Ultrafast fluorescence studies of excited-state hydrogen transfer reactions in solution
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Chapter 1

Introduction

Studies of molecular dynamics are of great interest to chemists because they contribute to a better understanding of the course of a chemical reaction [1-6]. On a molecular level, chemical reactivity is often discussed in terms of the free energy of the system as a function of the generalized reaction coordinate [7, 8]. The temporal evolution of the reaction coordinate is characteristic of the specific nuclear motions constituting the bond breaking(s) and bond fusion(s) during the reaction. For chemical reactions in the condensed phase, very often the nature of solute-solvent interactions influences the functional shape of the free energy or potential energy surface; in turn, this may be of great influence on the chemical reaction dynamics.

In this thesis we focus on a few molecular systems showing ultrafast intra- and intermolecular hydrogen transfer dynamics in the condensed phase. Hydrogen atom or proton transfer reactions are ubiquitous in chemistry and biology [9-13]. Proton/hydrogen atom transfer reactions may be initiated under various experimental conditions, e.g., by thermal activation [14], solvent mediation [13, 15] or photoexcitation [16]. To the experimentalist it is a challenge to study the behavior of the transfer reaction under a variety of different experimental conditions. Based on the information obtained in the experiments, it is attempted to visualize the functional characteristics of the potential energy surface and to indicate what reaction pathway is followed by the system as the reaction takes place.

Hydrogen atom transfer is often used synonymously with proton transfer. The latter involves a Zwitter-ionic structure and does not require significant electronic redistribution. In the case of hydrogen atom transfer, the product state is stabilized by electronic and nuclear redistribution. Quantum mechanical calculations and studies of the reaction in various polar solvents have been performed to distinguish between both mechanisms [17-19].

Hydrogen atom and proton transfer reactions have been investigated for molecules in both ground- and excited states. The pioneering work of excited-state hydrogen transfer research began in the 30-ies [20] and the late 40-ies [21]. All of these studies focused on intermolecular hydrogen transfer reactions. The first studies of excited-state intramolecular hydrogen atom transfer were reported in the mid 50-ies for the hydrogen atom transfer reaction in photoexcited methyl salicylate [22].
Studies of hydrogen transfer have been of great significance for the understanding of a wide variety of elementary reactions [23]. For instance, the unique properties of water stem from the ability of water molecules to form extensive networks through intermolecular hydrogen bonding [24, 25]. Elaborate calculations and experimental studies resulted in a model in which a continuous exchange of protons between nearest neighbor molecules is visualized [24]. In studies of catalysis, hydrogen bonding has often been found to be of vital importance [26]. Hydrogen bonding has been a key for determining the structural specificity of enzymes in restricted substrates [27] as for instance in membrane proteins [11] or in hydrogenation reactions [28]. For some excited-state intramolecular proton transfer (ESIPT) reactions, it has been shown that the ESIPT is driven by excited-state intramolecular charge transfer (ESICT) [29]. Energy stabilization by the polar medium of the possible product species has been found to determine the branching ratio of several possible ESIPT products. In DNA, proton - and charge transfer are entangled as well [30]. Proton motion was found to affect long range charge- and electron transfer in DNA [30, 31]. The main aim of all these studies is to gain insight in the photophysics and photochemistry of macromolecules that are of vital importance in nature. In addition, proton transfer studies have also led to a wide range of practical applications through the development of technological devices such as: solar collectors [32], energy storage systems [33], chemical lasers [34], high-energy detectors [35] and photolithography [36].

Photoinduced ESIPT can be investigated by employing time-resolved spectroscopy. Ultrafast laser technology has made it possible to study the ESIPT kinetics in real time with (sub)picosecond time-resolution [37, 38]. For fluorescent molecules, femtosecond fluorescence techniques are very powerful. The advantage is here that the temporal behavior of only the excited-state population is studied, without the interference of bleaching and excited-state absorption phenomena as in ultrafast transient absorption experiments [39-41].

In this thesis, we are mainly concerned with the excited-state proton transfer dynamics of a few organic fluorescent molecules of special interest, as detailed below. We focus on experimentally characterizing the excited-state dynamics of these molecules thereby attempting to also gain information on the nature of the reaction coordinate and the potential energy surface. To illustrate a few of the salient features of a photoinduced proton/hydrogen atom transfer reaction, we make use of the scheme of Figure 1.1. Two minima in the potential energy surfaces of the ground- and excited-states occur, corresponding to the tautomter forms, before and after the proton transfer, respectively. The abscis could for instance refer to the normal coordinate of a skeletal mode that promotes the transfer [42-44]. ‘Franck-Condon’ photo-excitation of the
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ground state population into the (first) excited-state will produce a non-equilibrated excited-state population. Subsequently, several population relaxation pathways may occur, as indicated in the figure by the downward arrows. These pathways include direct radiative (dashed) and nonradiative decay (wavy) relaxation of the reactant, decay by proton transfer from reactant to product in the excited-state (rate constant $k_{PT}$), and finally, radiative (dashed) and nonradiative decay (curly) from the excited product state to the product ground state, possibly followed by return to reactant ground state via a proton back-transfer (with rate $k_{PT'}$). The scheme in Figure 1.1 is illustrative of a single proton transfer process.

![Figure 1.1: Schematic representation of a possible photocycle for proton transfer. Photoexcitation leads to an excited-state proton transfer with reaction rate $k_{PT}$](image)

In many systems, however, a multi-proton transfer process may take place, for instance in the case of dimerization of 7-azaindole [45-47], and hydrogen-bridge formation in DNA [48-50].
In principle, the scheme of Figure 1.1 then has to be adapted and one has to plot the potential energy surfaces in multidimensional reaction coordinate space.

In Chapter 3, we study the proton transfer dynamics of the molecule [2,2'-bipyridyl]-3,3'-diol (BP(OH)$_2$), for structure see Figure 1.2. BP(OH)$_2$ has received great interest recently because it may be applied as a laser dye [51] and because it may be regarded as a model system for a double proton transfer process in the excited-state (ESIDPT) [52]. In previous studies it was concluded that photoexcitation of the dienol ground state population into the excited-state, induces an ESIDPT reaction that is essentially branched [53, 54], see Figure 1.2.

As illustrated in the figure, the reaction scheme comprises of a concerted and a consecutive double proton transfer. In Chapter 3 we present the results of our ultrafast fluorescence polarization spectroscopic study. Using time-resolved polarization techniques we were able to
investigate the reorientation dynamics of the emissive dipole [55]. The aim of our investigations is to obtain a better understanding of some of the details of the ESIDPT reaction of BP(OH)$_2$. In these studies it appeared possible to obtain information about the upper limit (~ 300 fs) for the lifetime of the fluorescent dienol reactant state. Furthermore, additional support for the existence of a branched photoreaction was obtained.

In Chapter 4, we present results for [2,2'-bipyridyl]-3,3'-diamine (BP(NH$_2$)$_2$), which is the diamine analogue of BP(OH)$_2$ and which appears to also show photo-induced double proton transfer. For BP(NH$_2$)$_2$, the optical properties and excited-state dynamics have not yet been studied previously. We will show that the photophysical and photochemical properties of BP(NH$_2$)$_2$ are quite similar to those of BP(OH)$_2$ [56]. After photoexcitation, both compounds give rise to ESIDPT.

The photophysics of BP(OH)$_2$ en BP(NH$_2$)$_2$ is also of great interest in studies of supramolecular stacks containing these molecules as functional groups. We present a typical example of such a supramolecule in Figure 1.3. Synthesized supramolecular architectures have drawn a lot of interest because they may serve as model systems for natural macromolecules [57]. Synthesized modifications of supramolecules may bridge the gap between synthetic architectures and biomacromolecules, and have the potential to be suitable to create newly functional systems [58].

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*Figure 1.3: Bipyridine based C$_3$-symmetrical disk (1) and its subgroup DAC (2)*
The $C_3$-symmetrical disk type molecules as presented in Figure 1.3, are able to self-assemble to stacks of molecules in apolar solvents. The large peripheral sidechains form solvophobic domains. Under these conditions of reduced influence of the solvent, interactions between neighboring molecules may be dominated by intermolecular hydrogen bonding and $\pi-\pi$ interactions. It has been found that the self-assembling of the discotic molecules gives rise to helical aggregates [59, 60]. This inherent helicity stems from the non-planarity of the discotic molecules, which restricts the mobility of the molecule within the aggregate. In polar solvents, solvation compensates for the secondary interactions and self-assembling of the aggregates is disrupted. In principle, the photophysics of the single disks or the aggregates can be selectively investigated by simply changing the polarity of the solvent medium. In Chapter 5, we present the results of our time-resolved fluorescence study of 1 and its photoactive subgroup 2, in polar and apolar solutions, applying ultrafast fluorescence spectroscopic techniques. It will be shown that the bipyridine functional groups, incorporated into large molecules 1 and 2, still show ESIDPT [61]. Even in the aggregated state, the $C_3$-symmetrical disk type molecules exhibit ESIDPT [61].

The studies provide information on the kinetics of the ESIDPT reaction. It will be shown that significant lengthening of the excited-state lifetime and drastic slowing down of the reorientation motions in the aggregate, when compared with the single disk, can be specifically attributed to the aggregated state; these phenomena are found to be representative of a rigid aggregate structure.

In some cases, proton transfer cannot occur directly. When the molecule comprises of proton-donating and -accepting groups that are unfavorably situated relative to one another, a direct intramolecular proton transfer does not occur. In such a case, the proton transfer may be facilitated by a protic solvent, [13, 46, 62, 63] or via hydrogen bonding in dimers [64, 65]. This type of reaction is then essentially an intermolecular proton transfer reaction. Solvent-assisted intermolecular proton transfer has also been found for aromatic thioketones. Two typical aromatic thioketones are presented in Figure 1.4.

![Benzophyranthione (BPT) and Thiocoumarine (TC)](image)

*Figure 1.4: Two typical aromatic thioketone: benzophyranthione (BPT) and thiocoumarine (TC)*
These aromatic thioketones were found to exhibit unusual fluorescence from the $S_2$ state and interesting relaxation dynamics in the $S_2$ state [66-68]. From transient absorption studies in $n$-alkane solutions [68-70], it was established that the $S_2$-state relaxation essentially involves intermolecular quenching by the hydrocarbon solvent. In particular, hydrogen bonding with the solvent was discussed to be involved in the quenching process. From these studies the reaction scheme of Figure 1.5 was proposed. The reaction coordinate involves the solute-hydrogen-carbon (SHC) internuclear coordinate, and long before it has a chance to form solute-hydrogen- and solvent molecule radicals, the system relaxes via a conical intersection, of the $S_2$ and $S_1$ surfaces [68], towards the $S_1$-state. This type of reaction is termed ‘aborted intermolecular hydrogen transfer’.

![Figure 1.5: Schematic electronic potential energy surface diagram corresponding with the aborted hydrogen abstraction from hydrocarbon (RH) in the $S_2$ state of the solute (S)](image-url)
In addition, photophysical studies of thioketones in polar and apolar solvents were performed to investigate how the nature of the solute-solvent interaction affects the \( S_2 \)-state dynamics \[68\]. In the polar solvent acetonitrile, it was concluded that in addition to the aborted intermolecular hydrogen transfer, exciplex formation with the solvent contributes to the \( S_2 \) state relaxation \[71\].

In Chapter 6 we investigate the \( S_2 \)-state photo dynamics for molecule 4H-1-benzopyrane-4-thione (BPT: Figure 1.4) in the protic solvents water and deuterated water. Of interest is to understand the mechanism of deactivation of the \( S_2 \)-state of BPT in water and deuterated water. From our studies we conclude that a hydrogen bonded solute-water complex is involved in the \( S_2 \)-state deactivation.

To gain additional information on the \( S_2 \)-state dynamics of BPT in solution, we performed fluorescence polarization experiments (Chapter 7). Our aim was to obtain additional information on the reorientation dynamics of the transition dipole during the \( S_2 \)-state relaxation. We examined the orientational anisotropy dynamics in a series of \( n \)-alkanes solution to determine the dependence of the reorientational motions on solvent viscosity. The dynamics for the orientational anisotropy decay are found to comply with a linear dependence on solvent viscosity.

As discussed throughout in all of the next Chapters, proton transfer is always accompanied by a variety of additional excited-state relaxation processes. In the condensed phase, excess energy is dissipated \textit{via} intra- and intermolecular relaxation processes \[72-75\]. The relaxation processes include: state-to-state internal conversion \[76, 77\], intersystem crossing \[78, 79\], intra- \[80-82\] and intermolecular vibrational relaxation \[83-85\] and solvation \[86-88\]. The time scales of these processes generally range from tens of femtoseconds to tens of picoseconds. Thus the investigation of excited-state relaxation, in particular of large molecules, confronts the experimentalist with a very complicated task indeed. In Chapter 8 we study an example of a highly fluorescent dye, showing relaxation from an excited electronic state higher than \( S_1 \). The structure of this dye molecule, 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP) is given in Figure 1.6.

The excited-state dynamics in the first excited-state mainly involves excited-state relaxation via spontaneous emission \[89\]. We have investigated the higher excited-state dynamics of fluorescent dye BDP-1 by means of ultrafast fluorescence spectroscopy measurements. It appeared possible to determine the \( S_n \rightarrow S_1 \) (\( n=2,3 \)) internal conversion time (typically between 100 and 230 fs) and the ensuing vibrational cooling in the excited \( S_1 \) state (~ 10-20 ps). BDP-1 represents one of the rare cases in which these relaxation processes could be followed using the femtosecond fluorescence upconversion technique.
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Figure 1.6: Scheme of boron-dipyrromethene (BDP) dyes

References

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