SYNOPSIS

Chemistry deals with the transformation of molecular entity through several elementary steps occurring in different timescales. Therefore, understanding the overall mechanism of a chemical reaction involves the investigation of the elementary processes at a molecular level. Many such processes occur with great rapidity involving many short-lived intermediate species, called the transients. Hence, creating such short-lived transients involved in a chemical reaction and then monitoring the characteristics of these transients are essential to obtain a deep insight into the microscopic mechanism of the reaction. Creation of electronic excited state using short light pulse and monitoring of subsequent evolution of the excited states are the key to explore reaction dynamics in real time. In 1949, Norris and Porter developed microsecond flash photolysis technique to monitor short lived reaction intermediate, for the first time. In following years, invention of pulsed lasers and pump probe technique revolutionized the field of time resolved spectroscopy. Advent of femtosecond laser pulses have offered direct observation of transition state of a chemical reaction. Importance of femtochemistry in studies of reaction dynamics was recognized by awarding a Nobel Prize to Prof. Ahmed Zewail in 1999.

Subpicosecond and femtosecond experiments allow monitoring fundamental chemical processes in real time. An electronically excited molecule undergoes a number of relaxation pathways, such as vibrational relaxation, charge transfer, energy transfer, proton transfer, solvent relaxation, configurational relaxation, intersystem crossing, internal conversion, etc. These excited state deactivation pathways are relevant to many chemical and biochemical processes. Electron transfer, proton transfer and proton coupled electron transfer are the most important reactions in photosynthesis and solar energy conversion reactions. Intramolecular charge transfer excited state serves to elucidate microscopic picture of solute solvent interaction and solvation dynamics. Large amplitude structural motion in donor-acceptor
molecules strongly influences extent of charge separation forming twisted intramolecular charge transfer (TICT) state. Time resolved measurements on TICT relaxation dynamics provide information about excited state potential energy surface.

Thus, fundamental understanding of excited state relaxation dynamics in real time holds crucial significance to unravel natural photoinduced processes as well as development of artificial photofunctional materials. Time resolved measurements on structurally simpler model molecules often provide in-depth understanding of the molecular level mechanism and timescale of these competing processes.

Employing femtosecond time resolved spectroscopy on several model molecular systems, the thesis aims at providing some important insights into the excited state dynamics of intramolecular charge transfer, proton transfer and structural relaxation and other electronic deactivation processes. For the convenience of presentation, the thesis is organized in the form of eight chapters. Chapter 1 and 2 describes the introduction of general photophysical aspects in electronic excited states and experimental techniques, respectively. Particular aspects of photoexcited state relaxation dynamics of model molecular systems are presented in self contained manner from chapter 3 to chapter 8. A concise description of the thesis is given below.

Chapter 1:

In this introductory chapter, some basic principles and concepts related to the present thesis have been discussed. The thesis deals with the photo-induced processes such as vibrational relaxation (VR), internal conversion (IC), intersystem crossing, charge transfer, proton transfer, TICT and solvation around the excited solute molecule. So a brief introduction to these interesting topics has been given in this chapter. The occurrence of a photo induced intramolecular process is strongly dependent on the geometry and electronic structure of the
molecule in the excited state as well as on the nature of interaction between chromophores and the surrounding solvent molecules. Role of solute-solvent interaction on the excited state dynamics has been discussed briefly in this chapter. Twisting induced charge transfer in donor-acceptor (D-A) molecules has been an interesting issue which has been discussed in the present thesis. Brief note on the objective and motivation of the present work has also been discussed in this introductory chapter.

**Chapter 2:**

This chapter provides the details of experimental methods used for the investigations of different processes presented in the thesis. Most of the work has been carried out using ultrafast transient absorption spectroscopic techniques. The basic principles of transient absorption spectroscopy and details of the femtosecond transient absorption instrument have been described in this chapter. Femtosecond fluorescence up conversion technique has been described which was used as a complementary technique to the transient absorption experiments. Basic principles of steady state absorption and fluorescence spectroscopic techniques have also been briefly described.

**Chapter 3:**

This chapter deals with the excited state relaxation dynamics of curcumin (figure 1), a natural pigment present in turmeric, in different protic and aprotic solvents. Structurally, Curcumin is a symmetrically substituted 1, 3-diketone which exist as keto-enol tautomer. The molecule possess strong charge transfer character in the S₁ state and shows strong solvent dependence of steady state photophysical propertires. Because of structural diversity and flexibility, the molecule may undergo photoinduced proton transfer, keto-enol tautomerization or isomerization around C=C double bond. Because of large charge transfer character in the excited state, solvation can play important role in the excited state relaxation. To unravel the exact relaxation pathways, transient absorption and fluorescence studies were performed in different solvents. It was observed that in polar solvents, both aprotic and protic, solvation is
the major relaxation process following photoexcitation. Solvation dynamics in protic solvents is multimodal, and the linear correlation between the longest component of the solvation process and the longitudinal relaxation time of the solvent suggests the specific hydrogen-bonding interaction between the solute and the solvent. In nonpolar solvents, the lifetime of the $S_1$ state was observed to be very short because of efficient nonradiative deactivation, which is an important consequence of the ultrafast excited-state intramolecular hydrogen transfer (ESIHT) reaction in the six-membered hydrogen-bonded chelate ring of the $cis$-enol form. Although intramolecular proton transfer may be occurring in ultrafast timescale, it has not been possible to monitor due to the symmetrical structure of the molecule with respect to the hydrogen-bonded chelate ring which forms symmetrical double minima potential energy surface in the ground as well as in the excited states.

**Figure 1:** Structure of curcumin in keto-enol tautomeric form.

**Chapter 4:**
This chapter describes the steady state and ultrafast time resolved spectroscopic studies on an unsymmetrically substituted 1,3-diketone system, namely 4-dimethylamino dibenzoyl ketone (figure 2). Unsymmetrical substitution allowed us to decipher the ESIPT as well as intramolecular charge transfer dynamics and their consequence to the photophysical properties of the molecule. Steady state photophysical studies reveal strong solvent polarity dependent fluorescence behavior. In solvents of low polarity, fluorescence yield increases with polarity, becomes maximum in the medium polarity solvents but decreases in high polarity region. Because of the unsymmetrical substitution, the molecule may exist in two possible cis-enol tautomeric forms (Enol-A and Enol-B) which are interconvertible via intramolecular proton
transfer. The relative energetics of two tautomers and their structural consequences determine the excited state properties. Structure and relative energy of the two tautomeric states in the first excited state were determined in gas phase as well as in polar solvents, which revealed that planar ICT state of Enol-A governs the photophysics in nonpolar solvents whereas dimethylanilino twisted TICT state of enol-B controls the photophysics in polar solvents. Transient absorption and fluorescence studies reveal that in low and medium polarity solvents, the excited Enol-B molecule (Enol-B*) undergoes ultrafast excited state intramolecular proton transfer (ESIPT) leading to the population of Enol-A*, which undergoes the ICT process without any significant change in the geometrical structure of the molecule. In polar solvents, ESIPT dynamics in the S1 state is reversed to populate Enol-B* and the relaxation process is mainly governed by solvation and twisting of the dimethylaniline group, leading to the population of the weakly emissive ‘twisted intramolecular charge transfer’ or the TICT state of Enol-B*.

Figure 2: Structure of 4-dimethylamino dibenzoyl ketone (DMADK) in keto and keto-enol tautomeric forms.

Chapter 5:

Investigation of the role of donor acceptor conjugation on the ICT-TICT dynamics of charge transfer molecules is the subject matter of this chapter. Two isomeric charge transfer dimethylaninochalcone derivatives were synthesized (DMAC-A and DMAC-B, figure 3), which differ in relative positioning of the donor and acceptor groups. Steady state
photophysical measurements revealed that both the molecules have highly charge transfer character in their first excited singlet state but fluorescence behavior has been observed to be remarkably different. Fluorescence quantum yields of DMAC-A decreases with polarity of the solvents, whereas for DMAC-B, fluorescence yield increases in higher polarity solvents. In polar solvents, DMAC-A is more than two order of magnitude weaker fluorescent than the DMAC-B. Moreover, fluorescence band width of DMAC-A is significantly larger than that of DMAC-B in polar solvents. Remarkable difference in the fluorescence quantum yield and fluorescence lifetime is explained by invoking the formation of non-fluorescent TICT state for DMAC-A, whereas, for DMAC-B, planar ICT state is the relaxed $S_1$ state without occurrence of twisting process. Femtosecond transient absorption measurements in different solvents of varying polarity and viscosity revealed the twisting dynamics of DMAC-A. The difference has been attributed to the strong coupling between the donor and acceptor groups in DMAC-A due to shorter distance, whereas in DMAC-B, planar ICT structure is more stable and large barrier is involved along the TICT coordinate due to longer separation of the donor-acceptor group.

![Figure 3](image.png)

**Figure 3:** Structure of two isomeric dimethylaminochalcones, DMAC-A and DMAC-B.

**Chapter 6:**

Chapter six deals with the charge transfer dynamics of a nitro substituted D-A systems. Nitro group being a very strong acceptor moiety, can induce large charge transfer in the excited state and may undergo twisting of the nitro group to facilitate complete charge separation. Moreover, photophysics of the nitroaromatic compounds are dictated by the properties of low energy triplet state, which is populated with a large yield. Thus charge transfer, structural relaxation and intersystem crossing may give rise to complex solvent dependent dynamics in the excited state. This issue has been addressed by exploration of the excited state dynamics of
1-(p-nitrophenyl)-2-(hydroxymethyl)pyrrolidine (p-NPP, figure 4)) in different solvents. Following photoexcitation using 400 nm light, conformational relaxation via twisting of the nitro group, internal conversion (IC) and the intersystem crossing (ISC) processes have been established to be the three major relaxation pathways responsible for the ultrafast deactivation of the excited singlet (S₁) state. Although the nitro-twisting process has been observed in all kinds of solvents, the relative probability of the occurrence of IC and ISC has been found to be extremely sensitive to solvent polarity, because of alteration of the relative energies of the S₁ and the triplet (T₀) states. In the solvents of lower polarity, the ISC is predominant over the IC process, because of near isoenergeticity of the S₁(ππ*) and T₃(nπ*) states. On the other hand, in the solvents of very large polarity, the energy of the S₁(ππ*) state becomes lower than those of both the T₃(nπ*) and T₂(nπ*/ππ*) states and the IC process to the ground electronic (S₀) state are predominant over the ISC, and hence the triplet yield is nearly negligible. However, in the solvents of medium polarity, the deactivation of the S₁ state is directed to both the IC and ISC channels. In the solvents of low and medium polarity, following the ISC process, the excited states undergo IC, vibrational relaxation, and solvation in the triplet manifold. On the other hand, in polar solvents, vibrational relaxation and reverse nitro-twisting process has been observed from the hot S₀ state following ultrafast IC.

Figure 4: Structure of 1-(p-Nitrophenyl)-2-hydroxymethylpyrrolidine.

Chapter 7:
This chapter discusses metal to ligand charge transfer dynamics of a mixed ligand ruthenium complex. Charge transfer dynamics in ruthenium polypyridyl complexes are important for the development of artificial solar energy harvesting system. Mixed ligand complexes are
especially important for broader solar energy absorption. Thus understanding the charge transfer dynamics in mixed ligand complex is highly desirable for development of efficient solar energy harvesting materials. We have probed dynamics of ultrafast vibrational energy relaxation and inter-ligand charge transfer processes of a heteroleptic ruthenium complex, [Ru(bpy)$_2$(pap)](ClO$_4$)$_2$ (where bpy is 2, 2’-bipyridine and pap is 2-(phenylazo)pyridine, figure 5) using femtosecond to nanosecond time-resolved transient absorption spectroscopic techniques. A good agreement between the TA spectrum of the lowest excited $^3$MLCT state of [Ru(bpy)$_2$(pap)](ClO$_4$)$_2$ complex and the anion radical spectrum of the pap ligand, which has been generated using pulse radiolysis technique, confirmed the charge localization at the pap ligand. While the lifetime of the inter-ligand charge transfer from the bpy to the pap ligand in the $^3$MLCT state is about 2.5 ps, vibrational cooling of the pap-localized $^3$MLCT state occurs in a much longer time scale with the lifetime of about 35 ps. Ultrafast charge localization dynamics observed here may have important consequences in artificial solar harvesting systems, which employ heteroleptic ruthenium complexes.

![Figure 5: Structure of [Ru(bpy)$_2$(pap)]$^{2+}$](image)

**Chapter 8:**
In this chapter, we describe the ultrafast electronic relaxation dynamics of uranyl ion in aqueous and methanolic solution following photoexcitation to the $S_1(^1\Phi_g)$ state using 400 nm light. The $S_1(^1\Phi_g)$ state undergoes ultrafast intersystem crossing ($<100$ fs) to the higher
vibrational levels of the $T_2(^3\Delta g)$ state, followed by the intramolecular vibrational relaxation (IVR) process in the later electronic state ($\tau_{\text{IVR}} \sim 0.85$ and 1 ps in aqueous and methanolic solutions, respectively). Subsequently, the $T_2(^3\Delta g)$ state undergoes an internal conversion (IC) process ($\tau_{\text{IC}} \sim 1.6$ and 4.5 ps in aqueous and methanol solutions, respectively) to the long-lived $T_1(^3\Phi g)$ state, which is responsible for the luminescent properties of the uranyl ion. In methanol, because of stronger interaction between the excited triplet, $T_1(^3\Phi g)$, state and the solvent via solvent to uranyl charge transfer, the U(VI) ion undergoes partial reduction to U(V) and the energy level of this state possibly lies lower than that of $(\text{UO}_2^{2+})^*$, which is the transient species existing in aqueous solution, and hence increasing the energy gap between the $T_2$ and $T_1$ states in methanol solution.

Summary:

The main aim of the thesis is to investigate the dynamics of intramolecular charge transfer, proton transfer, large amplitude structural relaxation and solvation dynamics in some model molecules. Competing relaxation pathways and their dependence on structure, functional group, solvent properties has been evaluated. Different aspects of the excited state relaxation processes were deciphered using specific model molecules. The main conclusions drawn from the different molecular systems studied in this thesis are as follows:

- Intramolecular charge transfer dynamics has been revealed to be associated with large amplitude structural relaxation of donor and acceptor moieties. Solvent polarity, viscosity and solvation dynamics were found to play significant role in ICT dynamics. Excited state properties have been revealed to be strongly dependent on the structure and functional group present in the molecular system. Solvent properties (i.e., polarity and proticity) have been found to significantly affect the excited state dynamics.

- In curcumin, six membered intramolecular hydrogen bonded system, excited state relaxation is mainly governed by solvation dynamics. The possible ESIPT dynamics
could not be resolved due to symmetrical structure of the molecule. Nonetheless, ESIPT was found to influence the excited state lifetime in nonpolar solvents.

- In a synthesized unsymmetrical diketone, namely DMADK, ESIPT process has been resolved which occurs in <200 fs timescale. Solvent polarity governs the direction of proton transfer and subsequent intramolecular charge transfer and structural relaxation.

- Effect of conjugation and coupling between donor and acceptor groups on twisted intramolecular charge transfer dynamics has been revealed from the comparative photophysics and excited state dynamics of the isomeric 4-dimethylaminochalcones.

- Studies on p-NPP revealed that twisting of nitro group governs the excited state charge transfer process followed by competing ultrafast internal conversion or Intersystem crossing depending on solvent polarity.

- Studies on two inorganic systems leads us to understand that excited state dynamics in inorganic molecules occurs on the triplet energy surface following ultrafast intersystem crossing. In uranyl nitrate, ultrafast ISC followed by vibtational relaxation and internal conversion to the lowest energy triplet state are the initial event upon photoexcitation. In a mixed ligand ruthenium complex, we observed the interligand electron transfer and vibrational relaxation to form lowest energy $^3$MLCT state.

The studies of excited state dynamics in various model molecules with different structures and functionality have revealed that excited state processes are strongly dependent on the structure and functional moieties present in the molecule. Effect of surrounding solvent environment has also been observed to determine the fate of the photo excited state. The knowledge gained from the present study on the dynamics of photo-induced intra- and inter-molecular processes in condensed phase may be useful for their applications in different fields such as molecular based photonic devices, nonlinear optics, photovoltaics, etc.
References: