Roll No. ....

239302

December, 2019
M.Sc. Chemistry - III SEMESTER
Spectroscopy - II (CH-302 A)

Time : 3 Hours]   ]Max. Marks : 75

Instructions :

1. *It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*

2. *Answer any four questions from Part-B in detail.*

3. *Different sub-parts of a question are to be attempted adjacent to each other.*

PART - A

1. (a) Calculate the degrees of freedom of acetylene and water molecule.   (1.5)

    (b) What is Born-oppenheimer approximation?   (1.5)

    (c) What are the factors which affect the intensity of the spectral line?   (1.5)

    (d) State the selection rule for Raman scattering.   (1.5)

(e) Which valence state of Cu^+ ion and Cu^{2+} ion will show an ESR spectrum and why? (1.5)

(f) Which of the following molecules show pure rotational Raman spectrum?

H_2, HBr, CH_3Br. (1.5)

(g) What do you understand by multiplicity of state? (1.5)

(h) Express McConnell relationship. (1.5)

(i) What is Patterson method? (1.5)

(j) Define stereographic projections. (1.5)

PART - B

2. (a) (i) Discuss the rotational spectra of linear and symmetric top molecules. (7)

(ii) Draw potential energy curve when force constant K is (a) large and (b) small. (3)

(b) The vibration frequency of $^1H^{35}Cl$ is 2990.6 cm^{-1}; estimate the frequency for (5)

$^1H^{37}Cl$, $^2D^{35}Cl$ and $^1D^{37}Cl$.

3. (a) Explain on the basis of nuclear spin-spin interactions the different peaks observed in the NMR spectrum of an acidified solution of ethanol. What types of absorption peaks are obtained for pure ethanol? (5)

(b) (i) Calculate the NQR energy levels for ^{55}Mn with $I = 5/2$ as a function of e^2Qq. Give the expressions for the transition frequencies. (7)

(ii) What are the various factors affecting chemical shift? (3)

4. (a) In the pure rotational Raman spectrum of a diatomic molecule, the separation from Rayleigh line of the first Stokes and anti-Stokes line is different from the subsequent line spacings. Find the ratio of these spacings when

(i) all the rotational levels are populated,

(ii) only the odd levels are populated, and

(iii) only the even levels are populated. (5)

(b) Predict the number of ESR lines in the spectrum of (a) CH_3CH_2-radical (b) C_6H_6- (benzene radical anion). (6)

(c) Why the ESR peak of a sample observed at liquid nitrogen temperature is nearly four times as intense as the same peak at 300 K? (4)

5. (a) Differentiate X-ray, electron and neutron diffraction techniques. (5)

(b) Determine the Miller indices (hkl) of the shaded planes below : (10)
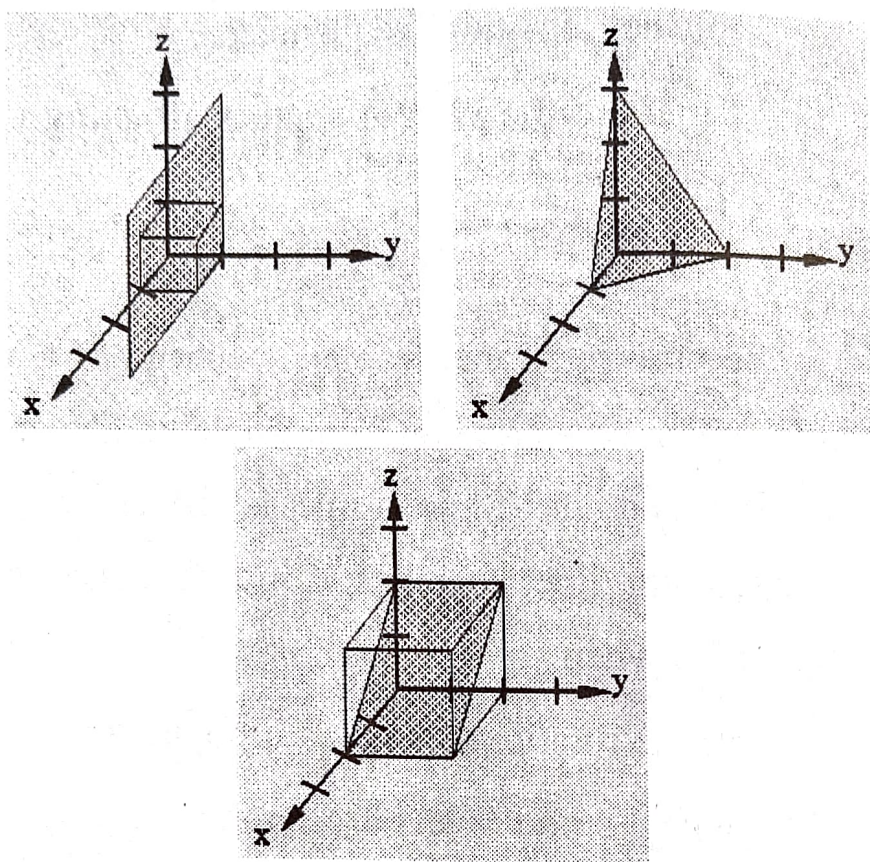
Q6 (a) Write short note on (i) spin lattice relaxation and (ii) nuclear overhauser effect. (5)

(b) (i) In an ESR spectrometer, the ESR frequency of the free electron is 9.5 GHz. Calculate the magnetic field at which the spectrometer is operating, $g_e = 2$ and $\mu_B = 9.273 \times 10^{-24}$ JT^{-1}

(3)

(ii) What type of vibration-rotation spectrum is obtained if the resolving power of the spectrometer is not so high? (5)

(iii) Why are the anti-Stokes lines less intense than Stokes lines in Raman spectrum? (2)

7. (i) What are O, P, Q, R, and S branches of the vibration-rotation raman spectrum? (8)

(ii) Which parameter differentiates the axially symmetric and axially non-symmetric molecules in NQR? (4)

(iii) How many PMR signals would you get from each of the following compounds?

CH_3OCH_3, $CH_3CH_2CH_2CH_3$,

and $C_6H_5CH_2CH_2CH_3$. (3)

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