Ultrafast fluorescence studies of excited-state dynamics of a few organic chromophores in solution
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Summary

The study of chemical reaction dynamics is central to obtain a deeper understanding of formation and breaking of bonds during a chemical reaction. An important problem in the field of chemical reaction dynamics is the determination of the reaction coordinate(s) i.e. a more detailed insight on the degrees of freedom that determine the reaction path. Many chemical reactions take place in solution. Besides internal molecular coordinates, also solvent molecular coordinates can influence the reaction. Chemical reactions on a time-scale of femto- to picoseconds are not unusual, in particular when the reaction is initiated by radiation with light (excitation) of appropriate color. The reaction then takes place for molecules in the “excited” state.

In this thesis, reactive excited states with a lifetime in the order of pico- to nanoseconds are investigated. Recent developments in ultrafast time-resolved spectroscopy make it possible to study in “real-time” chemical reaction dynamics on the order of femto- and picoseconds. We focus on fast molecular properties in the excited state in this time-range. Experiments were conducted with the fluorescence upconversion technique (time-resolution ~ 150 fs) and the single-photon counting technique (time-resolution of ~ 17 ps).

One of the properties of the investigated molecules is that after excitation with light they become fluorescent. Information about ultrafast processes in the excited state was collected by measuring the fluorescence transients with time-resolved fluorescence techniques. In this thesis we focus on ultrafast processes like rotational motions of functional groups inside a molecule, charge transfer (“electron transfer”) inside a molecule and the influence of fast reorientation motions of surrounding solvent molecules on the relaxation in the fluorescent state.
In the introduction of Chapter 1 we concentrate on several theoretical and experimental concepts for photo-induced chemical and physical processes. In particular, the influence of intramolecular rotational motions and solvation dynamics on the emission spectrum is considered.

Details concerning the experiments are presented in Chapter 2. The fluorescence upconversion and single-photon counting setups used in the experiments are described. Details of ultrafast fluorescence anisotropy measurements are also given.

Chapter 3 presents the results of the time-resolved spectroscopic investigation of a new class of organic light emitting diodes (OLED): Al(III)- and Ga(III)-tris-8-hydroxyquinoline and the free ligand 8-hydroxyquinoline. It is discussed that the measured spectral shift dynamics can be attributed to the influence of solvation on the emissive behavior of the “probe” molecules. One of the interesting conclusions is that the rate of photo-induced electron transfer in the “probe” molecules is dominated by solvation dynamics.

Chapter 4 describes the study of the time-resolved fluorescence anisotropy behavior of the OLED-molecules in the excited state. The anisotropy of the fluorescence shows a bi-exponential decay. The time-constant corresponding to the fastest component is similar to the solvation dynamics time-constant. This is a conformation for the already described mechanism for the electron transfer in the excited state discussed in Chapter 3. The fluorescence anisotropy decay on longer time-scale has been attributed to the rotational motion of the solute molecules. When the molecules are excited with UV-light (\( \lambda < 330 \text{ nm} \)) to higher electronic states, the dynamic anisotropy effects are lost. From this it could be concluded that
intramolecular relaxation from higher excited states to the lowest excited state takes place within 150 fs.

Chapter 5 presents some of the spectroscopic properties of two infrared laser dyes (IR1048 and IR1061) in the wavelength region of 800-1200 nm. The time-resolved emissions of the laser dyes are measured in solution and in a sol-gel solid matrix. The temporal behavior for these molecules in solution shows a bi-exponential behavior. For the fast component (~ 200 fs) it is argued that this component is due to vibrational relaxation. The slow component is typical for the lifetime of the excited state (~ 20 ps).

In Chapter 6 the time-resolved spectroscopic experimental results of two methanediphenyl dyes in solution are presented. The time-behavior of the emission is studied for Michler’s ketone (4,4’bis(N,N-dimethylamino)-benzophenone (MK)) and its bridged component (3,5-bis(dimethylamino)-10,10-dymethylanthrone (BMK)). MK has two phenyl groups that in principle can rotate freely around the bond with the central C-atom. This is impossible for the bridged component. The time-resolved emission spectrum of MK dissolved in an alcohol shows a dynamic Stokes shift; furthermore, the emission intensity shows a decay that is faster than expected for a solvation process. For BMK in the same solvent, only a dynamic Stokes shift with a time-constant similar to that for solvation was found. These findings were studied with various solvents of variable polarity and viscosity. The kinetics results were related to the internal rotation of the phenyl groups of MK and solvation of the used solvent. Different models were discussed. The model where the excited state was considered as an adiabatic mixture of an emitting and a dark state gives the best comparison with the experimental observations. The strength of the coupling between both states is dictated by the angle of rotation of the phenyl groups.
Chapter 7 presents a quantitative discussion of the coupling model of Chapter 6. The time-dependence of the emission spectra of MK in various solvents was simulated. For MK dissolved in an alcoholic solvent reasonable agreement between the simulated and the experimental time-resolved emission spectra was achieved. It appears that this model is less satisfactory for the simulation of the emission spectrum of MK dissolved in DMF. It was argued that a two-dimensional model, with rotational diffusion and solvation as reaction coordinates, could lead to a better agreement between experiment and simulation.