Preface

The subject of this thesis is the design and development of a unified set up for femtosecond transient absorption and ultrafast Raman loss spectroscopy and demonstrate its potential in capturing the ultrafast photophysical and photochemical processes with excellent time and frequency resolution. Ultrafast spectroscopy has been serving as a powerful tool for understanding the structural dynamical properties of molecules in the condensed and gas phase. The advent of ultrashort pulses with their high peak power enables the laser spectroscopic community to study molecular reaction dynamics and photophysics that happen at extremely short timescales, ranging from picosecond to femtosecond. These processes can be measured with extremely high time resolution, which helps to resolve the underlying molecular process. But in order to understand the global mechanism of the underlying molecular processes, we have to resolve the nuclear dynamics with the proper frequency resolution. However, achieving both, time and frequency resolutions simultaneously is not possible according to the Heisenberg uncertainty principle. Later, this limitation was overcome by femtosecond stimulated Raman spectroscopy (FSRS), a third order non-linear Raman spectroscopy. In this thesis we introduced the ultrafast Raman loss spectroscopic (URLS) technique which is analogous to FSRS, offering the modern ultrafast community to resolve molecular processes with better signal-to-noise ratio along with proper time and frequency resolution. We demonstrate the experimental procedure including the single shot detection scheme to measure whitelight background, ground state Raman, transient absorption and transient Raman in shot-to-shot detection fashion. URLS has been applied to understand the excited state planarization dynamics of 1,4-bis(phenylethynyl)benzene (BPEB) in different solvents. In addition, excitation wavelength dependent conformational reorganization dinamics of different sub-sets of thermally activated ground state population of BPEB are also dis-

cussed. Using the same techniques along with femtosecond transient absorption, we demonstrate the ultrafast vibrational energy transfer and the role of coherent oscillations of low frequency vibrations on the solution phase photo-isomerization of trans-stilbene from an optically excited state. The effects of solvents on the coherent nuclear motion are also discussed in the context of reaction rates.