Five Year Integrated M.Sc. Examination 2019

Semester-VI

Course: PH-3-6-5

(Spectroscopy-I)

Time: Three Hours **Full Marks: 40**

Questions are of equal value or as indicated in the margin.

Answer ***Question No.1*** and ***any three*** questions from the rest.

1. Answer ***any five*** questions: 5x2=10
   a) What is hot band and why it is called so?
   b) Which of the following molecules may show infrared absorption spectra: (i) H_2, (ii) CO_2, (iii) H_2O and (iv) N_2O?
   c) Discuss the factors that govern the intensity of the spectral lines.
   d) What are Stokes and anti-Stokes lines in Raman spectra? Which lines are more intense and why?
   e) What do you mean by internal conversion and intersystem crossing? Explain briefly.
   f) Why the triplet state of an organic molecule has a longer lifetime than a singlet state? Explain briefly.
   g) State and explain Kasha's rule.

2. a) Discuss about the vibration-rotational spectrum of a diatomic molecule. What are the PQR lines and what is the minimum energy separation between P and R lines in terms of rotational constant (B).
   b) What is degeneracy? Show that the maximum population observed for a rigid rotator at the nearest rotational level (J) = $\sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$. 6+(1+3) = 10

3. a) Draw pictures of polarizability ellipsoids for the normal modes of vibration of CO_2 molecule. Which of the modes is Raman active? Why? Define the "Principle of Mutual Exclusion".
   b) Using polarizability (α) of a molecule, explain the occurrence of Stokes and anti-Stokes lines in a Raman spectrum. (3+2+1)+4 = 10

4. a) For an AB_2 molecule, vibrational spectroscopy gives the following results:

ν (cm^{-1})	Infra-red	Raman
589	Strong: PQR contour	-----
1285	Very strong: PR contour	Very strong: polarized
2224	Very strong: PR contour	Strong: depolarized

   Identify the normal modes of vibration and give a structure of the molecule.
   b) The spectral lines of carbon monoxide follow the following equation:
   $\gamma_{P,R} = 2143.28 + 3.813m - 0.017m^2$ cm^{-1}. Find the band origin, B_1 and B_o (the rotational constants for the first and ground state rotational levels). 6+4 = 10

5. a) Pyridine, which is isoelectronic N-analogue of benzene, is non-fluorescent in non-polar solvent, but fluorescent in polar solvent. Why?

P.T.O.

b) All molecules are capable of absorbing light, but fluorescence is not observed in large number of molecules. Explain with suitable examples. 5+5 = 10

6. a) State and explain Franck-Condon principle.
   b) What do you mean by the dissociation energy of an organic molecule in the ground and excited states? Explain with diagram.
   c) Discuss how one can measure the dissociation energy of iodine molecule in the ground state.

3+2+5 = 10

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