15P2045

Reg. No..... Name.....

M. Sc. DEGREE END SEMESTER EXAMINATION APRIL 2017

SEMESTER – 2: M.Sc. CHEMISTRY/ APPLIED CHEMISTRY

COURSE: 15P2CHET08-15P2CPHT08 -MOLECULAR SPECTROSCOPY

(For Supplementary - 2015 Admission)

Time: Three Hours Max. Marks: 75

Section A

*(Answer any **Ten** questions. Each question carries **2** marks)*

1. Explain the term Fermi resonance.
2. Which of these molecules H_2, N_2, N_2O, CH_4 have a pure rotational spectra? Explain.
3. What is Franck-Condon Principle?
4. Differentiate between Stark effect and Zeeman effect.
5. Infrared absorption due to carbonyl stretching occurs at higher frequencies than stretching of C=C bond. Explain.
6. State "Mutual exclusion principle". Provide the selection rule for vibrational Raman spectra.
7. In a pure rotational Raman spectrum of $^{35}Cl_2$ the lines are separated by 0.9752 cm^{-1}. Calculate the bond length of the molecule.
8. What is nuclear quadrupole moment?
9. What is NOE effect?
10. What is meant by recoilless emission? Give the conditions under which Mossbauer effect is most likely to occur?
11. Why vibrations involving relatively neutral bonds such as **C-C,C-H,C=C** are strong Raman scatterers, while they are weak in IR absorption.
12. Why ^{13}C NMR spectra are difficult to record?
13. Briefly describe COSY and HETCOR.

(2 x 10 = 20)

Section B

*(Answer any **Five** questions, by attempting not more than 3 questions from each bunch. Each question carries **5 marks**)*

Bunch I

14. Write short notes on (a) Karplus relation (b) Karmers' degeneracy and (c) Mc Connell equation.
15. Explain radiative and non-radiative methods of energy dissipation in excited molecules.

16. What are the merits of Fourier Transform spectra over conventional spectroscopy?

17. With which type of spectroscopy would one observe the pure rotational spectra of Hydrogen molecule (H_2)? What would be the spacing of lines in the spectrum?

Bunch II

18. State Beer-Lambert law. The transmittance of an aqueous solution of $KMnO_4$ at a certain wavelength is **1%** for a **10^{-3}** molar solution in a **1** cm cell. What is its (a) absorbance (b) molar absorption coefficient of $KMnO_4$.

19. The rotational spectrum of CO shows a series of lines placed **3.84325 cm^{-1}** apart. Calculate the moment of inertia and bond length.

20. The equilibrium vibrational frequency of iodine molecule is 250 cm^{-1} and the anharmonicity constant $x_e = 0.003$.What is the intensity of the hot band? $\upsilon = 1$ to $\upsilon = 2$ relative to that of the fundamental $\upsilon = 0$ to $\upsilon = 1$, if the temperature is 300 K .

21. (a) The centre of the EPR spectrum of methyl radical occurred at 329.40 mT in a spectrometer operating at 9.2330 GHz. Calculate its g-value.

(b) At what magnetic field would the methyl radical come into resonance in a spectrometer operating at 34,000 GHz

(5 x 5 = 25)

Section C

*(Answer any **Two** questions. Each question carries **15 marks**)*

22. (a) Write short notes on (i) Predissociation (ii) magic angle spinning and (iii) Fermi resonance.

(b). Explain the principle of X-ray photoelectron spectroscopy.

23. (a) Describe the factors responsible for the width and intensity of spectral lines.

(b) Draw the energy level diagram and transition for the odd electron of the free radical in:

(i) $\bullet(CF_2H)$ and (ii) Naphthalene anion.

24. (a) What is Raman effect? Explain the origin of Stokes and anti-Stokes lines.

(b) Raman rotational spectra of H_2 was observed with Hg light with Rayleigh line at 2294 cm^{-1}. Stokes lines were observed at 2258.1, 2233.7, 2209.4 and 2185.1 cm^{-1}. Draw the rotational energy levels diagram for hydrogen molecule and show the stokes and anti-stokes transitions.

25. (a) Discuss the applications of Mossbauer spectroscopy in the study of Fe (II) and Fe (III) cyanides.

(b) Explain the principle and working of Ruby laser.

(15 x 2 = 30)

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