Karunya University
(Karunya Institute of Technology and Sciences)
(Declared as Deemed to be University under Sec.3 of the UGC Act, 1965)

End Semester Examinations - 2015-16 Even Semester - May 2016

15CH3006 Molecular Spectroscopy

Set B

Time : 3 hrs
Total Marks: 100

1. a. The internuclear distance of $H^{37}Cl$ is 1.28 Å. Calculate (a) reduced mass (b) rotational constant (c) frequency separation. (5 Marks)

b. Derive the energy equation for rigid symmetric top molecule which has $I_C \neq I_A = I_B$ in rotational spectrum. (5 marks)

c. Write the energy equation and draw the energy level diagram of the P, Q and R branches of rotation-vibration spectra of diatomic molecules. (5 marks)

d. For the molecule HCl, $\omega_e = 2368\ cm^{-1}$ and $\omega_e x_e = 49\ cm^{-1}$. Calculate the vibrational terms of the first four vibrational levels and determine the spacing between them. (5 Marks)

OR

2. a. Derive the energy equation and apply the selection rule for various transitions in the vibrational spectra of diatomic molecules–Anharmonic oscillator. (5 marks)

b. Assume the following data for the molecule $H^{35}Cl$: Bond length = 127.5 pm, Bond force constant = 516.3 Nm^{-1} atomic masses: $^1H = 1.673 \times 10^{-27}$ Kg, $^{35}Cl = 58.066 \times 10^{-27}$ Kg. Calculate (1) Fundamental frequency, (2) Zero point energy, (3) Rotational constant. (5 marks)

c. Explain overtone, combination bands and difference bands (5 marks)

d. Derive the energy equation and apply the selection rule for transition from J to J+1 of rotational spectra of non-rigid diatomic molecules. (5 marks)

3. a. Discuss the different types of chromic shift with examples. (5 Marks)

b. Derive the energy and wavenumber equation for rotational Raman spectrum of linear molecule. Explain their allowed transitions. (5 marks)

c. Explain the principles of inverse and coherent Anti-stokes Raman scattering. (5 Marks)

d. A molecule X_2Y_2 has the following Infra-red and Raman spectra: (5 Marks)

cm^{-1}	Infra-red	Raman spectra
3374	--------	Strong
3287	Very strong	--------
1973	--------	Very Strong
729	Very Strong	--------
612	---------	Weak

Deduce the structure of the molecule and assign the observed vibrations to particular molecule modes as far as possible.

OR

4. a. Discuss the dissociation and predissociation in electronic vibrational spectrum. (5 Marks)

b. Explain the IR and Raman vibrational modes of the following molecules based on the rule of mutual exclusion. (5 Marks)

(a) N_2 (b) trans-1 2-diphenylethylene (c) H_2O (d) PCl_3 (e) CO_2

c. Explain why: (2 + 3 Marks)

(1) The selection rule for rotational Raman spectroscopy of linear molecule is $\Delta J = \pm 2$.

(2) Phenol shows bathochromic shift by increasing pH, while aniline shows hypsochromic shift by decreasing pH.

d. Explain Franck-Condon principle. (5 Marks)

5. a. Describe the principles of Auger Electron Spectroscopy. (5 Marks)

b. Distinguish between Fluorescence and phosphorescence. (5 Marks)

c. Discuss Fluorescence lifetimes and quantum yield. (5 Marks)

d. What is mirror image rule? Explain the exceptions to the mirror-image rule in Fluorescence with examples. (5 Marks)

OR

6. a. Describe the confocal Fluorescence microscopy. (5 Marks)

b. Discuss Fluorescence quenching. (5 Marks)

c. Write short note on "Fluorescence resonance energy transfer". (5 Marks)

d. Explain the difference between Intersystem crossing and Triplet–triplet annihilation. (5 Marks)

7. a. Discuss the different mechanisms of relaxation in NMR spectroscopy. (5 Marks)

b. Determine which of the following molecules will show spin-spin splitting in their NMR. If the splitting is observed, give the multiplicity of each kind of protons and approximate chemical shift: (5 Marks)

(1) 2-methyl-1-propene (2) 3-hexyne (3) 1-bromo-1-chloroethene

(4) 3,3-Dimethyl-1-butyne (5) cis-4-octene

c. Explain the proton exchange reaction of ethanol in ^1H NMR spectroscopy. (5 Marks)

d. Give structures for each of the following compounds and explain the chemical shift of each of them. (2+2+1Marks)

(a) C_3H_7Br: δ 1.83 (6H, d); δ 3.58 (1H, septet)

(b) $C_7H_5O_3N$: δ 10.12 (1H, s); δ 8.11 (1H, s); δ 7.91 (1H, d); δ 7.62 (1H, d); δ 7.23 (1H, t)

(c) $C_5H_4Br_8$: δ 4.8 (4H, s)

OR

8. a. Describe Zeeman splitting of energy levels of bare proton. (5 Marks)

b. Why alkene protons appear at downfield than alkyne protons in ^1H NMR? Explain. (5 Marks)

c. Describe the chemically equivalent, chemically nonequivalent, magnetically equivalent and magnetically nonequivalent protons in ^1H NMR spectrum with examples. (5 Marks)

d. A compound X with the molecular formula $C_8H_{18}O_3$ and no O-H stretching absorption in its IR spectrum has the following proton NMR spectrum: δ 1.2 (3H, s); δ 1.4 (6H, t, J =7 Hz); δ 3.2 (9H, s); δ 3.8 (6H, s). Deduce the structure of X and explain with reason. (5 marks)

9. a. Explain Zero-field splitting and Karmer's degeneracy with examples. (5 Marks)

b. Write short note on "nuclear resonance absorption" (5 Marks)

c. Explain the ESR spectrum of bis(salicylaldiminato)copper(II). (5 Marks)

d. Compare the stick diagram and ESR spectrum of the following compounds. (5 Marks)

(a) $HO^{\bullet}CDCOOH$ (b) $DO^{\bullet}CHCOOH$

Wishing you All the Best
