

Synopsis

The present thesis deals with the detailed ultrafast experimental studies on the excited state vibrational dynamics of model chemical systems in condensed phase. The molecular systems are studied by means of Ultrafast Raman Loss Spectroscopy (URLS) and femtosecond transient absorption (TA) spectroscopy. The primary objective of the current thesis is to look at structural dynamics immediately after Franck-Condon excitation, influenced by surrounding solvent molecules.

The thesis is divided into six chapters and a brief summary of each chapter is given below.

In **Chapter 1**, I have included the concept of femtosecond time-resolved spectroscopy and nuclear dynamics. Some important aspects of spontaneous and stimulated Raman scattering are discussed. Subsequently, I have described the theoretical framework and methodologies that are important to understand non-linear spectroscopy. Important aspects of time-resolved stimulated Raman process are described here. A brief outline of the current thesis is also presented at the end of this chapter.

In **Chapter 2**, I have described in detail the instrumentation and data processing methods. A detailed explanation of spectroscopic techniques like transient absorption and femtosecond stimulated Raman spectroscopy and their experimental aspects are discussed. The optimization of the setup, detailed data analysis processes are described. Finally, I have described step-by-step data processing method using DaFitUma software which is developed in our lab.

In **Chapter 3**, I have studied the excited state isomerization dynamics of tetraphenylethylene in various solvents using femtosecond TA and URLS spectroscopy. Tetraphenylethylene, a model molecular motor, known to exhibit low-frequency torsional dynamics. TA measurements in the S_1 state reveal a step-wise structural rearrangement from Franck-Condon (FC) state \rightarrow relaxed state \rightarrow twisted state on photoexcitation. Furthermore, oscillation in TA kinetics was observed within 1 ps. Fourier transformation of this oscillation leads to a $\sim 130 \text{ cm}^{-1}$ low-frequency mode which is responsible for the excited state wavepacket dynamics during the course of FC state \rightarrow relaxed state structural rearrangement. Two vibrational marker bands $C_{et}=C_{et}$ stretching ($\sim 1512 \text{ cm}^{-1}$) and $C_{ph}=C_{ph}$ stretching ($\sim 1584 \text{ cm}^{-1}$) modes appear immediately after photoexcitation in URLS spectra. From the peak frequency shift, we confirm that the initial structural relaxation is dominated by phenyl torsion rather than central $C_{et}=C_{et}$ twist.

In **Chapter 4**, the structural dynamics and solvent induced internal conversion of 2-(2'-Hydroxyphenyl)benzothiazole (HBT), an extensively studied excited state intramolecular proton transfer (ESIPT) system, are investigated. We have obtained snapshots of vibrational spectra of the photoexcited HBT, by URLS, providing detailed structural change at an early time. From the URLS peak amplitude analysis we have observed ~ 400 fs amplitude decay in acetonitrile. This is assigned to a rapid structural change induced by polar acetonitrile due to the torsional motion. The ultrafast amplitude decay is associated with coherent excitation of torsional mode ($\sim 40 \text{ cm}^{-1}$). Oscillatory peak position in the high-frequency Raman modes indicates a coupling between low-frequency torsional and high-frequency vibrations. Activation of torsional motion in polar solvents provides an additional route for non-radiative decay, responsible for a short lifetime (~ 12 ps) and low fluorescence quantum yield. For hexane, the URLS spectral evolution is assigned to vibrational cooling (2-4 ps) followed by population relaxation (115 ps).

Chapter 5, deals with the ultrafast intersystem crossing (ISC) dynamics of thioxanthone (TX) in various solvents. It has striking solvent dependent photo-physical properties. For example, the fluorescence quantum yield (ϕ_f) and lifetime (τ_f) of the primarily populated singlet ($^1\pi\pi^*$) state strongly depends on the solvent properties. We have studied TX in three different solvents: acetonitrile (ACN; aprotic), methanol (MeOH; polar protic) and in cyclohexane (CX; nonpolar). Following electronic excitation to the S_1 ($^1\pi\pi^*$) state, the molecule relaxes to the lowest T_1 ($^3\pi\pi^*$) state in ~ 50 ps, ~ 4 ps in ACN and in CX respectively. In the case of TX in methanol, two stages of ISC with time constants of ~ 4 ps and > 2 ns were obtained. These two stages are assigned to direct (~ 4 ps) ISC to the T_2 state ($^1\pi\pi^* \rightarrow ^3n\pi^*$) followed by slow internal conversion (~ 2 ns) to the T_1 state ($^3\pi\pi^*$). Analysis of peak position dynamics further allows us to obtain vibrational relaxation times during ISC process. The present study sheds light on a complete understanding of the structural changes accompanying the ISC process.

Finally, in **Chapter 6**, we have briefly summarized the main results of the thesis. This chapter also includes our comments on some of the future extensions of the present work.