

## CHE-HC-5026: PHYSICAL CHEMISTRY V

**(Credits: Theory-04, Lab-02)**

**Theory: 60 Lectures**

**Course Objective:** *The aim of this course is to introduce the students with three important areas- quantum chemistry, molecular spectroscopy and photochemistry. In quantum chemistry unit the students will be taught the postulates of quantum mechanics and the application of quantum mechanical ideas in some simple systems such as particle in a box, rigid rotor, simple harmonic oscillator etc. In spectroscopy unit, rotational, vibrational, Raman, electronic, spin resonance, and electronic spectroscopy will be introduced.*

**Learning Outcome:** *After completion of this course the students are expected to understand the application of quantum mechanics in some simple chemical systems such as hydrogen atom or hydrogen like ions. The students will also learn chemical bonding in some simple molecular systems. They will be able to understand the basics of various kinds of spectroscopic techniques and photochemistry.*

### **Quantum Chemistry:**

Postulates of quantum mechanics, quantum mechanical operators, Schrödinger equation and its application to free particle and “particle-in-a-box” (rigorous treatment), quantization of energy levels, zero-point energy Extension to two and three dimensional boxes, separation of variables, degeneracy.

Qualitative treatment of simple harmonic oscillator model of vibrational motion: Setting up of Schrödinger equation and discussion of solution and wavefunctions. Vibrational energy of diatomic molecules and zero-point energy.

Angular momentum: Commutation rules, quantization of square of total angular momentum and z-component.

Rigid rotator model of rotation of diatomic molecule. Schrödinger equation, transformation to spherical polar coordinates. Separation of variables. Spherical harmonics. Discussion of solution.

Qualitative treatment of hydrogen atom and hydrogen-like ions: setting up of Schrödinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression). Average and most probable distances of electron from nucleus.

Setting up of Schrödinger equation for many-electron atoms (He, Li). Need for approximation methods. Statement of variation theorem and application to simple systems (particle-in-a-box, harmonic oscillator, hydrogen atom).

Chemical bonding: Covalent bonding, valence bond and molecular orbital approaches, LCAO-MO treatment of  $H_2^+$ . Bonding and antibonding orbitals. Qualitative extension to  $H_2$ . Comparison of LCAO-MO and VB treatments of  $H_2$  (only wavefunctions, detailed solution not required) and their limitations. Refinements of the two approaches (Configuration Interaction for MO, ionic terms in VB). Qualitative description of LCAO-MO treatment of homonuclear and heteronuclear diatomic molecules (HF, LiH). Localised and non-localised molecular orbitals treatment of triatomic ( $BeH_2$ ,  $H_2O$ ) molecules. Qualitative MO theory and its application to  $AH_2$  type molecules.

**(24 Lectures)**

### **Molecular Spectroscopy:**

Interaction of electromagnetic radiation with molecules and various types of spectra; Born-Oppenheimer approximation.

Rotation spectroscopy: Selection rules, intensities of spectral lines, determination of bond lengths of diatomic and linear triatomic molecules, isotopic substitution.

Vibrational spectroscopy: Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies. Vibration-rotation spectroscopy: diatomic vibrating rotator, P, Q, R branches.

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; Effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion.

Electronic spectroscopy: Franck-Condon principle, electronic transitions, singlet and triplet states, fluorescence and phosphorescence, dissociation and predissociation, calculation of electronic transitions of polyenes using free electron model.

**(24 Lectures)**

### **Photochemistry**

Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws, of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitised reactions, quenching. Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence.

**(12 Lectures)**

### **Recommended Books:**

1. Banwell, C. N. & McCash, E. M. Fundamentals of Molecular Spectroscopy 4th Ed. Tata McGraw-Hill: New Delhi (2006).
2. Chandra, A. K. Introductory Quantum Chemistry Tata McGraw-Hill (2001).
3. House, J. E. Fundamentals of Quantum Chemistry 2<sup>nd</sup> Ed. Elsevier: USA (2004).
4. Lowe, J. P. & Peterson, K. Quantum Chemistry, Academic Press (2005).
5. Kakkar, R. Atomic & Molecular Spectroscopy, Cambridge University Press (2015).

6. Kapoor, K. L. A Textbook of Physical Chemistry (Volume 4) McGraw Hill Education; 5<sup>th</sup> edition (2017)
  7. Sen, B. K. Quantum Chemistry- Including Spectroscopy, Kalyani Publishers; 4<sup>th</sup> edition (2011)
  8. McQuarrie, D. A. Quantum Chemistry, Viva Books (2016)
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## LAB

### 60 Lectures

#### UV/Visible spectroscopy

- I. Study the 200-500 nm absorbance spectra of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  (in 0.1 M  $\text{H}_2\text{SO}_4$ ) and determine the  $\lambda_{\text{max}}$  values. Calculate the energies of the two transitions in different units ( $\text{J molecule}^{-1}$ ,  $\text{kJ mol}^{-1}$ ,  $\text{cm}^{-1}$ , eV).
- II. Study the pH-dependence of the UV-Vis spectrum (200-500 nm) of  $\text{K}_2\text{Cr}_2\text{O}_7$ .
- III. Record the 200-350 nm UV spectra of the given compounds (acetone, acetaldehyde, 2-propanol, acetic acid) in water. Comment on the effect of structure on the UV spectra of organic compounds.

#### Colourimetry

- I. Verify Lambert-Beer's law and determine the concentration of  $\text{CuSO}_4/\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$  in a solution of unknown concentration
- II. Determine the concentrations of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  in a mixture.
- III. Study the kinetics of iodination of propanone in acidic medium.
- IV. Determine the amount of iron present in a sample using 1,10-phenanthroline.
- V. Determine the dissociation constant of an indicator (phenolphthalein).
- VI. Study the kinetics of interaction of crystal violet/ phenolphthalein with sodium hydroxide.
- VII. Analysis of the given vibration-rotation spectrum of  $\text{HCl}(\text{g})$

#### Recommended Books

1. Khosla, B. D.; Garg, V. C. & Gulati, A., *Senior Practical Physical Chemistry*, R. Chand & Co.: New Delhi (2011).
  2. Garland, C. W.; Nibler, J. W. & Shoemaker, D. P. *Experiments in Physical Chemistry 8th Ed.*; McGraw-Hill: New York (2003).
  3. Halpern, A. M. & McBane, G. C. *Experimental Physical Chemistry 3rd Ed.*; W.H. Freeman & Co.: New York (2003).
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