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Reg. No. | | | | | | | | |

II Semester M.Sc. Degree Examination, November - 2022

(CBCS 2014-15 Onwards Scheme Repeaters)

CHEMISTRY

Spectroscopy - I

Paper : C 204

Time : 3 Hours **Maximum Marks : 70**

Instruction to Candidates: Answer question No. 1 and ANY FIVE of the remaining questions Figures to the right indicate marks.

Answer any TEN of the following **(10×2=20)**

1. a) A molecule with more than one C_n-axis ($n > 1$) cannot have a dipole moment. Give reason.

b) Define the term "point group" and find the point group of tetrahedral CH_3Cl molecule.

c) List all the elements of the cyclic group generated by S_3 improper axis of rotation. What is the Schoenflies symbol for this point group?

d) Rotation about the bond axis of linear molecules is not responsible for absorption peak. Justify the statement.

e) Write the expression for rotational energy of rigid and non-rigid linear molecule and explain the terms involved.

f) What are hot bands? Mention the condition for their occurrence.

g) Calculate the normal modes of vibrations of N_2O and C_2H_2. Predict their IR activity.

h) The spacing between successive lines in the rotational Raman spectrum of a diatomic molecule is 36 cm^{-1}. What is the Raman shift of the first Stokes line?

i) Define the term polarisability and draw the polarisability ellipsoid for H_2O molecule.

j) The energy of each orbital varies considerably from atom to atom. Give reasons.

k) Distinguish between radioactive and non-radioactive decay.

1) How σ–and π- molecular orbitals are formed? Explain.

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2. a) List the complete set of operations included in the point group D_{4h}. Find all the subgroups of D_{4h}.

   b) Write a note on labelling of irreducible representation. **(5+5=10)**

3. a) Explain the terms axis of symmetry, centre of symmetry and rotation-reflection axis with examples.

   b) Construct the multiplication table for the symmetry operations of ammonia molecule. **(6+4=10)**

4. a) Obtain the expression for the energy of a diatomic molecule assuming it to be an anharmonic oscillator. Draw the energy level diagram and give the selection rules.

   b) Discuss the application of Stark effect in microwave spectroscopy for the determination of dipole moment of linear molecules. **(5+5=10)**

5. a) $H^{35}Cl$ has a B value of 10.593 cm^{-1} and a centrifugal distortion constant of $5.3 \times 10^{-4} cm^{-1}$. Estimate the vibrational frequency and force constant of the molecule.

   b) Write brief notes on

   i) Born-Oppenheimer approximation and

   ii) Q - branch in vibrational-rotational spectra of diatomic molecules. **(4+6=10)**

6. a) Sketch the normal modes of vibration for a linear and non-linear triatomic molecule. Discuss their IR and Raman activity.

   b) Derive the expression for the Raman shifts of the pure rotational- Raman lines of a linear molecule. **(6+4=10)**

7. a) With the help of Jablonski diagram illustrate the various photochemical pathways for the decay of excited states.

   b) State the Frank-Condon principle. How does it help in explaining the intensities of vibrational structure? **(5+5=10)**

8. a) Write the molecular orbital diagram of formaldehyde molecule and explain the possible electronic transitions involved in it.

   b) A diatomic molecule AB and its excited state (AB)* have the same equilibrium bond length. Draw a schematic plot of its vibrational course structure. **(6+4=10)**