

# Chapter 1

## Introduction

### 1.1 General aspects and outline of this thesis

Electron transfer (ET) is the simplest chemical reaction: an electron is transferred from a donor to an acceptor without the breaking or the creation of chemical bonds. ET is the basis of many fundamental biological and chemical processes, for instance photosynthesis. In nature, an electron is usually transferred from a molecular donor state into a particular molecular acceptor state, i.e. the ET is homogeneous. Around 1950 it became clear that the kinetics of ET reactions strongly vary between different molecular systems. At that time the theoretical description of ET reactions was mainly triggered by Marcus [1, 2, 3], who was awarded the Nobel prize in chemistry in 1992 "for his contributions to the theory of electron transfer reactions in chemical systems". Marcus realized the importance of nuclear configuration changes between reactants and products and the solvent contribution to the ET rate. A brief outline of the ET theory will be given in the following section.

A qualitatively different situation occurs if there are multiple acceptor states instead of one single molecular acceptor. Such a situation arises for molecules bound to the surface of a solid. If the excited states of the adsorbate overlap in energy with empty states of the solid, e.g. the conduction band of a semiconductor, a photoexcitation of the molecule will be followed by an ET from the molecule to the solid. Such heterogeneous ET is the initial process in applications like AgBr photography [4] and dye-sensitized solar cells (DSSC, also called Grätzel cells) [5, 6, 7]. In both systems a semiconductor with a large band gap is sensitized to visible light by surface-adsorbed dye molecules. O'Reagan and Grätzel were the first to report that such systems, consisting of a metal-organic chromophore and nano-structured titanium dioxide as semiconductor, are capable to convert sunlight into electrical energy with remarkable efficiency of about 10% [5]. This finding triggered numerous research activities as the DSSC promised to be a low-cost photovoltaic device and/or

a device for niche applications. It has been found that the functioning of the DSSC is based on a sequence of processes that differ in their kinetics by about 14 orders of magnitude: the timescale for the initial charge separation, i.e. the ET from the dye molecule into the conduction band, is typically tens of femtoseconds ( $1 \text{ fs} = 10^{-15} \text{ s}$ ), whereas migration of electrons within the nano-structured semiconductor to the back electrode takes up to seconds [8].

Apart from the technological importance, the initial photo-induced heterogeneous ET process, which is the main focus of this thesis, represents an interesting topic as it is a unique ET case. Surface electron transfer has been investigated over decades within the field of electrochemistry. The methods applied in electrochemistry usually address the overall rate of subsequent reactions, which of course is dominated by the slowest process. Furthermore, these methods are either stationary or have insufficient time-resolution to resolve the surface electron transfer.

The reason why the understanding of the basic physics of the heterogeneous ET is lagging behind the understanding of the homogeneous analog is inherent within the ET system, from both the theoreticians as well as from the experimenters point of view: an interesting aspect of the reaction is that it links molecular physics and solid state physics. In terms of symmetry, this means a transition from a localized wavefunction lacking any translational symmetry to delocalized wavefunctions with the three-dimensional symmetry of the lattice. For that reason, a proper theoretical description of such an ET system on a microscopic level requires extensive models, similar or even larger compared to theoretical surface science.

The experimenter faces the fascinating speed of the reaction - apart from the experimental difficulties of studying surfaces. Optical time-resolved spectroscopy is thus the only technique capable of a direct measurement of the ET kinetics. Starting in the nineties, a couple of groups studied electron injection for numerous systems [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23], whereas the time-resolution of most of these experiments only allowed the estimation of an upper limit of the ET time constant. The end of this chapter gives a brief overview of the state of the art in this field.

Apart from the mentioned existing applications, heterogeneous ET will be important if the proposed field of molecular electronics ever becomes reality [24]. Although this topic has been existing for more than 30 years now, e.g. the design of a molecular rectifier has been proposed by Aviram and Ratner in 1974 [25], it is still highly visionary. Nevertheless - for all of the proposed concepts at some point the molecular device has to be contacted with a conducting solid. Thus, the electronic interaction of a molecular unit with a solid is of vital importance also with respect to this visionary field.

**Outline of the thesis.** In this work electron injection from different perylene chromophores into the conduction band of nanostructured TiO<sub>2</sub> anatase is investigated. The outcome can be grouped in three categories, which are reflected by the three main chapters of the thesis.

Chapter 2 deals with the experimental setup. As the ET processes occur on a tens of femtosecond time-scale, the improvement of the time resolution, i.e. the generation of shorter laser pulses, was a major task within this thesis. A milestone in the generation of short tunable laser pulses was the realization of a proposed non-collinear amplification scheme [26] by Wilhelm, Piel and Riedle [27] for a 1 kHz repetition rate laser system. Within a collaboration between Riedle's group and the HMI, the non-collinear optical parametric amplification (NOPA) scheme was successfully adopted to the low pulse energy available from a high repetition rate laser system. This will be discussed in detail in chapter 2.

Another prerequisite for performing spectroscopy in defined conditions was the design and construction of an ultrahigh vacuum (UHV) chamber. Performing pump-probe spectroscopy in UHV offers two advantages: first, the photo-stability of the molecule is dramatically improved compared to ambient conditions. Secondly, the ET system is better defined and easier comparable to theoretical studies. Nevertheless, the effect of a particular solvent environment on the ET kinetics might be interesting. Therefore, the chamber was conceptualized such that it allows the introduction of gases and liquids at a high purity grade.

The investigated system is introduced in chapter 3. It is shown that the perylene chromophore is a very suitable molecule for the study of ET reactions for several reasons. As the molecular properties of the dye strongly affect the electron injection, the electronic properties of the molecule are investigated on the microscopic level by the use of molecular orbital calculations. The perylene chromophore is linked via different molecular bridge-anchor groups to the surface of nanostructured TiO<sub>2</sub>. Colloidal systems are inherently inhomogeneous. The microscopic properties of the semiconductor sensitively depend on details of the preparation procedure. It was found that the electron injection kinetics of an adsorbate is quite sensitive to certain parameters of the sample preparation. As a consequence the pure semiconductor as well as the sensitized system have been characterized with imaging techniques like REM and TEM (section 3.2.2) and different stationary spectroscopic techniques like FT-IR, Raman, and linear spectroscopy (sections 3.2.2 and 3.3). Furthermore, photoelectron spectroscopy (UPS and XPS) provides valuable information on the energetic position of molecular levels with respect to semiconductor states (section 3.4).

The results of the time-resolved measurements are presented in chapter 4. First, the chromophore directly linked to anatase via a carboxylate group is considered. This molecule is used as reference system for the investigation of the other perylene

derivatives. The origin of the pump-probe signals and its assignment to the temporal evolution of populations is discussed in detail in the first section of this chapter. The observed variations in the ET dynamics for the different anchor and bridge groups are related to microscopic properties of the adsorbates. These results represent the first study of a systematic variation of the electronic coupling in a heterogeneous ET system (section 4.2 and 4.3).

Effects arising from the glass substrate and the general comparability of differently prepared nanostructured samples are discussed in the following sections. Exemplary measurements on the effect of a solvent or gas environment on the ET kinetics are presented in section 4.4.4. Finally, analogies between forward electron transfer and the recombination kinetics are discussed in section 4.4.1.

Chapter 5 summarizes the results and gives some implications for applications utilizing heterogeneous ET.

The remaining chapter first gives a brief introduction into ET theory. Starting from homogeneous ET, the principles of interfacial ET will be derived more by illustrative rather than mathematically exact argumentation. Consecutively, the state of the art in the field of heterogeneous ET and open questions will be discussed.

## 1.2 Introduction to electron transfer theory

ET theory has been a vivid field for about 50 years now. Accordingly large is the number of publications on intramolecular ET. This section gives a brief outline of the description of ET reactions with the intention of giving a qualitative picture of the ET process. Interfacial ET will be discussed in terms and in the language of intramolecular ET. Readers interested in a more detailed discussion of the subject are referred to the cited literature.

### 1.2.1 Homogeneous electron transfer

#### 1.2.1.1 Non-adiabatic limit

Let us first consider a molecular system exhibiting intramolecular ET having two localized electronic states  $D$  (donor) and  $A$  (acceptor). The states are weakly coupled, optionally through a molecular bridge unit  $B$ , which does not alter the potential energy surfaces of  $D$  and  $A$ . Such a situation is illustrated in Fig. 1.1. The ET reaction thus reads



The standard quantum mechanical approach to describe such a non-adiabatic pro-

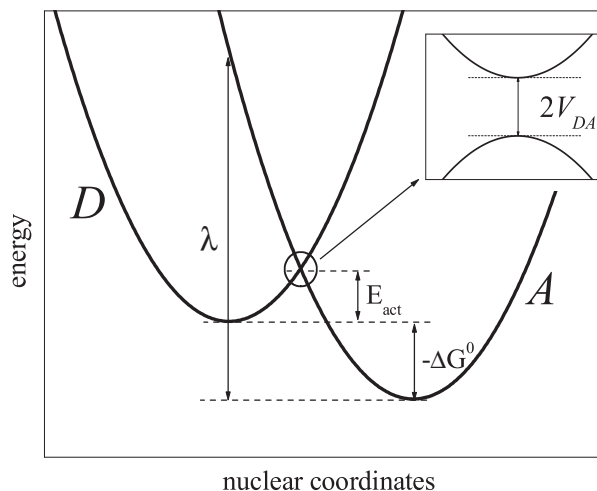


Figure 1.1: Two one-dimensional harmonic potential energy surfaces representing the donor ( $D$ ) and acceptor ( $A$ ) state of a DA complex in the non-adiabatic limit. The reorganization energy  $\lambda$ , the activation barrier  $E_{act}$  and the driving force of reaction, i.e. the standard Gibbs free energy difference  $-\Delta G^0$ , are indicated. The inset shows the region of the crossing point: the interaction of the two electronic states avoids a true crossing due to level splitting of twice the coupling strength.

cesses (weak perturbation) is an expansion in terms of the perturbation, i.e. the weak donor acceptor coupling. In the lowest order of perturbation theory one obtains a Fermi golden rule expression for the ET rate [7, 28, 29, 30, 31]

$$k_{ET} = \frac{2\pi}{\hbar} |V_{DA}|^2 FCWD, \quad (1.2)$$

with  $V_{DA}$  denoting the electronic coupling matrix element and  $FCWD$  the Franck-Condon-weighted density of states. The first term in Eq. 1.2 reflects the strength of the electronic interaction between  $D$  and  $A$ . Energetic aspects, i.e. the effect of nuclear configuration changes accompanying the ET reaction, enter via the second term. The simple structure of Eq. 1.2 bluffs with respect to the difficulty of calculating both terms on a microscopic level, which has been the intention of ET theory within the last 50 years.

**The Franck-Condon-weighted density of states.** Marcus first developed a formalism to express the electron transfer rate in terms of the nuclear configuration changes [1, 3]. Thereby, the potential energy surfaces of donor and acceptor are described as classical harmonic oscillators, as depicted in Fig. 1.1. The nuclear coordinates account for intra-molecular coordinates as well as the configuration of the immediate environment of the complex. In Marcus' classical description, Eq. 1.2

can be read as the following: the ET occurs at the crossing point of the two parabolas, the so-called transition state, with a probability proportional to the square of the electronic coupling  $|V_{DA}|$  (Landau-Zener equation [32]). Within this classical description, the *FCWD* are reflected by the probability of reaching the crossing point by the nuclear coordinates, which depends on the activation barrier and the temperature the temperature of the system:

$$FCWD_{\text{classical}} \propto \exp\left(-\frac{E_{act}}{k_B T}\right). \quad (1.3)$$

The well-known Marcus curve [33, 32] is obtained from Eq. 1.3 by expressing  $E_{act}$  in terms of the reorganization energy  $\lambda$  and the standard Gibbs free energy difference  $-\Delta G^0$ , i.e. the "driving force" of the reaction (Fig. 1.1),

$$FCWD_{\text{classical}} = (4\pi\lambda k_B T)^{-\frac{1}{2}} \exp\left[-\frac{(-\Delta G^0 - \lambda)^2}{4\lambda k_B T}\right]. \quad (1.4)$$

Eq. 1.4 states that the ET rate is maximal if the driving force  $-\Delta G^0$  matches the reorganization  $\lambda$ . This maximum separates the so-called *normal region* of ET with  $-\Delta G^0 < \lambda$  from the *inverted region* with  $-\Delta G^0 > \lambda$ . The prediction of a decrease of the reaction rate with increasing driving force stands in contradiction to the usual trend of a chemical reaction, but the existence of the *inverted region* has been verified experimentally, for instance by Miller, Calcaterra and Closs [34].

Levich and Dogonadze [35] first reported a quantum mechanical treatment of the motion of the solvent molecules. Bixon and Jortner [36, 37] extended the quantum mechanical description to the intramolecular vibrational motion. If the harmonic potential energy surfaces of  $D$  and  $A$  are treated quantum mechanically, the two electronic levels split around the crossing point by  $2|V_{DA}|$  due to the electronic interaction, and a true crossing is avoided (see inset in Fig. 1.1). Nevertheless, there is a descriptive explanation of the dependence of  $k_{ET}$ , which agrees with the behavior predicted by the classical Marcus approach (see for example illustration in Ref. [38]): the ET reaction in the non-adiabatic limit can be considered analogously to an optical transition between two electronic states within the Franck-Condon approximation. For the optical transition the two parabolas reflecting ground and excited state would be arranged vertically to each other in a scheme like Fig. 1.1. The probability of the transition between a particular vibrational eigenstate in the lower electronic state and one in the upper electronic state is proportional to the Franck-Condon factor, which is essentially the overlap of the vibrational wavefunctions. In the case of ET the parabolas are now arranged as in Fig. 1.1. Again one can define Franck-Condon factors  $FC_{n,n'}$  as the overlap between the vibrational states  $n$  in  $D$  and  $n'$  in  $A$ :

$$FC_{n,n'} \propto |\langle n | n' \rangle|^2. \quad (1.5)$$

The analogy to the classical Marcus approach becomes evident if one imagines the squared eigenfunctions of the harmonic oscillators [38]. As the eigenfunctions with increasing vibrational quantum number become more and more localized at the point where the potential energy surface reaches the total energy (classical: turning points), the overlap of the lowest vibrational eigenstate in the donor potential energy surface matches maximally a particular wavefunction in the acceptor potential energy surface for  $-\Delta G^0 = \lambda$  [39, 7].

Energy conservation enforces that ET only occurs between vibrational levels  $n$  and  $n'$  that differ in their energy eigenvalues by the standard Gibbs free energy of the reaction,

$$n' - n = m, \quad \text{with} \quad m\hbar\omega = \Delta G^0. \quad (1.6)$$

$\omega$  denotes the frequency of the harmonic oscillators, which is assumed to be the same for  $D$  and  $A$ . In order to obtain now the quantum mechanically correct *FCWD* in Eq. 1.2, one has to add up the Franck-Condon factors for all allowed transitions (constraint given by Eq. 1.6) and weight the single contributions by the population  $\rho_n$  of the different donor levels  $n$ :

$$FCWD = \frac{\sum_n \rho_n FC_{n,n+m}}{\sum_n \rho_n}. \quad (1.7)$$

So far ET has been discussed in a static picture. Most ET reactions are photo-induced, i.e. the donor state is a local excited state. An optical transition usually populates vibrationally higher excited levels within the vibronic manifold of the electronic excited state, especially if the transition is pumped by spectrally broad laser pulses. The optical excitation is followed by intramolecular thermalization within the first 100 fs and adjacent intramolecular cooling to the thermal equilibrium with the surrounding on the timescale of picoseconds [40]. Thus, depending on the kinetics of the ET reaction, the ET occurs from the vibrationally equilibrated or a hot excited state. In the latter case the populations  $\rho_n$  in Eq. 1.7 become time-dependent and the ET process must be described dynamically. Even more interesting is the situation of a coherent superposition, i.e. the generation of a vibrational wavepacket, in the electronic state, as treated by Jean, as this can provide a dynamical picture of the curve crossing process [41]. Furthermore, Jean's work revealed that the kinetics of the curve crossing process should be manipulable by selective preparation of the vibrational population. Mančal and May applied an optimal control scheme to study and to influence the transient populations of the different electronic levels involved in an intramolecular ET process in a DBA system [42].

**The electronic coupling.** Intramolecular ET can occur over large distances of tens of Ångströms, and can proceed with very different kinetics in systems with comparable D-A distance. In order to separate the contributions of the *FCWD* and

of the electronic coupling to the reaction rate, the effect of a systematic variation of the bridge unit in DBA systems has been investigated both theoretically and experimentally [43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 31]. If the electronic levels of the bridge are not close to resonance with the donor and the acceptor states, the energetics of the ET reaction, i.e. the *FCWD*, do not depend on the bridge as a first approximation. These studies therefore address the dependence of  $V_{DA}$  on the D-A distance and the chemical nature of the bridge. Regarding the distance dependence, as the electronic coupling between two states is proportional to the overlap of both electronic wavefunctions, the assumption of an exponential dependence of the coupling on the D-A distance,

$$|V_{DA}|^2 = V_0^2 \exp(-\beta R_{DA}), \quad (1.8)$$

is intuitive.  $V_0$  denotes some constant prefactor. In fact, this general behavior has been experimentally observed in different systems for intramolecular ET systems in the non-adiabatic limit (see for example Refs. [38, 24, 48] and references therein).

The theoretical determination of the electronic coupling matrix element  $V_{DA}$  has been subject of numerous studies [43, 44, 53, 54, 55, 56, 57, 45, 46, 58, 47, 51, 52, 31, 59]. Review articles from Newton [57, 45], Newton and Cave [60] and Jordan and Paddon-Row [46] provide a good overview of the field. The simplest approach for calculating  $V_{DA}$  in donor-bridge-acceptor (DBA) systems is based on Koopmans theorem (KT) [61] and addresses the electronic coupling by the calculation of energy splittings. As already mentioned, the level splitting at the transition state reflects  $2|V_{DA}|$  (inset in Fig. 1.1). With respect to the electronic eigenfunction a transition state is a nuclear configuration at which the electronic wavefunction is localized half-and-half both on donor and acceptor. These calculations have been performed at different computational levels, semi-empirical and *ab initio*. The computational costs of semi-empirical methods are about a factor thousand less than that of *ab initio* molecular orbital (MO) calculations, as only a minimal, parametrized atomic basis set are used. The parameters are usually matched to reproduce particular experimental data. Semi-empirical methods were found to provide a qualitative correct description of ET reactions ([51] and references therein) and can be applied to large ET systems like protein and DNA structures [62]. In section 4.3.3, this approach is applied for the estimation of the coupling through molecular bridge units in dependence on the chemical nature, i.e. the hybridization, of the bridge unit.

Different authors have addressed the nature of the interaction between molecular orbitals and in particular the question whether electronic interaction is mediated either through space or through bonds (TB). Hoffmann gave an introduction into that subject more than 30 years ago [63]. More recent and detailed discussions



have been given for instance by Newton [57] and Jordan and Paddon-Row [46]. In that context, it should be remarked that virtually all calculations of the electronic coupling in a DBA systems assumed vacuum conditions, whereas the experiments were performed under solvent conditions. Recently, the group around Waldeck and Zimmt investigated the role of the solvent electronic structure on the mediated electronic coupling for C-shaped DBA molecules, which exhibit a solvent accessible volume between donor and acceptor units [64, 65]. They observed a correlation between the energy of the solvent's lowest unoccupied molecular orbital (LUMO) and the electronic interaction mediated by the solvent. This aspect will be picked up in chapter 4.

### 1.2.1.2 Adiabatic limit

The non-adiabatic limit discussed so far can be seen as the situation of the frequency of the relevant nuclear motions being larger than the ET rate. With increasing electronic interaction and thus increasing level splitting (Fig. 1.1), donor and acceptor can no longer be regarded as two separate states but become one single potential energy surface. This is the adiabatic limit. Reactant and product can now be seen as two nuclear configurations of the ET system (inclusive environment) at which the same electronic wavefunction is mainly localized at the donor unit and at the acceptor unit, respectively. The system moves along the potential energy surface at the pace at which the nuclear configuration rearranges itself. This rearrangement localizes the electronic wavefunction at the acceptor. As solvent contributions to the reorganization energy  $\lambda$  usually outweigh the intramolecular contributions, the nuclear relaxation time of the surrounding medium determines the upper limit of the ET rate [66, 67, 7, 30]. This nuclear relaxation time is usually approximated by the longitudinal dielectric relaxation time of the environment.

## 1.2.2 Heterogeneous electron transfer

The most striking difference between a solid state electron acceptor and a molecular one is the number of electronic acceptor states, which results in an ET mechanism completely different from the traditional Marcus-Levich-Jortner-Gerischer description [3, 35, 36, 68]. We consider the case of a molecule chemically anchored on the surface of a semiconductor. The energy of the molecular donor level, which again is usually the excited state, may overlap with the conduction band which is assumed to be a continuum of states. If the difference in energy of donor level and conduction band minimum (CBM) is larger than the reorganization energy of the reaction, the vibronic donor state is in resonance with a particular acceptor state within the conduction band *for any nuclear configuration of the molecule* [69, 9, 10, 7, 17, 70, 71].

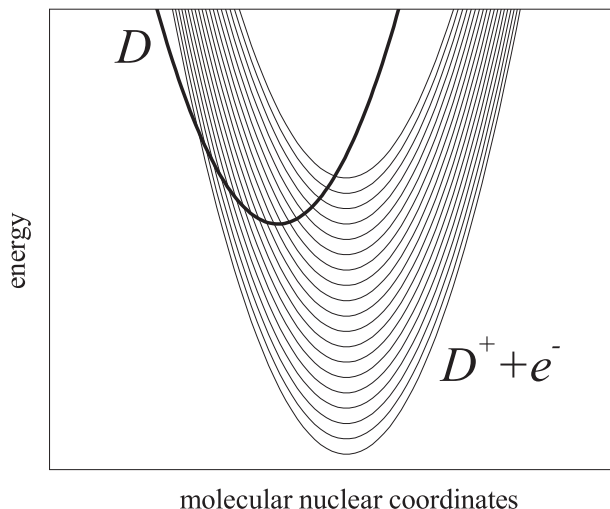


Figure 1.2: Illustration of non-adiabatic heterogeneous ET from a molecular donor state  $D$  to a solid in a classical picture. The continuum of acceptor states is represented by the manifold of product parabolas. See text for explanation.

This situation is the so-called "wide band limit" and is illustrated for the non-adiabatic limit in Fig. 1.2: the molecular donor level is again denoted as single potential energy surface  $D$ , whereas the continuum of acceptor states is symbolized by a manifold of parabolas. Each parabola in the manifold represents both products of the ET, namely an electron in a particular electronic state of the semiconductor together with the oxidized adsorbate in a particular vibrational state. The electronic energy is symbolized by the bottom of a given potential energy surface whereas the parabola itself represents a vibrational mode of the cationic molecule. The vibrational degrees of freedom of the solid are neglected in that description. In order to avoid confusion arising from the unusual crowd of parabolas one should be aware that each parabola does not only reflect one but two electronic states.

### 1.2.2.1 Non-adiabatic limit

The graphical illustration of Fig. 1.2 shows that every point on the donor potential energy surface is an avoided crossing point. As the electron can take along arbitrary energy the constraint to homogeneous ET given in Eq. 1.6 is not given to heterogeneous ET in the wide band limit. Thus, for each vibrational donor state  $n$  not only one particular Franck-Condon factor  $FC_{n,n+m}$  is realized, but the whole

Franck-Condon spectrum

$$\sum_{n'} FC_{n,n'} \propto \sum_{n'} |\langle n | n' \rangle|^2 = 1. \quad (1.9)$$

This implies different conclusions:

- Interfacial ET can become ultrafast, even for weak electronic interaction, as the ET rate is not limited by the frequency of nuclear motions that bring the system to a crossing point/transition state.
- In the wide band limit the Franck-Condon-weighted density of states (*FCWD*) (Eq. 1.7) becomes independent of the Franck-Condon factors. They become a pure density of states (DOS) factor, which depends on both the electronic DOS of the semiconductor as well as the vibrational DOS in the molecular cation [7, 70]. As these are characteristic stationary microscopic properties of the molecule-surface system under investigation, the DOS factor is a constant. Thus, recalling Eq. 1.2 *the ET kinetics directly reflect the strength of the (squared) electronic interaction*  $|V_{DA}|^2$ . This relation obtained here from an illustrative argumentation has been derived by Lanzafame, Miller, Muentert and Parkinson in 1992 by solving the Liouville equation for single electronic level coupled to a continuum [10]:

$$k_{ET} = 8\pi\hbar |V_{DA}|^2 \text{DOS}_{cont}, \quad (1.10)$$

where  $\text{DOS}_{cont}$  denotes the density of states of the continuum.

- If the wide band limit is not realized, e.g. for the situation that the donor level is located close to the conduction band minimum, the summation in Eq. 1.9 becomes restricted in dependence of the donor level  $n$ . Depending on the nuclear configuration of the donor, there are more or less acceptor states available. This is of particular interest if a vibrational coherence is generated in the donor state. The ET rate is then modulated with the coherent motion of the nuclear wavepacket. This subject and related questions have been addressed in several publications by Ramakrishna, Willig, and May [70, 71, 72, 73, 74]
- By the injection the electron enters a huge electronic phase space. In other words, the electron is transferred from a localized wavefunction without any translational symmetry to wavefunctions (ideally) delocalized in three (bulk state) or two (surface state) dimensions. Therefore, there is a very minor probability for the electron coming back to the donor shortly after the ET. However, if there would be no dephasing in the system, electron injection into

a quasi-continuum of states would result in echo-like periodical recurrences of the population on the injecting level. But in real systems electronic dephasing and inelastic scattering processes can occur within tens of femtoseconds, or even faster. Thus, the injected electron relaxes within the solid, making the initial ET irreversible.

### 1.2.2.2 Adiabatic limit

In the homogeneous case, the adiabatic limit has been classified as the situation, where donor and acceptor state are so strongly coupled that they become two nuclear configurations on a single potential energy surface. Having the Born-Oppenheimer approximation in mind, ET is an electronic "motion" coupled to nuclear motion in that case.

The situation is different for a continuum of acceptors. Let us first stick to a static picture and imagine the nature of the eigenfunctions and their eigenvalues, i.e. let us assume that we solve the stationary Schrödinger equation. These kind of calculations have been performed by Persson and co-workers for different molecules on TiO<sub>2</sub> clusters [75, 76, 77, 78]. If there is no coupling between adsorbate and surface, the eigenstates are either purely molecular or states of the solid. Switching on the strong coupling will lead to a "mixing" of the states, i.e. there are single eigenfunctions that are localized on both adsorbate and solid. Instead of one single molecular state there will be several mixed states that will be energetically in the vicinity of the energy eigenvalue of the uncoupled adsorbate. The energetic distribution of this states reflects the strength of the electronic coupling, equivalent to the level splitting at the nuclear configuration of the transition state in the homogeneous analog. The projected density of states (PDOS) on the adsorbate summed over the mixed states however will be close to unity. In such a situation, a photoexcitation with a spectrally broad ultrashort pump pulse creates a superposition of different electronic excited states (electronic wavepacket).

The most interesting heterogeneous ET systems are those where the molecular excited state is close to or above the CBM, and where the excitation energy of an electronic transition of the molecule is below the absorption edge of the solid. In those systems the highest occupied molecular orbital (HOMO) energetically lies in the band gap of the solid. Due to the low, ideally zero DOS of bulk states in the band gap the HOMO interacts much weaker with the solid compared to the excited state. Thus, it can be expected that the optical transition occurs from a clearly molecular state to mixed states. The extent to which the absorption spectrum of the adsorbed molecule differs from that of the free one might therefore be an experimental criteria of distinguishing between non-adiabatic and adiabatic ET.

The unknown nature of the excited state or states implies a problem in describing and discussing ET in the adiabatic limit as the clear definition of a donor state breaks down. In principle, by variation of adsorbate, anchor unit and substrate the whole range of adsorbate-surface systems from weakly coupled molecules with preserved molecular electronic structure to adsorbates, whose electronic structure is inseparable from those of the surface, should be continuously accessible. In terms of electron transfer, this wide range covers the spectrum from purely sequential heterogeneous electron transfer, which might be mediated by anchor or bridging units [73], to electron scattering from a photoexcited surface-like state.

The complex nature of the adiabatic ET process asks for a microscopic time-dependent description. However, the requirements for such a theory are demanding:

- The model must correctly reflect the high density of acceptor states to simulate electronic coupling, i.e. the mixing of the wavefunctions. This requires large models.
- The optical transition has to be treated microscopically under the condition of a time-dependent electromagnetic field. This could give an idea of the initial excited superposition of electronic states.
- The temporal evolution of the excited states has to be solved considering ultrafast electronic processes responsible for electronic dephasing and relaxation, with taking into account the nuclear degrees of freedom.

Recently, studies focusing on these topics have become available, which will be discussed in the following section.

## 1.3 State of the art and open questions

### 1.3.1 Experimental studies on heterogeneous electron transfer

The kinetics of electron injection have been studied with different techniques, for numerous systems, and in different environments. The spread of reported time constants is huge and ranges from 3 fs [79] to hundreds of picoseconds [80].

Most of the experimental studies on electron injection addressed ET into  $\text{TiO}_2$ . A handicap in most of these experiments is the lack of time-resolution, which often allowed only the estimation of an upper limit of the electron injection time constant. The molecules used to sensitize the semiconductor can be divided into two classes: transition metal-organic molecules and purely organic chromophores. The first class

is more interesting with respect to the DSSC due to the broad absorption spectra and the relatively good stability of these compounds. The most famous representatives are the Ru-complexes "N3" and "black dye" [81]. However, the advantageous absorption characteristics with respect to the solar cell are problematic for the spectroscopic investigation of these dyes as the absorption bands of the different electronic states strongly superimpose. For that reason, spectroscopic signatures were interpreted differently in the past [13, 14, 82, 83, 22]. For the N3 dye on TiO<sub>2</sub> under UHV conditions Willig and co-workers estimated the ET to occur faster than 25 fs. For the same dye in solution, Sundström *et al.* reported a 50 fs time constant for injection from the excited singlet state. An additional complication in the study of metal-organic complexes arises from the fact that these usually exhibit fast intramolecular electron dynamics like intersystem crossing [22] and inter-ligand transfer/localization [84]. These processes compete with the interfacial ET, and additionally give rise to vivid spectral features at early times, from which the spectral changes caused by the ET have to be separated. This culmination of unfavorable features makes the metal-organic dyes inappropriate for the study of ET if one is interested in a microscopic understanding of the process.

Lian and co-workers studied the injection kinetics in dependence on the length of a molecular bridge inserted between the anchor and the Re-polypyridyl chromophore [80]. These authors reported a dramatic deceleration of the electron injection by a factor of 200 due to insertion of only one CH<sub>2</sub> group. This observation has been ascribed to a transition from the adiabatic to the non-adiabatic limit caused by the insertion of the CH<sub>2</sub> group. However, in this study the influence of concurring intramolecular processes has not been clarified.

Recently, interfacial ET through long molecular bridge molecules have been investigated [85, 86]. These results will be discussed in section 4.3.4.

Also within the second class of sensitizers - the mentioned purely organic dyes - very different ET kinetics have been reported [12, 79, 21, 23]. The important aspect for the understanding of the ET process is the nature of the photoexcited state, as has been pointed out. Adsorbates like phenylfluorone [87], squaraine [88] and alizarin [89, 21, 90] give rise to a surface chelation, which results in the creation of a charge transfer complex. For the latter system Wachtveitl and co-workers reported a 6 fs dynamics, which they ascribed to the electron injection from a molecular excited state [21].

Schnadt *et al.* investigated electron injection from bi-isonicotinic acid adsorbed on a TiO<sub>2</sub> rutile single crystal surface by resonant photoemission spectroscopy. From the quenching of a core level peak these authors derived an excited state lifetime of 3 fs. This method is capable of resolving processes on the time scale of a few femtoseconds. However, it should be noted that this kinetics cannot be directly compared

to electron injection from an optically excited state, as the resonant photoemission spectroscopy inherently measures the electron injection from an ionized molecule (with the hole in a core level). Therefore, the higher molecular states, including the excited state, sink down in energy and cannot be directly compared with the situation after an optical excitation. For instance, the first excited state does not inject as its energy is pulled down below the conduction band minimum by the core hole in this experiment.

In summary, there is a large number of studies on different systems. Nevertheless, these do not provide a detailed understanding of the injection process, as different chromophores can hardly be compared without a microscopic understanding of the interfacial electronic structure. Furthermore, as will be pointed out in this work, the preparation of nano-structured anatase films is sensitive to details of the preparation procedure. As the ET kinetics is sensitive to the microscopic surface structure, the semiconductor moiety in the studies of different research groups might be not completely comparable. Thus, there is a lack of systematic investigations addressing the effect of single parameters on the interfacial ET.

### 1.3.2 Theoretical studies on heterogeneous electron transfer

Most of the theoretical descriptions of interfacial ET are based on the non-adiabatic perturbation theory approach. In its simplest form, this approach results in the Golden rule expression given in Eq. 1.10 [10]. S. Ramakrishna, F. Willig and V. May described the heterogeneous system with a model Hamiltonian, which incorporates vibrational degrees of freedom for the molecule [70, 71, 72]. Although this approach is not constrained with respect to the coupling strength, these authors obtained an equivalent expression for the ET rate [71] compared to the non-adiabatic perturbation theory. These studies focused on the effect of vibrational coherence on the ET kinetics. It was found that the extent, to which a vibrational wavepacket affects the ET process, is strongly dependent on the position of the injecting level with respect to the continuum of acceptor states. In the wide band limit the influence of the wavepacket motion on the ET process is rather minor. Recently, L. Wang and V. May applied an optimal control theory within this theoretical framework [91]. For the wide band limit, these authors find a poor controllability of the electron injection time by means of laser pulse shaping. The situation is different for an injection level close to the conduction band minimum, or if not the injection time but an intramolecular process is the target of control<sup>1</sup>.

Further aspects of the studies of Ramakrishna *et al.* are the influence of a molecular

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<sup>1</sup>The authors choose a particular vibrational level in the electronic ground state as target state, which is accessed via a pump-dump mechanism [91].

bridge unit [73] on the ET and the correlation between the spectroscopic pump-probe signal and the population kinetics in the presence of a vibrational wavepacket [74].

Petersson and co-workers obtained an analytical expression within a tight-binding approach, which describes the semiconductor as a one-dimensional semi-infinite chain of atoms [92]. This approach incorporates only the interfacial electronic coupling but neglects the vibrational modes of the adsorbate.

The electronic coupling, which is the key parameter, is treated as empirical parameter in the models mentioned above. As discussed in the previous section, the requirements for a microscopic calculation of the interfacial electronic structure are demanding. P. Persson *et al.* studied the electronic structure of different adsorbate-TiO<sub>2</sub> systems within a stationary approach [75, 76, 77, 78]. In chapter 4 latest results of P. Persson and M. Lundqvist for the perylene-anatase system are compared with the experimental results.

Recently, also time-dependent calculations on the molecular level have been published [93, 94, 95, 96]. O. Prezhdo and co-workers performed *ab initio* molecular dynamics calculations for strongly coupled chromophores like isonicotinic acid and alizarin on TiO<sub>2</sub> [93, 95, 96]. In this approach, the electronic structure is calculated within the density functional theory (DFT), whereas the nuclear degrees of freedom are treated classically. Non-adiabatic transitions between electronic states are included. The calculation describes the ET reaction in real time, and allows the study of a temperature-dependence.

A very interesting aspect in these studies is the separation of adiabatic and non-adiabatic ET pathways. The temporal evolution of the ET is described in terms of the electron density  $\rho_{dye}$  of the excited state  $\Psi(r)$  on the dye molecule [95]

$$\rho_{dye} = \int_{dye} |\Psi(r)|^2 dr = \sum_{i,j} c_i^* c_j \int_{dye} \phi_i^*(r) \phi_j(r) dr . \quad (1.11)$$

In the second identity, the excited state wavefunction is expressed in terms of the basis functions as  $\sum_i c_i \phi_i$ . The index "dye" indicates the restriction of the integration to the space occupied by the dye molecule. The time-derivative of  $\rho_{dye}$  reads

$$\dot{\rho}_{dye} = \sum_{i,j} \left[ \frac{d(c_i^* c_j)}{dt} \int_{dye} \phi_i^*(r) \phi_j(r) dr + c_i^* c_j \frac{d \int_{dye} \phi_i^*(r) \phi_j(r) dr}{dt} \right] , \quad (1.12)$$

according to the product rule. The first term corresponds to the non-adiabatic ET, as it describes the changes in the occupations of the electronic states. The second term reflects changes in the localizations of the adiabatic states and thus describes adiabatic ET [95, 96]. From this description of electron injection W. Stier, W. Duncan and O. Prezhdo conclude several interesting aspects of the heterogeneous ET reaction:



- For any electronic coupling strength there are both adiabatic and non-adiabatic contributions to the ET.
- The non-adiabatic contributions are temperature-independent and dominate the ET at low temperature (50 K) in the case of isonicotinic acid.
- The adiabatic contributions show a dependence on the temperature, as this ET mechanism is driven by nuclear motions. In the case of alizarin at 350 K the electron injection is determined by these contributions.
- In the case of alizarin, the photoexcited state is already localized in the semiconductor by 30 to 40%. This is a quantitative statement on the CT contribution of the optical excitation.

In summary, recent developments in computational physics (in combination with the continuously increasing computing power) are able to cope with the description of interfacial ET on the molecular level. The results of this thesis with respect to the influence of the bridge-anchor group on the ET can provide the basis for future theoretical studies.

