

II Semester M.Sc. Degree Examination, June/July 2018  
(CBCS Scheme)

CHEMISTRY

C - 204 : Spectroscopy - I

Time : 3 Hours

Max. Marks : 70

**Instruction :** Answer question no.1 and any five of the remaining.

1. Answer any ten of the following : (10×2=20)

- a) Define the term rotation-reflection axis with an example. Write systematically the operations are generated by  $S_5$ -axis.
- b) Prove that  $C_3\sigma_v \neq \sigma_v C_3$  and  $C_3^2 \equiv C_3^{-1}$ .
- c) Show that three reflections of ammonia constitute a class.
- d) Classify the following molecules are microwave active or inactive. Justify your choice.
 

i) $C_2H_2$	ii) HCN	iii) $CO_2$	iv) HF
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- e) A non-linear triatomic molecule belongs to  $C_{2v}$  - point group. How many bending and stretching modes are present in it?
- f) What are hot bands? Mention the conditions for their occurrence.
- g) Depict polarizability ellipsoid for  $CO_2$ .
- h) Give the meaning of the term Fermi resonance with an example.
- i) The odd-even classification of orbitals arise in homonuclear diatomic molecules. Account it.
- j) The parallel vibration of  $AB_2$  shows PR branches, while that of  $XY_2$  shows PQR branches. Suggest the possible structures of  $AB_2$  and  $XY_2$ .
- k) Outline the electronic structure of  $N_2$ . Calculate the bond order of  $N_2$  and  $N_2^+$ .
- l) Define the terms : vibrational relaxation and internal conversion.

2. a) What point group is obtained when operation of inversion centre is added to the following symmetry groups?

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| i) $D_3$ | ii) $C_3$ and | iii) $C_{4v}$ |
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- b) Write the matrix notations for the symmetry operations of  $C_{2v}$  - point group. By matrix multiplication, prove that it is an Abelian group.
- c) List the main characteristic features of  $D_{nh}$  and  $D_{nd}$  - point groups. To which group  $X_6F_4$  and  $C_3H_4$  molecules belong? (3+3+4=10)
3. a) Construct a character table for the operations of  $C_{3v}$  - point group. Explain each area in detail.
- b) State and explain the selection rules for electronic transitions. Classify the following transitions are allowed or forbidden :  
 $\Sigma^+ \leftrightarrow \Sigma^+$ ,  $g \leftrightarrow u$ ,  $g \leftrightarrow g$ ,  $\Sigma^- \leftrightarrow \Sigma^-$ . (5+5=10)
4. a) The first line in the pure rotational spectrum  $^1H^{35}Cl$  appears at  $21.18 \text{ cm}^{-1}$ . Calculate the bond length of the molecule.
- b) Discuss the rotation spectra of a linear polyatomic molecule. Interpret the results to obtain the bond length. (4+6=10)
5. a) Write briefly on the main components of infrared spectrometer.
- b) Sketch schematically the normal modes of  $AB_3$  - pyramidal molecule and comment on its IR and Raman activity.
- c) Describe the classical theory of Raman effect. (3+3+4=10)
6. a) Depict the electronic configuration of the ground and excited states of HCHO molecule. Explain the electronic transitions involved in it.
- b) Write briefly on non-radiative decay process. (6+4=10)
7. a) State the rule of mutual exclusion. Which of the following molecule(s) obey this rule? Justify  $C_3O_2$ ,  $C_2H_2$ ,  $NO_2$ ,  $N_2O$  and HCl.
- b) Give comprehensive notes on : Franck-Condon principle and Fortrat diagram. (5+5=10)
8. a) A sample was excited by a radiation of  $4500 \text{ \AA}$  wavelength. A Raman line was observed at  $4600 \text{ \AA}$ . Calculate the Raman shift in  $\text{cm}^{-1}$  and comment on the nature of Raman line.
- b) Give a brief account on vibration rotation spectra of symmetric top molecules. (4+6=10)