 MHz. **3+2+3+2=10**

   b. The ESR spectrum of hydrogen atom exhibits two lines at 0.3573 T and 0.3066 T in a spectrometer operating at 9,302 MHz. Find the hyperfine coupling constant.

   c. Find the ratio of the equilibrium population of α (Ms = +1/2) and β (Ms = - 1/2) spin states of electrons at 27 °C in a magnetic field of 0.34 T. Consider g_e = 2.00.

   d. How many lines are expected for the anion radical of anthracene in a fully resolved ESR spectrum? Justify your answer.

5. **a.** Mössbauer spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ are given below. Explain which is for which one? **4+3+3 =10**



b. Which of the following compounds show higher quadrupole splitting: *cis* or *trans*-$Fe(CO)_4Cl_2$? Justify your answer.

c. Explain why the Mössbauer spectrum of $Fe(CN)_6^{4-}$ shows a single peak while that of $[Fe(CN)_5NH_3)]^{3-}$ shows a pair of peaks.

6. **a.** A Mössbauer nucleus of mass 57.0 amu emits radiation of wavelength 0.1 nm. Find the recoil velocity, energy, and Doppler shift to an observer. **4+3+3 =10**

b. The half-life of $^{57}Fe^*$ is 1.5×10^{-7}s. Calculate the line width of the γ ray emission.

c. Predict the expected variation in isomer shift of Sn^{2+}, Sn^{4+} and Sn covalently bonded to four groups.

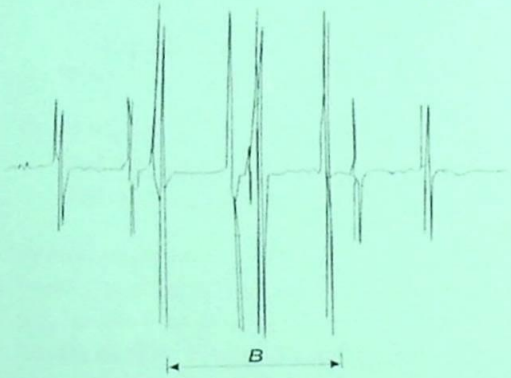
7. **a.** Explain with diagram the stimulated emission of radiation. Discuss the mechanism of light amplification in a laser. What are the requirements of laser action? **2+3+2 =7**

b. Mention the properties of laser radiation. Why a four level laser is superior to three level laser? **3**

8. **a.** Discuss the expected ESR spectrum for $^{\cdot}NH_3$ radical taking $a_N > a_H$. **3+3+4 =10**

b. A radical containing three equivalent protons shows a quartet with intensities 1:3:3:1. The lines occur at 331.4 mT, 333.6 mT, 335.8 and 338.0 mT. Find the coupling constant and the g value of the radical for the spectrometer operating at 9.332 GHz.

c. Interpret the following ESR spectrum of CH_3CHOH radical produced as a transient species in the ultraviolet photolysis of a solution containing
H_2O_2 and ethanol.



= = *** = =