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

Chemical reactions involving the transfer of protons or hydrogen atoms are of utmost importance in chemistry and biology. In many cases, proton transfer is induced by photoexcitation. Excited-state proton transfer reactions can be either intramolecular or intermolecular, in which case the reaction is sometimes facilitated by protic solvents.

Recent developments in laser technology have provided new ways for the study of chemical reaction dynamics on ultrafast time scales, down to femtoseconds (1 fs = 10^{-15} s). In this thesis, results of fluorescence experiments are presented employing fluorescence upconversion and single-photon counting detection techniques (with time resolutions of ~ 150 fs and ~ 17 ps, respectively). From the time-resolved spectroscopic data, the dynamics of intra- and intermolecular proton transfer as well as dissipation of excess energy for a number of model molecular systems are investigated.

In the Introduction (Chapter 1) we review in brief a few of the characteristics of proton transfer. Some background information of the molecular systems studied in the next Chapters is also presented.

In Chapter 2 we present the experimental setups used in the experiments. The principles of fluorescence anisotropy are also presented.

In Chapter 3 we present results of our study of excited-state intramolecular double proton transfer (ESIDPT) in [2,2'-bipyridyl]-3,3'-diol (BP(OH)₂), in polar and apolar liquid solutions. BP(OH)₂ is of interest because it represents a model system for ESIDPT and shows branching of the photoreaction in which ESIDPT can occur in a concerted as well as in a consecutive fashion. The fluorescence data reveal a fast fluorescence decay (~ 300 fs) in the blue edge of the emission band and a similar time component for the rise of the fluorescence band of the 'product' state, which leads us to conclude that the subpicosecond time component is a measure of the rate of ESIDPT. The subps component is also found in the fluorescence anisotropy decay, providing additional evidence for the kinetics of the ESIDPT reaction. Furthermore, the temporal behavior of the anisotropy shows two additional time components. One time component (~ 10 ps) is similar to the time being found for the conversion of the monoketo to diketo species in the consecutive ESIDPT. A somewhat slower time component (~ 20-40 ps) is due to orientational diffusion motions of the solute in the liquid.

In Chapter 4, the excited-state dynamics of [2,2'-bipyridyl]-3,3'-diamine (BP(NH₂)₂) is investigated. The photophysics of BP(NH₂)₂ is of great interest in studies of supramolecular stacks (Chapter 5) containing these molecules as functional groups. It is concluded that photoexcited BP(NH₂)₂ undergoes a branched intramolecular double proton transfer reaction
comprising of two trajectories: (i) a consecutive scheme involving ultrafast double proton transfer (within \( \sim 100 \) fs), followed by twisting (\( \sim 250 \) fs) and (ii) a direct transfer governed by a simultaneous twisting motion and proton transfer (within \( \sim 250 \) fs). For the photoproduct state, an additional picosecond fluorescence decay is found, the decay being characteristic of the cooling of vibrationally hot ‘product’ states in which excess vibrational energy is lost by energy dissipation to the bath of solvent molecules. The very short lifetime of the tautomer product (\( \sim 10 \) ps in \( n \)-alkanes) is related to relaxation via conical intersection between the product- and the ground state potential energy surfaces.

In Chapter 5, we present a comparative time-resolved spectroscopic study of a \( C_3 \)-symmetrical disk molecule and its asymmetrical building block (hereafter labeled Tab and DAC, respectively), in which \( \text{BP(NH}_2)_2 \) is incorporated as a functional group. In apolar solution, TAB is able to form supramolecular stacks of single disk molecules via secondary interactions, whereas in polar solution solvation is able to compensate for the secondary interactions, such that stacking is disrupted. In order to characterize the photophysics of supramolecular stacks of TAB molecules, a comparative study is made with model systems \( \text{BP(OH)}_2 \) and \( \text{BP(NH}_2)_2 \) (Chapters 3 and 4). A major finding from these studies is that when photoexcited, TAB and DAC exhibit ultrafast ESIDPT (within \( \sim 200 – 300 \) fs); in TAB ESIDPT occurs irrespective whether the molecule is either in the aggregated- or in the non-aggregated state. The fluorescence decay of the photoproduct states of TAB and DAC is multiexponential. Initial ps fluorescence decay (\( \sim 3-25 \) ps) is representative of cooling of vibrationally hot ‘product’ molecules, to the solvent bath. Fluorescence anisotropy measurements revealed a \( \sim 1 \) ps decay component that is only observed in the aggregated state. It is discussed that the rapid loss of fluorescence polarization is characteristic of excited-state energy transfer among neighboring disk molecules in the stacks. Long-time multi-exponential decays are observed for molecularly dissolved TAB and DAC (0.1 - 0.4 ns) and aggregated TAB (0.1 - 4 ns). These time components are attributed to the excited-state lifetime; the spread in the lifetimes is attributed to structural inhomogeneities of the stacks in solution. The influence of aggregation on the excited-state lifetime in TAB is also briefly discussed.

In Chapters 6 and 7, the \( S_2 \)-state relaxation dynamics for the molecule 4H-1-benzopyrane-4-thione (BPT) are investigated. This molecule exhibits fluorescence from its \( S_2 \) state, which is unusual. In Chapter 6, the \( S_2 \)-state photophysics of BPT in water and deuterated water is investigated, by using femtosecond fluorescence up-conversion and transient absorption spectroscopic techniques. The results show that the \( S_2 \)-state relaxation involves a mechanism of
intracomplex deactivation within a BPT-water complex promoted by high-frequency O-H / O-D stretching modes.

In Chapter 7, a study of the fluorescence anisotropy decay of 4H-1-benzopyrane-4-thione (BPT) in the \( S_2 \)-state, in hydrocarbon solution, shows that the reorientational dynamics of BPT is linearly dependent on the solvent viscosity. The results are in agreement with the Stokes-Einstein-Debye hydrodynamics theory, applied for slip conditions.

In Chapter 8, we study the higher excited-state dynamics of 2,6-diethyl-1,3,5,7-tetramethyl-8-phenyl-4-difluorobora-3a,4a-diaza-(s)-indacene (BDP) dye in polar and apolar solvents. Internal conversion and vibrational relaxation times from this state are \( \sim 100-230 \) fs. Fluorescence anisotropy measurements with high-time resolution show that the \( S_3 \leftarrow S_0 \) transition moment is perpendicular to that for the \( S_2 \leftarrow S_0 \) and \( S_1 \leftarrow S_0 \) transitions. The anisotropy measurements also reveal that vibrational cooling in the \( S_1 \) state is vibronic rather than vibrational in nature.