

18/12/17



DOON UNIVERSITY, DEHRADUN

End Sem Examination, Odd Semester, 2016–2017

School of Physical Sciences (SoPS)

5th semester, Integrated M.Sc. 5 Years (Chemistry)

Dated: 18 Dec, 2017

Course: Phys. Chem. V: Quantum Chemistry & Spectroscopy Course Code: CYC-302

Time Allowed: 3 Hours

Maximum Marks: 30

Note: Attempt All Questions from Sections A, B and C. (All terms have their usual meaning)

SECTION: A

(Marks: 5)

- [1] Calculate the force constant of HCl molecule, when fundamental vibrational frequency of is 2890 cm^{-1} . Molar masses of $^1\text{H} = 1.67 \times 10^{-27} \text{ kg}$; $^{35}\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$. [1]
- [2] (i) Exchange integral term (H_{ij}) in the approximate energy expression of a molecular orbital model represents: [1/2]
- a) Energy of electronic interaction of e⁻s in the atomic orbital
 - b) Energy of interaction of e⁻s in the influence of i and j nuclei
 - c) Overlapping integral factor of orbitals centred at nuclei i and j
 - d) None of the above
- (ii) The correct order of bond strength of the species O_2 , O_2^+ , O_2^- and O_2^{2-} is: [1/2]
- a) $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$
 - b) $\text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+$
 - c) $\text{O}_2 > \text{O}_2^- > \text{O}_2^+ > \text{O}_2^{2-}$
 - d) $\text{O}_2^- > \text{O}_2^+ > \text{O}_2^{2-} > \text{O}_2$
- [3] Illustrate:
- (a) Raman rotational vibrational transitions and bands [1/2]
 - (b) ESR spectra for methyl radical [1/2]

- [4] Calculate the equivalent, non-equivalent protons and draw the NMR spectra for: [1/2 + 1/2]
- But-1-ene
 - isopentane
- [5] Calculate the degree of freedom for BF_3 , C_2H_2 [1/2+1/2]
- BF_3
 - C_2H_2

SECTION: B

(Marks: 10)

- [6] Define quantum yield. What are the reasons for abnormal quantum yield? [2]
- [7] What are the basic differences between Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). [2]
- [8] Derive expression for Lambert-Beer law. What are its limitations? [2]
- [9] Using free electron model approach, illustrate the number of electronic transitions for conjugated system of hexa-1,3,5-triene. [2]
- [10] Define: [1/2 x 4]
- Law of mutual exclusion
 - Frank Condon Principle
 - Spin spin coupling
 - Principle of NMR spectroscopy

SECTION: C

(Marks: 15)

- [11] Show that the average value of $1/r$ for an electron in 1s orbital of hydrogen atom is $1/a_0$, given that $\psi_{1s} = (e^{-r/a_0})/(\pi a_0^3)^{1/2}$ [3]
- [12] What is variational principle? Using this principle, deduce the expression for $E_\alpha(\text{min})$ and $\phi_\alpha(\text{min})$ of a Simple Harmonic Oscillator (S.H.O.) having wave function expression,

$$\phi(x) = e^{-\alpha x^2}$$

[4]

- [13] What is isotope substitution method? How is it used in determination of bond length for linear triatomic molecule? [3]
- [14] Derive an expression for vibrational energy in terms of wave number for a diatomic molecular transition for fundamental vibrational frequency, third overtone and hot band. [2]
- [15] What are radiative and non-radiative transitions taking place in absorption and emission pathways? Discuss in details. [3]