REV-01
MSC/04/10

2023/06

SET A

M.Sc. CHEMISTRY
SECOND SEMESTER
QUANTUM CHEMISTRY & MOLECULAR SPECTROSCOPY II
MSC – 204 [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: ***1X20=20***

1. The solvent residue peak for CD_3CN in ^1H-NMR is a
   a. doublet b. triplet
   c. quartet d. quintet

2. Among the following, those act as Mössbauer nuclei are
   1) ^{129}I 2) ^{57}Co 3) ^{57}Fe 4) ^{121}Sb
   a. 1, 2, 3, 4 b. 2, 3, 4
   c. 1, 2, 4 only d. 1, 3, 4 only

3. 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

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

5. The energy levels of cyclobutadieneare $\alpha + 2\beta$, α, α and $\alpha - 2\beta$. The delocalization energy of this molecule is
   a. 4α b. -4β
   c. -8β d. zero

6. The spatial part of the wave function of the atom in its ground state is 1s (1) 1s (2). The spin part would be
   a. $\alpha(1)\beta(2)$ b. $\beta(1)\alpha(2)$
   c. $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)] - \beta(1)\alpha(2)]$ d. $[\alpha(1)\beta(2)] + \beta(1)\alpha(2)]$

7. 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, $\Delta E_j \propto J^2$

8. 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. $r_e' << r_e''$

9. For hydrogen like atom with a nuclear charge z, the energy of orbital with principal quantum number 'n' follow the relation
   a. $E_n \infty n^2 z^2$ b. $E_n \infty -\frac{z^2}{n}$
   c. $E_n \infty -\frac{z^2}{n^2}$ d. $E_n \infty -\frac{z}{n}$

10. 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. $\frac{h}{2\sqrt{E_K}}$

11. How many signals will be seen for CD_2Cl_2 in ^{13}C NMR in 100 MHz instrument?
   a. 4 b. 5
   c. 3 d. 1

12. 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

13. The ESR spectrum of $[Cu(NH_3)_6]^{2+}$ complex will have
   a. Single 'g' value b. $g\| = g^{\perp}$
   c. $g\| > g^{\perp}$ d. $g\| < g^{\perp}$

14. Stimulated emission is most likely in which of the region of the region of electromagnetic radiation?
   a. Microwave b. Infra red
   c. Visible d. Ultra violet

15. 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. $E_2 \rightarrow E_3$

16. 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. $16384\ cm^{-1}$

17. e^{-2x^2} is an eigen function of the operator $(\frac{d^2}{dx^2} - 16x^2)$. The corresponding eigen value is

a. +2
b. -2
c. +4
d. -4

18. 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. $^3\sum \rightarrow {}^3\prod$

19. In a d^1 complex, the ESR signal occurs at 326 mT and the reference signal at 332 mT, g_{ref} = 2.0028. The g value of the sample will be

a. 2.23
b. 2.32
c. 2.04
d. 2.40

20. Which of the following having nuclear spin, I =3/2?

a. ^{19}F
b. ^{13}C
c. ^{35}Cl
d. ^{31}P

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Descriptive

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

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

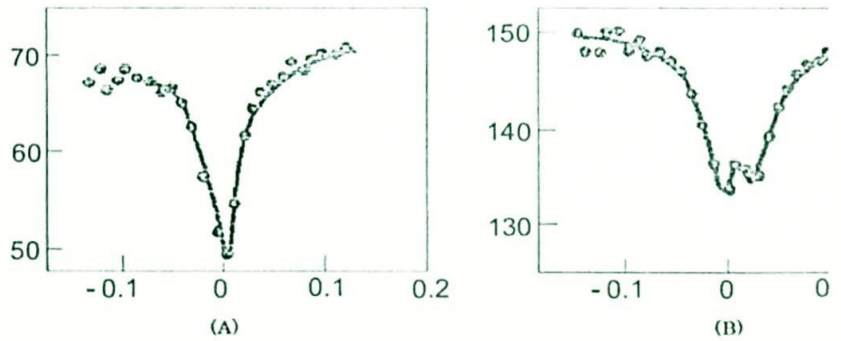
1. a. What is meant by a rigid rotator? Write down the Schrodinger wave equation of the rigid rotator in spherical polar coordinate and separate the Φ and θ equations. Find the energy of the rigid rotator and show that it is quantized. 7+3=10

   b. Show that energy difference between two successive energy levels of a rigid diatomic rotator is $\frac{h^2}{4\pi^2 I}(J+1)$, where J is the rotational quantum number of the lower rotational level.

2. 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

3. 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.

4. a. Acetonitrile (CH_3CN) has resonance at 1.97 ppm, whereas methyl chloride (CH_3Cl) has resonance at 3.05 ppm in ^1H-NMR, even though the dipole moment of acetonitrile is 3.92 D and that of methyl chloride is only 1.85 D. The larger dipole moment for the cyano group suggests that the electronegativity of this group is greater than that of the chlorine atom. The methyl hydrogens on acetonitrile are actually more shielded than those in methyl chloride, in contrast with the results expected on the basis of electronegativity. Explain why? **2+3+5 =10**

b. Define chemical shift in NMR spectroscopy? Calculate the chemical shifts of the different hydrogen atoms of (E)-1-chloro-2-nitroethene. [NO_2: $\delta_{gem} = 1.87$, $\delta_{cis} = 1.30$, $\delta_{trans} = 0.62$ and Cl: $\delta_{gem} = 1.08$, $\delta_{cis} = 0.19$, $\delta_{trans} = 0.13$]

c. Depict the ^1H NMR spectrum of ethyl acetate with multiplet skewing. Explain the terms (i) Chemical shift and (ii) Coupling constant with ethylacetate as an example.

5. a. What is meant by effective potential acting on the electron in hydrogen atom? Give the expression of effective potential. Discuss how effective potential changes with distance from the nucleus and various levels of orbital angular quantum numbers. **7+3=10**

b. Explain the differences between orbit and orbital.

6. 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.

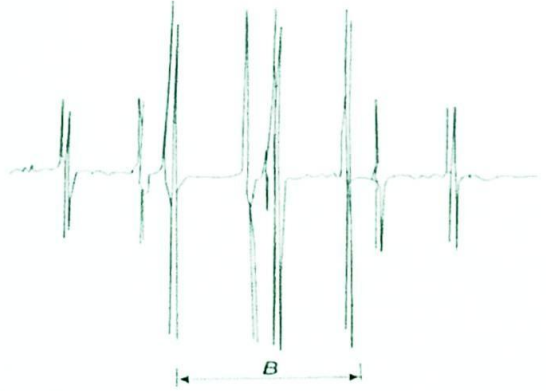
c. Find the ratio of the equilibrium population of α (Ms = +1/2) and β (Ms = - 1/2) spin states of electrons at 27 °C in a magnetic field of 0.34 T. Consider g_e = 2.00.

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

7. a. Discuss the expected ESR spectrum for $\dot{N}H_3$ 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 $CH_3\dot{C}HOH$ radical produced as a transient species in the ultraviolet photolysis of a solution containing H_2O_2 and ethanol.



8. State the assumptions on which Hückel Molecular orbital (HMO) theory is based. Obtain HMO energies and Hückel Molecualar orbitals of ethylene. Hence obtain the total π electron energies of a classical double bond. Discuss the bonding and symmetry properties of Hückel Molecualar orbitals. **10**

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