

ABSTRACT

In this thesis, two important aspects of non-adiabatic effects are explored. In the first part, the focus is on understanding structural aspects of conical intersection (CI) and its seam. The second part utilizes current computational methods of ab initio electronic structure non-adiabatic dynamics to understand electronic relaxation and photochemical pathways in two small organic molecules. The first part of the thesis involves two research works - one H⁺⁺ molecular system and 3⁺⁺ the other on H₃ and ethylene molecules. The work on H₃ is motivated by the fact that structure of CI seams, which are usually highly-complex multi-dimensional geometric entities for polyatomic molecules, does become simpler for triatomic molecules. Further, there have been limited number of studies so far on global aspects of CI seams such as seam branch connectivities and their relation to 3-state intersections. In this work, a study of global structural features of CI seam by considering a simple one-electron triatomic molecular system - H₃⁺⁺. Using a simple numerical approach to track the seam in nuclear configuration space, a seam of this system exhibiting several branches of different types of CIs has been constructed in a large part of the coordinate space. A visualization of the seam in hyperspherical coordinates has revealed interesting seam-connectivity pattern. The second work on ethylene and H₃ molecules, explores the possibility to indirectly infer the local geometric/topographic structure of CI seam in polyatomic molecule using series of non-adiabatic coupling calculations (NACTs). The simpler H₃ study helps in interpretation of such calculations on larger ethylene. The second part of the thesis has been motivated by use of substituent effects, which have been recently used in experiments to understanding electronic relaxation mechanisms. Two distinct classes of substituents, methyl and heteroatom substitutions, have considered in two prototype reactions, cis-trans isomerization and 1,3-electrocyclization. The experimentally observed differences in electronic relaxation behaviour of acrolein with that of its methylated derivatives, despite similarities in their electronic structures is considered. While static calculations support similarity, dynamics simulations clearly establish that ultrafast relaxation in S₂ state is indeed very similar for acrolein and crotonaldehyde. Our studies did not turn out to be conclusive enough to attribute the experimentally observed differences to the corresponding differences in ultrafast relaxation from S₁ state. The heteroatom substitution effect in photoelectrocyclic reaction is the focus of another work. Taking formaldonitrone (FN) as prototype, we carried out a detailed computational study on a nitron-oxaziridine interconversion. Based on high-level calculations, a barrierless pathway for photochemical reaction for FN has been proposed. A 200fs dynamics simulation confirms ultrafast deactivation and barrierless relaxation from S₁ state.