



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student : TOUSIF HOSSEN
Roll Number : 156122043
Programme of Study : Ph.D.
Thesis Title: Photoinduced Electron, Proton and Proton-Coupled Electron Transfer in H-Bonded Complexes
Name of Thesis Supervisor(s) : Dr. KALYANASIS SAHU
Thesis Submitted to the Department/ Center : Chemistry
Date of completion of Thesis Viva-Voce Exam : 10-02-2021
Key words for description of Thesis Work : Excited state H-bonding dynamics, PET, ESPT, PCET

SHORT ABSTRACT

The thesis includes investigations on some simple but interesting hydrogen-bonded complexes and their photophysical processes like photoinduced electron transfer (PET), excited-state proton transfer (ESPT), and proton-coupled electron transfer (PECT). The thesis utilized seven chapters to distribute its contents.

Chapter 1 presents a brief account of recent experimental and theoretical advancements of the primary excited-state processes in H-bonded systems. Chapter 2 summarizes theoretical methods and experimental strategies adopted throughout the thesis. In chapter 3, molecular dynamics (MD) simulation was employed to unveil the exact H-bonding configuration of an experimental system comprising of a coumarin 102 (C102) as acceptor with varying number of phenol and cyclohexane molecules as a donor and a non-interacting partner, respectively. The main aim of this chapter was to get molecular insights of the molecular arrangement around the acceptor (C102) at different mole fractions of the phenol-cyclohexane mixture. The results assist to understand the unusual fluorescence modulation of C102 observed in the mixture in a previous experimental study. In chapter 4, time-dependent density functional theory (TD-DFT) reveals the possibility of PCET as an alternative mechanism for the experimentally observed fluorescence quenching of the H-bonded C102-phenol complex. Chapter 5 deals with another H-bonded system methylbipyridine/methoxyphenol complex, which shows quite controversial spectroscopic signatures, which may be due to conventional PET or PCET. TD-DFT calculations presented in this chapter indicates that conventional PET is a more favorable excited-state pathway than PCET in the system. Finally, in chapter 6, the fluorescence modulation of three photoacids (2-naphthol, 6-sulfonate-2-naphthol, and 6-cyano-2-naphthol) was investigated inside the nanocavity of β -cyclodextrin (β -CD). The differential fluorescence modulation of the photoacid was found to be not due to very different hydration environment around the deprotonation site (hydroxyl group), but is linked to the intrinsic chemical nature (pK_a^*) of the photoacids. Chapter 7 reports very different pK_a shift and fluorescence modulation of the strong photoacid 6-cyano-2-naphthol inside α -cyclodextrin (α -CD) vs β -CD.