Synopsis

In this thesis, I have presented my work on properties of hydrogen(H) bonded systems, H-atom transfer reaction in solution and molecular vibrational spectra through theoretical investigations. The studies are based on two simple models namely, the Empirical Valence Bond (EVB) model and the local-mode based description of vibrations. **Chapter 1** is an introduction to these theoretical models. I also briefly introduce the systems investigated along with the model used. Using a EVB based approach, H-bonded O-H vibrations and H atom abstraction reaction by CN radical from ethanol in solution are studied, while a local mode based approach is used for analysing the gas-phase C-H stretch infra-red spectrum of napthalene. A brief description of the contents of the following chapters is presented below.

In **Chapter 2**, I present our work on the quantum effect of H-motion on H-bonding properties. An EVB based model based on a symmetric O-H···O type of H-bonded system is used for the study. Here I discuss the details of the two-diabatic state model used and the subsequent quantization along one dimensional H-atom motion which is parametric in the donor-acceptor distance. The vibrational states so obtained from the quantization are used to analyse various H-bonding properties such as bond-length, frequency shift and isotope effect. An analysis of the secondary geometric isotope effect (SGIE) using an extension of the two-state model is also presented. The role of bending motion on the H-bond properties are also discussed.

Chapter 3 of the thesis presents our work where we have analysed the correlation of H-bond strength with isotopic fractionation based on the same two-state model. The relative contribution of O-H stretch and bend vibrations, tunneling splitting and SGIE are considered in the analysis.

In **Chapter 4** I present our work on the intensity variation associated with O-H stretch vibration involved in a O-H···O type of H-bonded system. Extending the model from **Chapter 2** with a Mecke function-based dipole moment the transition intensity is computed. An analysis of variation in fundamental and overtone intensities with H-bond strength and isotope effect (including SGIE) on fundamental intensity are discussed. A study of the trend of these

transition intensities due to variation of Mecke parameters of the dipole moment function is also discussed in this chapter.

Chapter 5 discusses our work on H-atom abstraction reaction of the CN radical with ethanol in solution based on an EVB model approach coupled with molecular dynamics simulations. A two-state EVB model is used to define the reaction system and the details of the reaction-system models are described. The reaction system in solvated H_2O and $CHCl_3$ and the dynamics of the H-abstraction are analysed in terms of the energy profile and post-transition state energetics. An analysis of solvent involvement in the processes for the two solvents are also presented.

Our study on the C-H stretch infrared region of Napthalene employing a local-mode normal-model based approach is presented in **Chapter 6**. Using a curvilinear coordinate framework to set up the vibrational Hamiltonian, the calculated spectra is presented. The details of this Hamiltonian and the use of its eigenstates to describe the coupled states that make up the spectral bands are presented in this chapter.

Chapter 7 briefly summarize the works undertaken and highlight the important results obtained from our studies.