PHOTOINDUCED ELECTRON TRANSFER AT THE TETRAPYRROLE-TIO₂ INTERFACE: EFFECT OF THE ENERGY ALIGNMENT

by

Jesus S. Nieto-Pescador

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

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ABSTRACT

Photoinduced electron transfer is a ubiquitous process behind several physical, chemical, and biological processes. Its potential applications, ranging from solar cell technologies to photodynamic cancer therapy, require a thorough understanding of the basics of the reaction. This dissertation addresses open questions for a particular case of electron transfer processes: Heterogeneous Electron Transfer (HET). In this process, an electron is transferred between a localized donor and a multitude of delocalized acceptor states. HET between photoexcited tetrapyrroles and colloidal TiO_2 has been investigated using femtosecond transient absorption spectroscopy. Specifically, this work explores the not well-understood influence of the availability of states on the HET reaction. This problem is addressed by measuring electron injection times as a function of the energy difference between the LUMO and the conduction band of TiO_2 . The change in the energy alignment was done using two experimental strategies. The first one employs a recently synthesized phlorin with two different excited states above the conduction band of TiO_2 . This molecule allows comparing HET rates from two different excited states. The phlorin presents the rare case in which electron transfer process can be measured from various excited states with the same experimental condition. The second strategy measures the electron injection rates after exciting the same electronic state of a set of specially designed porphyrins. The novelty of the approach is that the difference in energy alignment is attained by the introduction of dipole groups within the bridge group of the molecule. This strategy generates a difference in energy alignment of up to 200 meV. The reported measurements were carried in a high vacuum environment with an apparatus capable of resolving sub 30 fs processes. Disentanglement of the electron transfer processes was done, after careful study of the relaxation dynamics of the molecules in solution, by monitoring the decay of the excited state absorption and the rise of the cation spectral signatures. Within our time resolution, our results show that the increase in the availability of acceptor states does not influence the electron injection dynamics. The results suggest that the injection process takes place into a spectrum of states different from those obtained by steady state calculations.

Chapter 1 INTRODUCTION

Photoinduced electron transfer (ET) is a ubiquitous process that can be considered one of the simplest chemical reactions. In this process, a photoexcited electron is transferred between a donor and acceptor state without modifying the chemical structure of the involved species. Despite its simple description, electron transfer reactions are of utmost importance and are the subject of study of physicists, chemists, and biologists. To start with, these type of processes drive all the photosynthetic machinery on Earth. They can also be found at the heart of a multitude of current and promising photoactivated technologies like xerography, film photography, solar energy conversion, photo catalyzers, and molecular electronic devices.

Given the overwhelming number of scenarios where the electron transfer process takes place, it is important to introduce some classification at this point. Electron transfer processes can be classified into two groups. On the one hand, the electron transfer can be homogeneous, meaning that the electron moves from a single defined molecular state into an acceptor state of the same nature. On the other hand, heterogeneous electron transfer (HET) takes place between a well-defined molecular state and an acceptor composed of the multiple states within an electronic band. An example of the latter case is the electron injection between a photoexcited molecule and a semiconductor conduction band.

The study of homogeneous ET, being simpler, was tackled since the early 1950s. At that time, the focus of the research was to understand the underlying parameters that influenced the ET rate. A significant achievement in the field was the realization of the importance that nuclear configurations play in the process. [1-3] These important ideas built what is now known as Marcus Theory of electron transfer.¹

The theory of HET reactions is less developed than the homogeneous case. Studying HET has proved to be a challenging task, mainly due to the hybrid description of the system. One one side, the molecular part of the system can be treated, from a theoretical point of view, with a quantum description based on localized wave functions. Conversely, the semiconductor side is usually well understood under the assumption of a delocalized wave function. However, a description of the interface requires merging these two radically different formalisms. The experimentalists, in a similar way, face the challenge of dealing with a hybrid system, the inherent difficulties of studying surfaces [4], and the femtosecond time-scale of the HET reactions.

Despite the challenges, and motivated by the promising dye-sensitized solar cell (DSSC) technology, [5] the study of HET increased in the last decades. The first experimental studies aimed to resolve fundamental questions regarding the nature of the reaction and to develop the necessary techniques to measure these ultrafast processes. The theorists, on their part, tried to extend the ideas presented by Marcus and developed models to calculate the parameters of the reaction from quantum mechanical principles. [6–11] More recently, the availability of femtosecond laser sources brought a new tool to study HET, and several works have provided a good qualitative picture of the process. [12] However, the extrapolation of these qualitative results has produced, in some cases, an apparent contradiction in the expected properties of different molecule-semiconductor systems. [13] Thus, it is now clear that a careful, and better designed systematic approach should be used to address open questions regarding HET.

An example of the mentioned extrapolations is the usually assumed understanding of the effect of the so-called energy level alignment on the HET process. This important parameter in the design of molecule-semiconductor systems refers to the

¹ Rudolph A. Marcus received the 1992 Nobel Prize in Chemistry "for his contributions to the theory of electron transfer reactions in chemical systems"

relative energy alignment between the ground and excited state of the molecules and the semiconductor bands. In this dissertation, an experimental study of photoinduced heterogeneous electron transfer is presented. The goal of this work was to address the following fundamental question regarding the HET process: What is the relation between the ET rate, the energy level alignment, and the density of states? This thesis addresses the issue in the following order:

The remainder of **Chapter 1** gives an introduction to the ET process and sets the tone for the discussion on the topic. Then, a short discussion regarding the parameters involved the energy level alignment is also presented. This discussion is followed by a quick review of the previous work in the field of HET. Finally, at the end of the chapter, two different experimental approaches addressing the question posed in this dissertation, are described. The specific goals of each approach are stated and discussed regarding their contribution to the development of the field.

Chapter 2 aims to specify and describe the basic physical and chemical properties of the experimental system used in this work, namely, the molecules and semiconductors. The chapter starts by giving a brief introduction to the basic of photochemistry. Subsequently, the common properties and characteristics of the tetrapyrrole family of molecular systems employed in this study are discussed. This discussion is followed by a description of the two tetrapyrroles, a phlorin and a ZnTPP-porphyrin, which were used to implement the experimental design. Then, in a similar fashion, the characteristics of the semiconductor used in this work (TiO₂) are presented and discussed regarding its application in the proposed experiments. Finally, the chapter ends with a description of the sample preparation methods and protocols followed for the realization of this work.

Chapter 3 presents the experimental details of this work. First, a description of the laser system and the experimental transient absorption setup are presented. These descriptions are accompanied by a brief introduction to the relevant theory behind the spectroscopic techniques. A thorough description of the data analysis procedure used to extract the HET rates from the transient absorption signals is also given. The level of detail in the description of the experimental procedures aims for an easy replication of the obtained results as well as to serve as a reference for future members in the laboratory. With this in mind, the chapter ends with the description of additional instrumentation developed for parallel projects outside the scope of this dissertation.

Chapter 4 is the first of two chapters presenting the results obtained in this work. This chapter shows the results achieved by studying a novel phlorin system, $3H(Phl^F)$. This molecular system allows studying the HET process as a function of energy level alignment. The change in level alignment was obtained by exciting different electronic states. The chapter starts by presenting and discussing the spectral properties and relaxation dynamics of the $3H(Phl^F)$ chromophore and its $3H(Phl^{CO_2H})$ derivative. Then, measurements of the HET rates from different electronic states are presented and discussed in relation to their energy level alignment. The results showed an independence of the HET rate on the energy level alignment for this system. Hence, they point to the presence of intermediate states mediating the reaction. Finally, these results are summarized, and their implications are discussed.

Chapter 5 presents the results of the second experimental strategy in this work. Mainly, the energy level alignment was changed by the use of dipole groups attached to a common Zn-porphyrin chromophore (ZnTPP). The chapter starts by presenting the relaxation model of the molecules in solution, validating the usefulness of the proposed strategy. Then, the results of the HET rates on TiO_2 are presented, discussed, and compared with a theoretical model. The results show that within the experimental resolution, the energy level alignment does not affect the HET rates and support the results presented in chapter four. The chapter ends by summarizing and discussing the implications and potential applications suggested by these results.

Chapter 6 summarizes the results herein presented.

In the process of writing this dissertation, several published and unpublished works on the topic were consulted and are referenced in the appropriate context. Nevertheless, a special mention is required for the following dissertations [14–17]. These works inspired some of the contents, figures, and style used in this document, and a specific reference in the remainder text was not considered necessary.

1.1 Photoinduced Heterogeneous Electron Transfer

To start the discussion of photoinduced HET and to explicitly set the goals of this study, an understanding of homogeneous ET is a pre-requisite. The homogeneous electron transfer between a single donor and acceptor state can be thought as the two-level system shown in Figure 1.1. The equation describing the reaction is

$$D + A \longrightarrow D^+ + A^- \tag{1.1}$$

where D and A denote the donor and acceptor respectively, and D^+ , A^- refers to the oxidized and reduced product pair. From the mentioned figure, the multidimensional energy surfaces of the system can be represented as parabolas depending on a suitable choice of an appropriate abstract coordinate. Then, for a particular value of this reaction coordinate (Q) the transition is energetically allowed. With this picture in mind, the electron transfer rate k_{ET} can be described as being proportional to the product of the following two probabilities denoted by $\mathcal{P}(x)$:

$$k_{ET} \propto \mathcal{P}(\text{Electron tunneling}) \times \mathcal{P}(\text{Reactant diffusion to crossing point}).$$
 (1.2)

Considering this simple approach, the electron transfer rate can be written as

$$k_{ET} = \kappa \nu \exp\left(\frac{-E_a}{k_B T}\right). \tag{1.3}$$

In the above expression, κ is the tunneling coefficient, ν is the frequency of reaching the crossing area, E_a is the height of the energetic barrier, and $k_B T$ is the usual Boltzmann factor. The tunneling transition coefficient is calculated from the Landau-Zener equation as

$$\kappa = \frac{2P}{1+P},\tag{1.4}$$



Figure 1.1: Schematic of the energy parabolas of the two-level system composed of reactant and product states. E_a and E_r are respectively, the activation and reorganization energy, ΔG^0 is the Gibbs free energy, and V_{DA} is the donor-acceptor coupling.

where,

$$P = 1 - \exp\left[\frac{-4\pi^2 V_{DA}^2}{h\nu(\mathcal{S}_r - \mathcal{S}_p)}\right]$$
(1.5)

is calculated from the frequency of nuclear motion ν , the coupling potential V_{DA} , and the slope of the reactant and product parabolas at the point of tunneling S_r , S_p . [18] The ET process can be treated in two liming cases depending on the coupling strength:

Adiabatic Limit. On the one hand, for $P \longrightarrow 1$, meaning a strong V_{DA} coupling, the process can be addressed as being adiabatic. In the adiabatic picture, the coupling is so strong that donor and acceptor can no longer be treated as two separate states, but rather as two different nuclear configurations of the same electronic state. The average time the system spends in the coordinate space Q is longer than the mean time for tunneling. Thus, $\mathcal{P}(\text{Electron tunneling}) \approx 1$ and the electron transfer rate is

limited by the thermodynamics of the system following an Arrhenius or Eyring equation.²

Nonadiabatic Limit. On the other hand, when P is small, meaning weak V_{DA} coupling, a nonadiabatic treatment is possible. Under this approximation, the system reaches the point Q in coordinate space several times before the electron tunneling can occur. Thus, $\mathcal{P}(\text{Reactant diffusion to crossing point}) \approx 1$ and the reaction is now controlled by the internal quantum parameters of the reaction. In this scenario, the weak coupling can be considered a small perturbation and the transfer rate can be calculated with a Fermi golden rule equation

$$k_{ET} = \frac{2\pi}{\hbar} |V_{DA}|^2 \mathcal{F}.$$
(1.6)

In the above expression, the term \mathcal{F} is the so-called Franck-Condon Weighted Density of States (FCWD); this factor takes into account the probability of tunneling as a consequence of nuclear motion. The FCWD is proportional to

$$\mathcal{F} \propto \frac{\sum_{n} \rho_{n} |\langle \psi_{n} | \psi_{n+m} \rangle|^{2}}{\sum_{n} \rho_{n}}, \qquad (1.7)$$

where ρ_n is the probability density of the population being in the n-th vibrational state (ψ_n) subject to the energy restriction

$$|E_n - E_{n+m}| = \Delta G^0, \qquad (1.8)$$

with ΔG^0 being the Gibbs free energy of the system.

Building on the previous homogeneous electron transfer formalism, HET can be

 $^{^2}$ The Arrhenius equation is an empirical relation for the temperature dependence of a reaction rate. It was proposed by Svante Arrhenius in 1889 and is trivially equivalently to the equation derived in 1935 by Henry Eyring from statistical thermodynamics.



Figure 1.2: Representation of the simplest picture of an HET process between the excited state of a molecular dye and the conduction band of TiO_2 .

now discussed. The general system where HET takes place is composed of a light absorber that is photoexcited and acts as the donor, and an electron accepting material. The most commonly studied system consists of an organometallic molecule chemisorbed onto a semiconductor as depicted in Figure 1.2. Different light absorbers, like nanoparticles, have also been studied. [19] However, due to current technological applications, the number of previous studies, and the feasibility of tuning the different parameters of the reaction, this study focuses on the organometallic chromophore. Correspondingly, for the electron acceptor, semiconductors are usually preferred to generate a long-lived charge separated state. The primary requirement for the semiconductor material is the availability of empty levels aligned with the excited state of the chromophore. A detailed description of the organic molecules (also called dyes) and the semiconductor used in this study can be found in chapter 2.

The HET reaction can also be treated in the adiabatic and nonadiabatic approximation. Similarly to the homogeneous case, adiabatic HET is assumed to show an Arrhenius temperature dependence, while the nonadiabatic picture is again treated by the Fermi golden rule presented in equation 1.6. Nonetheless, a distinction must be



Figure 1.3: Schematic of a nonadiabatic HET process under the wide band limit assumption (WBL).

made on the interpretation of the FCWD factor \mathcal{F} . An specific case of nonadiabatic HET that has received special attention is the so-called wideband limit (WBL). This situation is the one shown in Figure 1.3 and consists on having the whole vibrational spectrum of the donor energetically above the conduction band minimum. Under this condition, the donor state is in resonance with an acceptor state for any relevant nuclear configuration of the molecule. The WBL also allows the reaction to be ultrafast (< 100 fs) because is not limited by the frequency of nuclear motion to bring the system to a crossing point.

This work focuses in the wide band limit case of nonadiabatic HET. Under this assumption, the sum appearing in the FCWD equation 1.7 is simplified as

$$\sum_{n} |\langle \psi_n | \psi_{n+m} \rangle|^2 = 1, \qquad (1.9)$$

and the FCWD is now a pure density of states (DOS) which depends on the electronic DOS in the semiconductor and the vibrational DOS in the molecule. The exact calculation, from Liouville's equation, was carried out by Lanzafame et al. in 1992 [11]. The result is that nonadibatic HET rates under the WBL can be expressed using the

following relation

$$k_{ET} \propto |V_{DA}|^2 \mathcal{DOS},$$
 (1.10)

In the above equation, \mathcal{DOS} denotes the electronic density of states of the continuum of product states. The simplicity of equation 1.10 is misleading; calculating both terms, V_{DA} and \mathcal{DOS} , on a microscopic level has been a hard task for theoreticians for several decades. The first parameter is the coupling potential V_{DA} which is proportional to the overlap of the electronic wavefunctions of donor and acceptor state and can be approximated by the following relation

$$|V_{DA}|^2 = V_0^2 \exp\left(-\beta_0 R\right). \tag{1.11}$$

In the above expression, R is the distance between chromophore and electrode, while V_0 and β_0 are constant prefactors. This behavior has been observed for homogeneous ET in the nonadiabatic limit. [20,21] For the case of HET a similar qualitative behavior has also been reported. [22–25] However, these results must be taken with care, especially for HET, due to the experimental limitations of the studies. Theoretical calculations of the coupling matrix element V_{DA} has been the subject of extensive work. [26–28] The basis of most of these theoretical work can be derived from the use of Koopmans³ theorem. [29] Where the calculation of V is addressed from considerations of the energy splitting at the crossing point of the transition.

The second parameter in equation 1.10 is the density of states (DOS) in the semiconductor. The first approach estimating this parameter can be done from considering a 3-dimensional, defect free, bulk semiconductor. By doing this, the DOS will have the known \sqrt{E} dependence. Specifically,

$$\mathcal{DOS}(E) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3}\sqrt{E},$$
(1.12)

³ Tjalling Koopmans, a mathematician and economist, shared the Nobel Prize in economics in 1975 together with Leonid Kantorovich "for their contributions to the theory of optimum allocation of resources".



Figure 1.4: Calculated electron transfer rates into SnO_2 as a function of the driving force (the difference between the energy of the LUMO and the conduction band edge) for different reorganizational energies ($E_r = \lambda$). Reprinted from [30], Copyright (2004), with permission from Elsevier.

where m^* is the effective mass of electrons in the conduction band, and E is the energy position above the conduction band minimum. Using the above dependence of the density of states, and assuming an energy-independent coupling term, equation 1.10 gives rise to an increase in the electron transfer rate as a function of the energy above the conduction band minimum where the electron injection takes place. This is what is called the enrgy level alignment of the HET reaction. This behavior can be seen in the graph shown in Figure 1.4. It is important to emphasize that the real energy dependence of the DOS is far more complicated than the one described in equation 1.12. The calculation of the surface density of states of a real semiconductor, including defect and surface effects, is by itself a field of active research. Nonetheless, regardless of the level of calculation, all DOS show an increase in the number of available states that goes from zero in the band gap to a peak somewhere above the conduction band (CB). For this reason, it is usually assumed that HET rates from excited states, higher in the CB, will be faster. However, this may not be the case, and this work aims to test this assumption.

1.2 Energy Level Alignment

The last section discussed how HET, in the nonadiabatic limit, and under the wideband assumption is directly proportional to the DOS of the semiconductor available for the transition. Hence, predictions on the transfer rate for a given system require the knowledge of two parameters. The first one is, clearly, the DOS of the electrode. The influence of this parameter was briefly discussed in the last section, and for the system under study–anatase TiO_2 (101)– it will be further addressed in section 2.3. The second parameter is the energy position of the molecular excited state within the conduction band of the semiconductor. This is the so-called energy level alignment of the molecule-semiconductor system. This alignment determines how much of the available DOS can be sampled by the excited donor state. In this section, a general picture of the parameters governing the level alignment, and how they can be calculated from experimental techniques is presented.

The different quantities defining the level alignment at the molecule-semiconductor interface are shown in figure 1.5. This figure also illustrates how the parameters can be extracted from experimental measurements, mainly, ultraviolet photoemission spectroscopy (UPS). We can group the various parameters in two categories, energy levels, and energy gaps. On the semiconductor side, we have the following elements. The Fermi level (E_F) is the total chemical potential for electrons. It can be thought as the required thermodynamic work required to add one electron to the body in question. Under the band structure model, it is the hypothetical level which will have a 50% probability of being occupied by an electron at thermodynamic equilibrium. The work function (ϕ) is the work required to remove an electron from a solid to a vacuum point just on the solid surface; the work function is the energy gap between the Fermi level and the vacuum level (E_{vac}) . Finally, the band gap (BG) is the energy region where no electron states can exist.

On the molecular side, the highest occupied molecular orbital (HOMO) is analogous to the valence band maximum in a semiconductor. Similarly, the lowest unoccupied molecular orbital (LUMO) is comparable to the semiconductor conduction band



Figure 1.5: (a) Schematic of the different parameters involved in the energy level alignment at the molecule semiconductor interface. (b) Valence photoemission spectrum of an organic molecule (top) and an organic/metaloxide (bottom). (c) Secondary electron spectrum of an organic molecule (top) and an organic/metal-oxide (bottom). Modified by permission from Macmillan Publishers Ltd: Nature Materials [31], copyright 2011.

minimum (CBM). The ionization energy (IE_{org}) is the work required to remove one electron from the HOMO into the vacuum level of the organic molecule. It is important to notice that, although initially assumed to be the same, the vacuum levels on the electrode and molecular side rarely align at the surface interface. [32] The last parameter in the figure is the HOMO offset (ΔE_H) which represents the energy difference between the Fermi and HOMO levels.

Due to its importance in the operation of a multitude of technological applications, the ability to predict the energy level alignment from fundamental parameters of the system has been extensively investigated. [32–39] Recently, Greiner et. al. [31] found a universal relationship that relates the offset between the HOMO and the Fermi level ΔE_H to the difference of the work function ϕ and the organic molecule's ionization



Figure 1.6: Level alignemnt of about 40 organic/metal-oxide interfaces. The dashed line is the best fit line. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [31], copyright 2011.

energy IE_{org} . The proposed relation, plotted in Figure 1.6, can reproduce the alignment of 40 different organic/metal-oxide interfaces. A physical interpretation of the parameters involved in the proposed relation was partially done by the same Greiner et al., and was further developed by Ley et al. [40]

Given that the work function for anatase and the ionization potentials of the molecules used in this study are well-known values, the graph shown in Figure 1.6 was used in this work to calculate the energy level alignment of the systems under investigation.

1.3 Current State of the Field

The first experimental studies on HET aimed to reveal if the reaction was an electron transfer process or an energy transfer. Soon it was proved that the process was indeed electronic transfer. [6] Most of the seminal studies involved the measurement of photocurrent densities generated in redox reactions. [7] These early experiments

were characterized by a lack of time-resolution, and only allowed getting upper limit estimations of the electron injection rates. However, these studies raised important questions regarding the fundamental parameters of the injection mechanisms. The first time-resolved measurements, using flash photolysis on the μ s time scale, were performed between the 70s and 80s. These measurements studied homogeneous ET between quinones. [8] Later, HET was reported between an organic molecule and semiconducting TiO_2 nanoparticles on the nanosecond time scale. [9] Further improvement in the time resolution using pulsed dye lasers produced picosecond time-resolved electron transfer measurements between organic molecules and inorganic crystals. [10, 11] Being that the HET process typically occurs on the femtosecond time scale, an increasing number of experiments were reported after the rapid development of ultrafast optics in the late 80s. Similarly, the field received a boost after the publication of solar energy conversion using ruthenium sensitized TiO_2 nanoparticles and again after the report of a 12% efficient solar cell using a similar technology. [5,41] After this publications, the research on HET took two main paths. One of them took an applied approach and focused on the understanding and improvement of the technology behind DSSC. The second one focused on addressing the fundamental mechanisms of the reaction and is the direction this dissertation follows. Studies regarding the basic elements of HET advocate for the use of smaller molecules with simple electronic structures that are accessible to ab initio calculations.

For example, measurements on the enediol/TiO₂ system were useful to understand details of the HET process, and they reported a strong donor-acceptor coupling to the point where the excited state is predominantly localized on the TiO₂ orbitals. This gave rise to mostly adiabatic HET with time scales that were hard to resolve. [42] In particular, the catechol/TiO₂ system allowed to study the short-lived intermediate states at the surface of the semiconductor without the influence of molecular states. [43] Other systems worth mentioning with a strong coupling interaction are the alizarin/TiO₂ and the bi-isonicotinic acid on TiO₂. The first interface was studied by Wachtveitl, Grätzel, and coworkers using transient absorption spectroscopy. [44, 45] The second interface was addressed by Schnadt et al. [46] and a record 3 fs injection time, using resonant photoemission spectroscopy, was deduced.

Likewise, extensive experiments on the hundreds of femtosecond time-scale were carried out by the Lian group on ruthenium dyes attached to TiO_2 . Their measurements monitored the infrared absorption of injected electrons in the semiconductor. They concluded that the injection dynamics was biphasic, with an ultrafast component <100 fs arising from nonthermalized excited states, and a slower component corresponding to injection from a relaxed states. [12, 47]

A system that proved to be very productive for fundamental HET studies is the perylene/TiO₂ system studied by Willig's group mostly using femtosecond timeresolved spectroscopy. [48] The following research was carried on, using perylene derivative as sensitizers: the HET temperature dependence was measured, [49] the vibrational wave packet motion was studied, [50] the influence of different bridge groups on HET was investigated, [51] and the influence of the anchor group was also studied. [52] These studies indicated that the coherent wave packet created in the donor molecule by the pump pulse survived the ET process and could be detected in the cation by the probe pulse. This observation challenged the usual model of HET, which assumed that the reaction starts from a thermally equilibrated state in the donor, and motivated theoretical studies of the injection dynamics. Also, Willig et al. [53] probed the absorption of the injected electrons and found that the rise in the injected electron signal was identical to the rise in the donor cation signal. Thus, demonstrating that after injection, the electron was not trapped on the surface but indeed entered the bulk of TiO_2 . More recently, using two-photon photoemission spectroscopy, the spectrum of the injected electrons showing the effect of the Franck-Condon factors on nonadiabatic HET was resolved for the first time. [54]

To date, from a fundamental perspective, the crucial points that are still not well understood in the HET process are:

1. The distinction and transition between the adiabatic and nonadiabatic case of HET, including possible electronic coherence between the excited donor and the

acceptor state.

- 2. The influence of vibrational degrees of freedom on HET, including the effect of coherent vibrational phenomena.
- 3. The influence of the available density of states for reactant and product that includes short-lived intermediates near the surface.

Currently, experimental work addressing the first point is rare. However, several theoretical studies deal with the transition between the nonadiabatic and the adiabatic regime on HET. [55] Moreover, work tackling the second point has been carried out by collaborators [56] and it is a current research topic in our research group. This dissertation presents studies concerning the third point and addresses these open questions.

Specifically, nonadiabatic HET, as was discussed in section 1.1 depends mainly on two parameters: electronic coupling between a donor molecule and acceptor states and the density of acceptor states. The effects of changing the first parameter have been studied by introducing different bridge and anchor groups between the donor molecule and the semiconductor. [57-60] The second parameter, the Franck-Condon weighted density of states (\mathcal{F}) accounts for the accessible acceptor states weighted by Franck-Condon factors. The latter parameter has been investigated by comparing different substrates and different dye molecules that vary the density of states (DOS) and the level alignment. For example, several studies examined injection times of various dyes into the same semiconductor. [30, 47, 61, 62] These studies gave some support to the idea of having slower HET rates when the excited state was closer to the conduction band edge. On the other hand, measurements on the Alizarin-TiO₂ system were found to be ultrafast even though the donor level is located close to the conduction band minimum. [45, 63] However, these experimental approaches have several shortenings and are not conclusive. Mainly, the use of different molecules introduces the possibility of significant differences in the electronic coupling. An alternative method to test the HET rate dependence on the density of states is by modifying the position of the conduction band edge. These modifications have been done by varying the pH or ion concentration [64, 65] or by applying a voltage to an electrochemical cell. [66, 67]

However, the latter approaches are not free of shortcomings because of the complex solvent environment and the effect it introduce in the adsorbate energetics and its binding with the nanoparticle. [68, 69].

More recent experimental results have been discussed in terms of the steadystate density of surface and surface defect states, level alignment, and Coulomb interaction. Nevertheless, these interpretations have led to controversial conclusions. Some studies compared different metal-oxide electrodes and concluded that surface states are critical for HET. [70] Instead, the importance of electron-hole Coulomb interaction at the interface was pointed out by Nêmec et al. and Stockwell et al. [71,72] On its part, Strothkaemper et al. concluded from a multi-technique study that HET proceeds into surface states formed by the anchor group before charge separation occurs. However, the influence of Coulomb interactions could not be observed in this study. [73] Timeresolved THz studies by Tiwana et al. pointed in the same direction and concluded that local binding, and orbital overlap of the sensitizer on the metal-oxide surface were the prevailing parameters. [74]

This work addresses the issue of the effect of the density of available acceptor states by measuring the HET rates of several systems with different energy level alignments. This was done by implementing two distinct experimental strategies that aim to resolve most of the issues previously discussed. A description of the strategies and the specific goals of this study are presented in the following section (1.4).

1.4 Objectives of this Study

After discussing the basics of the HET process and a brief review of the previous work in the field, the goals of this study can be specified.

The primary objective of this research is to measure and compare the HET rates for systems with different energy level alignments. This work presents a systematic approach to answer this question by following two different strategies.



Figure 1.7: Scheme depicting the general idea behind the first proposed approach to change the level alignment. HET occurs from the first (S_1) or the second (S_2) excited state.

In The first approach the energy level alignment of the reaction is changed by selectively initiating HET from the first or second excited state of the same chromophore. The general idea behind this approach is depicted in the scheme shown in Figure 1.7. This approach involves the use of a phlorin macrocycle attached to TiO_2 via an anchor-bridge group. The details and properties about the phlorin system will be discussed in section 2.2.2. By using this chromophore, the change in the level alignment is achieved without additional changes in the experimental conditions. It is important to stress this point because previous studies in this direction changed the energy level alignment as a result of more than one variation in the experimental conditions. The advantages of the proposed approach are: first, the phlorin used in this study can be excited into two different states that lie above the conduction band minimum of TiO_2 . This excitation can be achieved for both states using pulses in the same energy range. Second, the phlorin macrocycle, being a tetrapyrrole (see section 2.2.1), has a well understood intramolecular relaxation dynamics.

The second approach is based on a set of molecules with the same chromophor. In this case, the change in energy level alignment is achieved by the introduction of dipole-groups in the molecular architecture. The modification of the energy



Figure 1.8: Parallel capacitor model to explain the change in energy level alignment introduced by the use of dipole groups.

level alignment produced by the presence of a dipole in the chromophore can be understood using a parallel plate capacitor model. Considering the molecular arrangement shown in Figure 1.8, the potential difference between the capacitor plates is

$$V = \frac{D_{proj}}{\epsilon A}.$$
(1.13)

In the above expression, D_{proj} is the projection of the dipole moment normal to the surface, ϵ is the permittivity, and A is the surface area of the molecule. This approach allows modifying the energy level alignment by reorientation of the dipole moment as shown in Figure 1.9. Details about the chromophore employed in this experiment (ZnTPP) are given in section 2.2.3.

The advantages of this experimental design are: it only requires small changes to the bridge element and no changes to the semiconductor or the anchor group of the chromophore. In other words, the electron injection occurs from the same electronic state of the same chromophore into the same semiconductor. This assures that the coupling parameter remains the same for the different molecules. Second, the relaxation dynamics of ZnTPP and the electron transfer into different semiconductors have been previously reported.

Both systems were investigated in an UHV environment to remove solvent effects and minimize photodamage of the samples.


Figure 1.9: Scheme showing the basic idea followed in the second experimental approach. The same chromophore is used, and the energy alignment is modified by dipole groups.

Specific goals set for the second experimental scheme are: first, establish if the addition of the dipole groups affects the intramolecular relaxation dynamics of the fairly well understood ZnTPP chromophore. Second, HET rates after the excitation of the S_2 excited state will be measured and compared.

Chapter 2 EXPERIMENTAL SYSTEM

Pursuing the objectives underlined in the last section (Section 1.4), demands a set of appropriate molecule-semiconductor systems. The ideal experimental system for the experimental study of HET must satisfy a set of requirements. First, the HOMO-LUMO gap of the chromophore must be smaller than the semiconductor bandgap to allow selective excitation of the molecular excited state. Second, the relaxation dynamics of the molecular species must be relatively simple or fairly well understood to allow the disentanglement of contributions arising from HET process. Additionally, the absorption and emission bands of the molecule should be separated to allow distinguishing different processes. Finally, the relaxation timescales of the molecule should not compete with the expected ultrafast HET reactions.

The remainder of this chapter gives additional details on the employed experimental system. First, an elementary description of the photophysical process that can be observed after photoexcitation of molecules is presented. Then, the tetrapyrrole molecules employed in this study are introduced and clearly specified. Subsequently, the specific characteristics of the substrate acting as the electrode are also discussed.

2.1 Basic Photophysics

Photophysics is the usual name given to the study of the processes that include the photoexcitation of a molecular species, as well as all the subsequent process taking place after the generation of the excited state. The most basic process can be explained by using elementary quantum mechanics concepts and the corpuscular nature of light. Given a light-molecule interaction, there are two processes that can occur (only first order processes are considered in this section). Absorption takes place when a photon with an energy equal to the energy difference between two molecular levels interacts with an electron on the lower level. Photoemission is the reverse process that brings an electron to a lower state with the emission of a photon. The strength of the transition will be determined by the transition dipole moment between the levels involved in the reaction. Another type of energy levels that play a crucial role in the relaxation of molecules are vibrational levels originated by periodic motion of the nuclei of the atoms within a molecule. A common schematic representation of the possible absorption process and the fate of the excited states is the so-called Jablonski diagram.¹ An example of this type of diagrams showing the possible relaxation pathways is shown in Figure 2.1. Referencing to this figure the different process displayed in the diagram are:



Figure 2.1: Jablonski diagram showing different relaxation process after photoexciting a molecule.

¹ Aleksander Jablonski was a Polish academic who introduced this diagrammatic representation in 1933 [75]

Vibrational relaxation (VR) is a non-radiative process where the energy obtained after the absorption process is given away as kinetic energy. Two cases can be identified. The first one leaves the kinetic energy within the same molecule by activating vibrational modes in the same electronic level and is called Internal Vibrational Relaxation (IVR), Another possibility is that the energy may be transfer to the solvent molecules around the excited species; this is called Vibrational Cooling (VC).

Internal conversion (IC) is a nonradiative process between two different electronic states of the same multiplicity. The process takes place when vibrational energy levels from a high energy electronic state overlap with the vibrational levels of a lower lying electronic level.

Fluorescence is the radiative process that relaxes one electron from an energy level with singlet multiplicity into the ground state. This process is usually only seen with appreciable yield from the lowest excited state of a particular molecule (this is known as Kasha's rule) because higher energy levels are more likely to relax via the faster VR and IC processes. The energy of the photons emitted through this pathway is usually less than that of the initially exciting photons. This difference in the absorption and emission wavelength is known as the Stokes' shift of the transition and is caused by the energy lost in internal conversion and vibrational relaxation processes.

Intersystem crossing (ISC) is the process analogous to internal conversion between states from different multiplicity, i.e., singlet to triplet electronic transitions. The process is usually slower than IC due to the transition being forbidden based on electronic selection rules. However the coupling of the electron spin with the orbital angular momentum usually seen in heavy-atom molecules softens the selection rule.

Phosphorescence is a radiative transition between the lowest triplet state and the ground state. This process is analogous to ISC and is also very slow due to the forbidden nature of the transition. Most molecules usually relax into the ground state via a radiationless transition and phosphorescence will be typically observed for relatively high energy triplet states.

Transition	Time Scale	Radiative?
Absorption	$10^{-15} { m s}$	yes
Internal Conversion	$10^{-15} 10^{-11} \text{ s}$	no
Vibrational Relaxation	$10^{-15} 10^{-11} \text{ s}$	no
Fluorescence	$10^{-9} 10^{-7} \text{ s}$	yes
Intersystem Crossing	$10^{-8} 10^{-3} \text{ s}$	no
Phosphorescence	$10^{-4} 10^{-1} \text{ s}$	yes

 Table 2.1:
 Typical timescales of different molecular photophysical process.

2.2 Molecular systems

To conduct the experiments specified in section 1.4 we used a class of molecules know as tetrapyrroles. Tetrapyrroles are a family of compounds containing four pyrrole rings (Figure 2.2) held together by covalent bonds. These molecules can be found in either a linear or a cyclic arrangement, and they show a high degree of conjugation.² Some members of this family of molecules play crucial roles in biochemistry and living systems, for example, hemoglobin and chlorophyll. Since early times, natural and synthetic tetrapyrroles have been used as model systems for understanding fundamental photophysical and photochemistry process. Currently, they can be found in technological applications such as photovoltaic and photocatalytic devices. Specifically, this work uses two different tetrapyrroles. One is a phlorin, employed to test the effect of injecting from two different electronic states on the HET rate. The second molecule is a porphyrin, where energy alignment was tuned by the introduction of dipole bridge

 $^{^2\,}$ In chemistry, a conjugated system is composed of connected p-orbitals with delocalized electrons in molecules with alternating single and multiple bonds. This structure, in general, lowers the overall energy of the molecule and increases stability.



Figure 2.2: Pyrrole groups are the building blocks of tetrapyrroles (left). Examples of cyclic tetrapyrroles (right).

groups. Both molecules, belonging to the same family, display similarities in their photophysical behavior. In the following, some basic properties of the family of molecules are presented. Then, details of each molecule and how they fit into the proposed experiments, are also discussed.

2.2.1 Basic tetrapyrrole properties

An exemplary cyclic tetrapyrrole is the porphin (also called free base porphyrin) shown in Figure 2.3. The macrocycle possesses different binding positions categorized in three groups. There are α -positions where the carbon atom is next to a nitrogen atom, β -positions with two carbon atoms apart from a nitrogen atom, and *meso*positions located in between two α positions. It posses 18 π -electrons, and obeys Hückels aromaticity rule. As a consequence of the aromaticity, the macrocycles possess multiple absorption bands in the ultraviolet and visible range. The addition of substituents can spectrally shift and alter the relative intensity of these bands. In general, cyclic tetrapyrroles show a so-called Q band, which is a broad but weak absorption



Figure 2.3: Porphin, a prototypical tetrapyrrole. The basic structure and nomenclature used in the substitution of functional groups are shown in the figure.

in the visible range. This absorption band corresponds to the first electronically excited singlet state S_1 . The degrees of symmetry present in a particular tetrapyrrole will introduce or remove degeneracies that modify the number of bands showing up in the visible region. The more intense absorption band, 5 to 100 times stronger than the Q band in common tetrapyrroles, is called the Soret or B band. This band is caused by transitions into the second excited singlet state S_2 , and is located at around 400 nm.

The aforementioned bands cannot be explained by a simple molecular orbital theory using a single HOMO and LUMO orbital. As a result, Gouterman developed a model explaining the essential features of most standard cyclic tetrapyrroles. Despite more accurate modern models based on density functional theory [76], Gouterman's model is still in use since the 1960's for its intuitive explanations of the observed photophysics.

Gouterman's model starts by considering a pair of HOMOs and LUMOs orbitals calculated via Hückel theory. The requirement of two HOMOs and LUMOs originates from the fact that cyclic tetrapyrroles show degenerate orbitals. Applying the configuration interaction method to the proposed orbitals generates the new effective states involved in the optical transitions observed in the molecules. Thus, the transitions are not directly related to a single molecular orbital but rather to a superposition of them. This explains the observed difference in absorption strength that depends on the degree of shared symmetry as well as the energy gap between the effective states. Using Figure 2.4 as a reference, the pair of HOMOs are labeled as Ψ_1 , Ψ_2 . Similarly the LUMOs are identified as Ψ_3 , Ψ_4 . If we denote by $\Psi_i \Psi_f$ the singlet state originated after the transition $\Psi_i \longrightarrow \Psi_f$, the new effective states can be written as a mixture of these elementary transitions in the following manner,

$$Q_x = \frac{1}{\sqrt{2}} (\Psi_1 \Psi_4 + \Psi_2 \Psi_3) \tag{2.1}$$

$$Q_y = \frac{1}{\sqrt{2}} (\Psi_1 \Psi_3 - \Psi_2 \Psi_4) \tag{2.2}$$

$$B_x = \frac{1}{\sqrt{2}} (\Psi_1 \Psi_4 - \Psi_2 \Psi_3) \tag{2.3}$$

$$B_y = \frac{1}{\sqrt{2}} (\Psi_1 \Psi_3 + \Psi_2 \Psi_4), \qquad (2.4)$$

with x and y being the directions of the resultant dipole moment of the transition. Depending on the symmetries introduced or removed by the different substitutions in the macrocycle, some of the above transitions will have a larger dipole magnitude or can even be forbidden. In this way, the four orbital model is able to explain the observed absorption spectra of a large group of cyclic tetrapyrroles.

2.2.2 Phlorin (3H(Phl^F)) molecular system

The first experimental approach in this work uses a phlorin to investigate HET occurring from two different excited states. Phlorins share a lot of the common characteristics previously discussed for tetrapyrroles. However, the phlorin macrocycle contains a sp³ hybridized carbon at one of the meso positions. This structure gives rise to multielectron redox properties and photophysical characteristics, which distinguish it from more common tetrapyrrole architectures. The synthesis of the phlorin macrocycle has proved to be a challenging task causing to be seldom reported in the literature. Nevertheless, the synthesis of a novel and stable fluorinated phlorin $(3H(Phl^F))$ has



Figure 2.4: The four orbitals that build Gouterman's model of porphyrins (a). The model gives rise to the two different absorption bands shown in panel (b).

been achieved by Pistner et al. [77] The addition of the fluoride anions significantly perturbs the absorption bands of the chromophore. For the purpose of this research, the phlorin derivative is useful because it shows strong absorption in the Q band. The phlorin derivatives shown in Figure 2.5 allow to compare electron injection rates after excitation in the Q and Soret bands without the need of for major changes in excitation fluence or concentration of molecules. This situation permits the study of the effect of the density of acceptor states on the HET process.

The ground state absorption and emission spectra of $3H(Phl^F)$ and $3H(Phl^{CO_2H})$ are shown in Figure 2.6 and agree in general with the reported measurements on cyclic tetrapyrroles. [78, 79] The phlorin has a Soret band at ~440 nm and a Q band at ~650 nm. These absorption bands correspond to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively. The emission spectra show a maximum at ~730 nm. Correspondingly, the phlorin with the acid anchor group (used for the experiments on the electrode) shows a slight red shift of the Q band and consequently a shift in the emission spectra.



Figure 2.5: (a) Freebase phlorin derivatives utilized in this study. (b) Solid state structure of 3H(Phl^F) shown from above the plane of the macrocycle (left) and side one (right). A molecule of cocrystallized CHCl₃ and all non-nitrogen bound hydrogen atoms have been omitted for clarity.

2.2.3 Porphyrin (ZnTPP) molecular systems

It was mentioned in section 1.4 that the second approach in this research consisted in modifying the level alignment by means of a dipole-bridge molecular architecture. Three different molecules, based on a Zn porphyrin, were used for this purpose. The selection of this chromophore, a zinc tetraphenylporphyrin (ZnTPP), followed two reasons. First, it has been shown that the photophysical properties of ZnTPP are mostly unaffected by the functionalization at the meso positions (see Figure 2.3). [80–84] Second, the use of ZnTPP allows a direct comparison with previous studies of similar porphyrins bound to TiO₂ and ZnO. [80,82–84]

The compounds used in this study and their steady state absorption spectra are shown in Figure 2.7. Details on the chemical synthesis of the three compounds have



Figure 2.6: The ground state absorption and static fluorescence spectra of $3H(Phl^{F})$ and $3H(Phl^{CO_2H})$ in toluene.

been previously reported in two publications. [80, 85] All three compounds, labeled as 1, 2, and 3 are composed of a ZnTPP chromophore, a bridge group, and an anchor group. The bridge group in 2 is a phenyl ring, whereas in 1 and 3 it is a N,Ndimethyl-4-nitroaniline group. The three dyes are terminated by an isophthalic acid group (Ipa) as the anchor unit. The anchor group binds efficiently to metal oxides through the carboxylate groups, and its successful use has been reported in previous studies. [81, 86, 87]

The introduction of the nitroaniline group in 1 and 3 is the key aspect of the molecular design. This group has an electric dipole moment with a component that is oriented along the molecule. The direction of the dipole can be changed to point towards or away from the anchoring group, without influencing the photophysical properties of the ZnTPP chromophore. [88]

It has been shown by our collaborators that the introduction of the dipole group alters the energy level alignment. UPS measurements by the Bartynski group demonstrated that the nitroaniline group introduces a dipole moment that shifts the energy level alignment by 200 meV. This shift depends on the orientation of the dipole, where **1** is 100 meV higher in energy than **2** and 200 meV higher than **3** on a ZnO (11-20) surface. [88] The shift in the energy alignment follows the order $\mathbf{1} > \mathbf{2} > \mathbf{3}$.



Figure 2.7: UV-Vis spectrum and structure of the three Zn-porphyrin derivatives used in this study.

Going back to Figure 2.7 the steady-state absorption and fluorescence spectra of the compounds is shown for solutions prepared in tetrahydrofuran (THF). The absorption and emission of the compounds include a two-fold degenerate Soret band (423 nm in THF), and a weaker Q_1 (555 nm) and Q_0 (595 nm) bands. Except for a small shift that has been attributed to the phenyl linkers, [80,89] the spectra resemble the one of regular ZnTPP porphyrin. [90–92]

2.3 Electron acceptor substrate

One side of the HET reaction is the molecular light absorber just described in the previous section. The other side is the electron acceptor substrate. In this work, the electron acceptor material is a semiconductor cast on a transparent glass window. In this section, we will go in detail over the electron acceptor substrate used for the HET measurements.



Figure 2.8: Crystal structure of TiO_2 (anatase). Titanium atoms are in grey, while the red ones represent oxygen atoms.

In this study, the semiconductor providing the multitude of acceptor states required for HET was titanium dioxide. Specifically, colloidal nanoparticles of anatase TiO₂. Anatase is one of the three naturally occurring mineral forms of TiO₂, with brookite and rutile being the other two. The anatase phase is always found as small, isolated and sharply developed crystals belonging to a tetragonal system. The basic structure of anatase is an octahedron with a titanium center surrounded by six oxygens as seen in Figure 2.8. Bonds in metal oxide crystals as TiO₂ usually are placed between the covalent bonded III-V semiconductors and the ionic I-VII salts. [93] Hence, stoichiometric TiO₂ has a large band gap and imperfections result in n-doped TiO₂. [94]

The dependence of HET on the density of acceptor states in the semiconductor (DOS) was discussed in section 1.1. Thus, an estimation of this parameter, either by experimental or theoretical means is important. The DOS of the anatase TiO_2 is taken as the (101) surface DOS calculated using density functional theory. Figure 2.9 shows this calculated DOS and the details of the calculations can be found in reference [95].

A requirement for spectroscopy on molecule-semiconductor systems is a sufficiently large number of adsorbate molecules that provides an adequate signal to noise ratio. Nanoporous anatase TiO₂ films provides an effective surface area of around $140 \text{ m}^2/\text{g}$ [96] satisfying this requirement.

The nanoporous anatase TiO_2 films utilized in this study were prepared in



Figure 2.9: Band structure (a) and density of states (b) of a (101) TiO_2 anatase perfect surface. Image reprinted from reference [95], licensed under CC BY 3.0.

two steps. First, the colloidal TiO₂ solution was synthesized by hydrolysis of Ti(IV)isopropylate and autoclaving of the acidified solution. The description of this sol-gel technique can be found in the literature e.g. [84] Next, the colloidal solution was cast onto 50 μ m thin AF45 glass (Schott Displayglas, AF stands for "alkali-free") via doctor blading. The choice of the glass substrate obeys two considerations. One of them is that the glass substrate is likely to generate coherent signals artifacts in transient absorption measurements. Thus, these contributions are reduced by the use of thin glass substrates. Second, it has been observed that the alkali content of the glass substrate affects the molecule-TiO₂ interface by the diffusion of alkali atoms into the anatase lattice. [97] Hence, to avoid this effect, alkali-free glass was used (alkali content <0.25%).

The above-described method resulted in mesoporous films of $\sim 10 \ \mu m$ thickness consisting of nanoparticles with an average diameter of $\sim 20 \ nm$ as seen in Figure 2.10. The glass-TiO₂ substrates were kept in a dry low vacuum environment before they were sensitized with the molecular chromophore.



Figure 2.10: SEM image (left) of the cross-section of nanoporous anatase on a glass substrate similar to the one used in this work. Right: TEM image of fragments of a film. The TEM image is reprinted from reference [97].

2.4 Sample preparation

In order to effectively disentangle the HET rates it is fundamental to understand the relaxation dynamics of the molecules in solution phase. This because the relaxation dynamics in solution compete with the electron injection process. Hence, measurements in solution were performed as a prerequisite to explain the observed HET processes. The experiments in solution were performed in spectroscopy grade solvents. The solvents used for the phlorin molecule were: methanol, toluene, dimethylformamide (DMF), and cyclohexane from Fisher Scientific. Correspondingly, for the ZnTPP molecules the solvents used were: diethyl ether (ether), and tetrahydrofuran (THF) also from Fisher Scientific. The employed solvents were chosen for the following reasons. First, the sample must be highly soluble in the solvent to avoid the formation of aggregates. Second, when comparing solution measurements with the ones done on the sensitized film, the use of a nonpolar solvent is advantageous because it better reproduces the vacuum conditions. Third, the grade of coordination between solvent and the molecules must also be considered.

For binding the dyes onto the nanoporous TiO_2 substrates, the following process was observed. Firstly, a thin glass film covered with TiO_2 was annealed in a furnace at 450°C. Next, the film was immersed in a 100 μ M solution of the chromophore with an anchor group for about 20 to 45 minutes. Afterward, the dye-covered film was rinsed six times by squirting clear solvent with a pipette and blown dry with argon. The rinsing process was validated by measuring the decrease of fluorescence from the film and the disappearance of fluorescence from the supernatant.

An important consideration when performing transient absorption experiments is how to deal and minimize the effects of photobleaching. Photobleaching of dyes when absorbed into TiO_2 has been reported when measuring HET rates. [97]. Similarly, bleaching of porphyrin samples in solutions has been reported after excitation at 397 nm. [90] Solution phase measurements were performed without using a flow cell since convection was sufficient for replenishing the sample. For the film measurements, a reduction around 30% in the transient absorption signal during the first 20 min of irradiation was observed. This was usually accompanied by a decoloration of the sample. Similar photobleaching processes have been described previously [97]. Bleaching has been ascribed to photo-oxidation of unbound molecules in the film residing in a photoexcited, highly reactive state for a prolonged time. Properly bound molecules, on the other hand, undergo rapid HET transfer resulting in the molecular cation. The high vacuum environment employed in this study slows down the photobleaching process and allows for comparing measurements at the beginning and the end of this process. After the mentioned bleaching process, no changes in the absorption, emission spectra, or dynamics was observed. Thus, all measurements were performed after an initial 20 min bleach period that can be thought as an additional step in the sample preparation procedure.

Chapter 3 EXPERIMENTAL METHODS

The primary goal of this study was to measure the electron transfer rate from different tetrapyrrole systems into TiO_2 colloidal nanoparticles. These measurements require a spectroscopic technique with femtosecond resolution and capable of identifying electronic transitions in the molecular systems. Femtosecond transient absorption spectroscopy satisfies the above requirements. Compared with time-resolved fluorescence, it allows tracking the evolution of non-emissive states. Hence, transient absorption spectroscopy, combined with additional steady-state and conventional transient spectroscopies, is capable of elucidating the fast relaxation pathways of the studied molecules in solution and when attached to the semiconductor film. This chapter presents the details of the experimental setup and data analysis.

3.1 Laser System

The laser system used in this work was composed of a commercial Ti:Sapphire oscillator (Coherent Mantis) and a regenerative amplifier (Coherent Legend-Elite). The regenerative amplifier takes the pulses from the oscillator and stretches them for amplification on a Ti:Sapphire crystal pumped by a Nd:YLF (Coherent Evolution) laser. After leaving the amplification stage, the pulses are compressed to deliver 35 fs pulses centered at 800 nm with a repetition rate of 10 kHz and 620 μ J of energy. A fraction of this power was used to perform the spectroscopic experiments.

3.1.1 Overview of Non-Linear Optics

All classical electromagnetic phenomena, including optics, and the interaction of light with matter can be explained with Maxwell equations, the Lorentz force, and the constitutive equations. A relatively new phenomenon is the field of nonlinear optics. This area remained largely unexplored until the development of the first lasers in 1960. In fact, the first reported experimental observation of nonlinear optical phenomena was the observation of second harmonic generation in 1961.¹ [98] This observation and all nonlinear optical phenomena arise from the properties of certain materials to react in a nonlinear way to intense electromagnetic fields. This nonlinear reaction can be understood in terms of the induced polarization. In general, the polarization field P(x, t), generated by an external electric field E(x, t) in an isotropic linear dielectric material with susceptibility χ can be written as

$$\boldsymbol{P}(\boldsymbol{x},t) = \epsilon_0 \chi \boldsymbol{E}(\boldsymbol{x},t). \tag{3.1}$$

For the case of a losless² nonlinear medium the previous expression can be approximated by the Taylor expansion

$$\boldsymbol{P}(\boldsymbol{x},t) = \epsilon_0 \left[\chi^{(1)} \boldsymbol{E}(\boldsymbol{x},t) + \chi^{(2)} \boldsymbol{E}^2(\boldsymbol{x},t) + \chi^{(3)} \boldsymbol{E}^3(\boldsymbol{x},t) + \dots \right]$$
(3.2)

$$=\epsilon_0 \chi^{(1)} \boldsymbol{E}(\boldsymbol{x}, t) + \boldsymbol{P}^{NL}, \qquad (3.3)$$

where the coefficients $\chi^{(n)}$ are the n-th order electric susceptibility (in general a n + 1 order tensor). By taking the curl of the Maxwell-Faraday equation, using vector identities, and substituting Ampere's law, the following wave equation can be derived

¹ Franken et al. focused a 694 nm ruby laser into a quartz sample. Afterward, the light was dispersed and recorded on photographic paper. Famously, the editor thought the spot at 347 nm (the reported second harmonic) was a speck of dirt and removed it from the publication.

 $^{^2}$ Nonlinear lossless processes represent a family of phenomena also called parametric. These processes are characterized by leaving the quantum state of the material unchanged. Contrary, non-parametric processes, are lossless processes where the quantum state of the material is altered, and their study requires the quantum mechanical approach described in section 3.2

for a source free region of space:³

$$\nabla^2 \boldsymbol{E} - \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{E} = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{P}^{NL}, \qquad (3.4)$$

where \mathbf{P}^{NL} makes reference to the non-linear part of the polarization. The solution to the above equation is composed of the solution of the homgeneous equation plus the solution due to the driving term. For example, considering a second order non linearity

$$\boldsymbol{P}^{NL} = \epsilon_0 \chi^{(2)} \boldsymbol{E}^2(t), \qquad (3.5)$$

with an assumed electric field of the form

$$\boldsymbol{E}(t) = \frac{1}{2}\boldsymbol{E}_1 \exp\left(-i\omega_1 t\right) + \frac{1}{2}\boldsymbol{E}_2 \exp\left(-i\omega_2 t\right) + \mathcal{C}.\mathcal{C}.$$
(3.6)

 $(\mathcal{C}.\mathcal{C}.$ stands for complex conjugate) gives the following non-linear driving term

$$\mathbf{P}^{NL} = \frac{\epsilon_0}{4} \chi^{(2)} \{ |\mathbf{E}_1|^2 \exp(-i2\omega_1 t) + \\
|\mathbf{E}_2|^2 \exp(-i2\omega_2 t) + \\
2\mathbf{E}_1 \cdot \mathbf{E}_2 \exp[-i(\omega_1 + \omega_2)t] + \\
2\mathbf{E}_1 \cdot \mathbf{E}_2^* \exp[-i(\omega_1 - \omega_2)t] + \\
(|\mathbf{E}_1|^2 + |\mathbf{E}_2|^2) + \mathcal{C}.\mathcal{C}. \}.$$
(3.7)

If the above expression is introduced back in equation 3.4 we will have a wave equation with several driving terms. Each of these driving terms, originated from a second order non-linearity, will generate electric fields oscillating with different frequencies. These fields correspond to the following wave-mixing process: second harmonic generation, sum frequency generation, difference frequency generation, and optical rectification.

³ The identity used is $\nabla \times \nabla \times \boldsymbol{E} = \nabla(\nabla \cdot \boldsymbol{V}) - \nabla^2 \boldsymbol{V}$. When applied to $\nabla \times \boldsymbol{E} = -\partial \boldsymbol{B}/\partial t$ it leads to the appearance of the term $\nabla \cdot \boldsymbol{E}$ which in a non-linear media its not necessarily equal to zero. However its contribution is often negligible and has been ignored in equation 3.4. [99]

These second order effects represent the most common non-linear phenomena and are exploited in the experimental setup of this work. For higher order effects, the discussion follows in a similar way and gives rise to two important non-linear phenomena. The Kerr effect ($\chi^{(3)}$ process) exploited in the femtosecond oscillator used in this study (section 3.1.2), and supercontinuum generation (combination of higher order process) used in this work to generate the seed for optical parametric amplification (section 3.1.4) and as the probe for the transient absorption setup (section 3.3.1).

3.1.2 Femtosecond Oscillator

The backbone of the experimental setup is a Ti:Sapphire femtosecond laser. This type of lasers was first built in 1982 [100] and is commercially available since 1990. Nowadays, most of these systems rely on the self-mode-locking technique to produce a train of pulses with femtosecond duration. When compared to conventional continuous wave (CW) lasers, femtosecond lasers require two particular elements in their design. First, a gain medium that allows amplification of light over a broad spectrum. Second, an element that selectively permits the travel of high-intensity short pulses within the laser cavity, while suppressing the low-intensity continuous wave radiation. These two required elements are responsible for the generation of short pulses in a way that can be understood from the time-energy uncertainty relation⁴

$$\sigma_E \sigma_t \ge \frac{\hbar}{2}.\tag{3.8}$$

For the case of a light pulse, photons can be considered to be distributed around a central energy value E_0 . Furthermore, recalling the expression that relates the energy

⁴ The uncertainty relation was originally presented for the momentum and position of a particle by Heisenberg in 1927 as $\Delta x \Delta p \gtrsim h$. [101, 102] Also in 1927, Kennard first proved the inequality in terms of the standard deviation $\sigma_x \sigma_p \geq \frac{\hbar}{2}$. [103] Nowadays, in the Hilbert space formulation of quantum mechanics, it is usually written as $\Delta x \Delta p \geq \frac{\hbar}{2}$ where Δ refers to the uncertainty of the expectation value of an Hermitian operator. Since there is no time operator in standard quantum mechanical theories, a formal derivation of the energy-time relation gave rise to several discussions on the topic. [104] It was finally formally proved, in the way shown in equation 3.8 by Mandelshtam and Tamm in 1945. [105]

of a photon E_p with the wavelength λ , the speed of light c, and the Planck constant h, i.e.,

$$E_p = \frac{hc}{\lambda},\tag{3.9}$$

the standard deviation of the energy in equation 3.8 can be recast to get a more useful relation from an experimental point of view

$$\Delta \lambda \Delta t \ge K \frac{\lambda_0^2}{c}.$$
(3.10)

In the above expression, Δ now represents the full width at half maximum (FWHM) of the corresponding quantity, and K is a constant that relates the FWHM with the standard deviation σ of the photon distribution. From the last equation, it can be concluded that the only way of having a femtosecond laser pulse is by forcing the laser to amplify a considerably broad spectrum in a manner that allows all the frequencies to interfere constructively. This process is what is called mode-locking. To achieve this, state of the art lasers implement a design in which they use a broad emission crystal that also plays the role of a modulator. The most common example of this crystal is sapphire (Al₂O₃) doped with titanium ions (Ti:Sapphire); its characteristic emission spectrum is shown in Figure 3.1. Because the crystal acting as the shutter needs to react in the femtosecond scale, the modulation of this element can only be done by the same short pulse itself. Achieving this fast modulation is done by exploiting the Kerr effect. [107] This effect is a non-linear process in which a material changes its index of refraction n as the direct response to the presence of a high-intensity electromagnetic field, i.e.,

$$n(\boldsymbol{x},t) = n_0 + n_2 I(\boldsymbol{x},t).$$
 (3.11)

In plain words, the light will be slower in areas where the intensity of the beam is higher than the average. If the propagating beam has a transversal Gaussian spatial intensity profile, the Kerr effect will generate a Kerr-lens leading to self-focusing of the propagating beam. This intensity dependent change in focus is exploited by designing



Figure 3.1: Absorption and emission spectra of a typical Ti:Sapphire crystal. Image reprinted from Reference [106].

a cavity that blocks or attenuates the unfocused low-intensity light. On the other hand, a Gaussian temporal intensity profile will produce a red shift at the front part of the pulse and a blue shift at the tail of it; this effectively broadens the pulse. Under these circumstances, once the light in the cavity achieves the required power to cause a Kerrlens, the two processes mentioned earlier will reinforce themselves producing broader and more intense pulses after each roundtrip. The initial fluctuation that triggers the described process can arise from random fluctuations, or more conveniently, from a controlled perturbation of the system.

3.1.3 Chirped Pulse Regenerative Amplifier

The pulses generated by the oscillator, despite being short, still have a relatively low intensity to be useful in a modern spectroscopy laboratory. Thus, an additional amplification process is required. The current state of the art in laser amplification is the so-called chirped pulse amplifier developed in the mid-1980s. [108] Before the development of this technique, conventional amplifiers were limited by the damage threshold of the gain medium. Chirped amplification overcomes this limitation by stretching the laser pulses in time creating a low-peak intensity long pulse. To achieve this, the first stage of the amplifier separates the pulse into its spectral components. This separation is usually done employing a diffracting grating, and effectively introduces different path lengths for the various spectral components. Thus, the grating produces a temporally stretched, low-peak power, pulse. Once the intensity of a pulse is lowered enough, it bounces within a cavity containing a gain medium like a Ti:Sapphire crystal. After each roundtrip, the pulse increases its energy in the pumped amplification crystal. The number of roundtrips in the cavity is controlled by the Pockels cell.⁵ This gating process produces the desired repetition rate of the laser system. Finally, after the amplification stage, the pulse is compressed again in a grating compressor to deliver a short high-peak intensity beam.

3.1.4 Parametric Amplifiers

Ti:Saphire lasers are limited by the emission wavelength of the fundamental (800 nm). To overcome this limitation parametric amplifiers are used. Specifically, the experimental setup in this work employs a Non-collinear Parametric Amplifier (NOPA). The purpose of this tool is to take the 800 nm pulses from the laser system and generate energy tunable pulses. In particular, the NOPA used in this work can generate pulses in the visible (450-750 nm), and with minor modifications, in the near infrared region (840-1600 nm). A sketch of the device is shown in Figure 3.2 This NOPA delivers sub 30 fs pulses after a compression stage with a pair of fused silica prisms. The output pulses, depending on the system under study, can either be used right after the compression stage or after second harmonic generation in a 0.1 mm BBO crystal. In the later case, the pulses are pre-compressed to achieve the same 30 fs pulses after generation of the second harmonic. An excellent introduction to the operation and design of these type of optical instruments can be found in the review by Cerullo. [109] In detail, the setup in the laboratory was built using a β -barium borate (BBO)

 $^{^{5}}$ The effect is named after Friedrich Carl Alwin Pockels who studied the phenomenon in 1893. The effect consists in a change of the index of refraction in an optical medium induced by an electric field.



Figure 3.2: Schematic of the NOPA used in this study. This tool generates sub 30 fs tunable pulses in the visible and near infrared.

crystal similar to NOPAs by the Riedle group. [110–112] These instruments perform an energy conversion process by exploiting non-linear optical phenomena driven by the spatiotemporal overlap of two high-intensity light pulses. The nonlinear process in question is known as difference frequency generation (DFG). This is a $\chi^{(2)}$ process described in section 3.1.1 and it is characterized by the generation of a third radiation field with a wavelength corresponding to the difference in energy between the two original ones. By a suitable selection of the intensity, polarization and overlap geometry of the two incoming pulses; it is possible to use this process to amplify one of the incoming pulses using the energy of the second one. The most common configuration is to overlap in the BBO crystal a weak but broad supercontinuum pulse (generated by focusing an 800 nm beam on a sapphire window), referred as the seed, with a highintensity 400 nm pump pulse (generated by frequency doubling of an 800 nm beam). With careful alignment, it is possible to amplify the desired portion of the broad seed spectra generating in the process an idler pulse with the mentioned energy difference. The characterization of the NOPA pulses used in this work was done using both a home built autocorrelator and a commercial FROG⁶ (Mesa Photonics).

3.2 Introduction to Non-Linear Spectroscopy

Conventional linear spectroscopies like absorption, emission, and Raman, treat light matter interactions with one weak electric field. Thus, this interaction can be treated as a linear response to the interaction field. On the other hand, nonlinear spectroscopies deal with light matter interaction where more than one electric field is involved, or when linear response theory is inadequate to describe the material's behavior. This section gives a brief introduction to the framework, mainly developed by Shaul Mukamel, [114] used to describe this nonlinear interactions.

Transient absorption spectroscopy-the technique employed in this work-is by itself a nonlinear spectroscopy technique. However, due to its simple interpretation in terms of basic photophysical and phenomenological ideas, this technique is seldom treated under the formalism herein described. Nevertheless, it is important to understand the microscopic origin of the spectroscopic signals.

Spectroscopic signals arise from the interaction of light and matter. First, an incident electromagnetic wave⁷ described by the wave equation

$$\nabla^2 \boldsymbol{E} - \frac{1}{c^2} \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = 0 \tag{3.12}$$

encounters a non linear material. Second, the microscopic dipoles in the material interact with the electric field and the latter generates a macroscopic oscillating polarization given by

$$\boldsymbol{P}(\boldsymbol{x},t) = \epsilon_0 \left[\chi^{(1)} \boldsymbol{E}(\boldsymbol{x},t) + \chi^{(2)} \boldsymbol{E}^2(\boldsymbol{x},t) + \chi^{(3)} \boldsymbol{E}^3(\boldsymbol{x},t) + \dots \right]$$
(3.13)

⁶ FROG stands for frequency-resolved optical gating; it is a method for characterizing short optical pulses developed by Trebino and Kane in 1991 [113]

⁷ Interactions with the magnetic field are usually ignored due to their relatively small strenght.

Third, this macroscopic polarization acts as the source of a new signal field E_{sig} described by the equation

$$\nabla^2 \boldsymbol{E}_{sig} - \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{E}_{sig} = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{P}, \qquad (3.14)$$

To solve for the signal field E_{sig} it is useful to assume the following forms for the polarization and the signal fields as an ansatz

$$\boldsymbol{P}(\boldsymbol{r},t) = \tilde{\boldsymbol{P}}(t)e^{(i\boldsymbol{k}'_{sig}\cdot\boldsymbol{r}-i\omega_{sig}t)},\tag{3.15}$$

$$\boldsymbol{E}_{sig}(\boldsymbol{r},t) = \boldsymbol{E}_0(\boldsymbol{r},t)e^{(i\boldsymbol{k}_{sig}\cdot\boldsymbol{r}-i\omega_{sig}t)}.$$
(3.16)

Introducing the previous assumptions in equation 3.14 and considering the signal field originates from a thin sample of length l, for which the radiated amplitude grows and becomes directional as it propagates through it, the signal field can be written as,

$$\boldsymbol{E}_{sig}(t) = i \frac{2\pi\omega_{sig}}{nc} l \tilde{\boldsymbol{P}}(t) \operatorname{sinc}\left(\frac{\Delta kl}{2}\right) e^{i\Delta kl/2}, \qquad (3.17)$$

where $\Delta k = |\mathbf{k}_{sig} - \mathbf{k}'_{sig}|$. Now, to get an expression that relates the signal field to the microscopic parameters it is required to turn to quantum mechanics. The problem can be described with the semi-classical time dependent Hamiltonian,

$$\hat{H} = \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t), \qquad (3.18)$$

where the time dependence arises from the interaction of electric field $\boldsymbol{E}(t)$ with the electric dipole operator $\hat{\boldsymbol{\mu}}$. The desired induced polarization is calculated as the expectation value of the electric dipole operator, and the problem is better treated by describing the state of the system with the density matrix operator in the interaction picture

$$\rho_I(t) = U^{\dagger}(t, t_0)\rho(t)U(t, t_0).$$
(3.19)

The last equation introduces the unitary evolution operator U and the time evolution of the density matrix in the interaction picture is described by the Luoiville-Von Newmann euquation,

$$i\hbar \frac{d}{dt}\rho_I(t) = [\hat{V}_I(t), \rho_I(t)].$$
(3.20)

The problem can be solved perturbatively using an expansion of the form

$$\rho_I(t) = \rho_I^{(0)} + \sum_{n=1}^{\infty} \rho_I^{(n)}(t).$$
(3.21)

The zero order term corresponds to the solution of the system without the perturbation, $\rho_I^{(0)} = \rho_{eq}$, so it is more interesting to write an expression for the n-th order expansion of the density matrix as

$$\rho_{I}^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^{n} \int_{-\infty}^{t} dt_{n} \int_{-\infty}^{t_{n}} dt_{n-1} \cdots$$

$$\int_{-\infty}^{t_{2}} dt_{1} \left\{ \left[\hat{V}_{I}(t_{n}), \left[\hat{V}_{I}(t_{n-1}), \left[\cdots, \left[\hat{V}_{I}(t_{1}), \rho_{eq}\right]\cdots\right]\right]\right] \right\}.$$
(3.22)

Once we have an expression for the density matrix, the polarization can be calculated as the expectation value of the dipole operator

$$\tilde{\boldsymbol{P}}(t) = \langle \hat{\boldsymbol{\mu}}(t) \rangle = \operatorname{Tr}(\boldsymbol{\mu}_{I}(t)\rho_{I}(t)) = \operatorname{Tr}(\boldsymbol{\mu}_{I}\rho_{I}^{(0)}) + \operatorname{Tr}(\boldsymbol{\mu}_{I}\rho_{I}^{(1)}) + \operatorname{Tr}(\boldsymbol{\mu}_{I}\rho_{I}^{(2)}) + \cdots \quad (3.23)$$

As can be seen from the above expression, the level of complexity of the description, even for lower order terms is discouraging. Given this, Feynman diagrams are usually employed to track the different interaction terms contributing to the polarization. Transient absorption spectroscopy corresponds to a third order nonlinear spectroscopy originated from two interactions with the pump field and one interaction with the probe field. However, this spectroscopic technique can be explained and understood with a phenomenological approach. This phenomenological description will be the topic of the following section and the reader interested in a full nonlinear description of the technique is referred to the following books and notes in the subject [114–116].

3.3 Transient Absorption Spectroscopy

As mentioned before, the main results of this work involve the measurement of the transient absorption response of different molecular and molecule/semiconductor systems with femtosecond resolution. In this work, optical femtosecond transient absorption spectroscopy (TA) was used. This spectroscopy technique is classified as a pump-probe experiment. For a phenomenological description, the process can be separated into two parts. First, a transient state is produced by a relatively intense pump pulse. This intense pulse should be capable of exciting a noticeable fraction of the sample species (typically above 0.1%). Second, a weak probe pulse, that does not change the state of the population, is delayed a time τ relative to the pump. Then, the change in the probe intensity caused by the pump beam is measured at different wavelengths λ . In this way, a difference absorption spectrum at the given delay τ is generated. By repeating this process for different delay times, the transient absorption spectra can be reconstructed in a similar way to a stroboscopic measurement.

The measured absorption difference signal, $\Delta A(\lambda, \tau)$, is calculated as:

$$\Delta A(\lambda,\tau) = \log\left[\frac{I_0(\lambda)}{I(\lambda,\tau)}\right]_{on} - \log\left[\frac{I_0(\lambda)}{I(\lambda,\tau)}\right]_{off}.$$
(3.24)

In the above equation I refers to the transmitted intensity of the probe beam, and the subindexes 0, on, and of f respectively refer to the blank, pump on, and pump off cases. Due to the high correlation between two subsequent pulses from current laser systems, it was shown that the error introduced by assuming $[I_0]_{on} = [I_0]_{off}$ [117, 118] is smaller than other noise sources. Thus, it is common to simplify expression 3.24 as

$$\Delta A(\lambda,\tau) = \log\left[\frac{I_{off}(\lambda,\tau)}{I_{on}(\lambda,\tau)}\right].$$
(3.25)

The above expression can take either positive or negative values. The origin of the contributions are depicted in Figure 3.3 and can be grouped in the following five



Figure 3.3: Schematic of a transient absorption experiment (a). Origin of the different contributions to the $\Delta A(\lambda, \tau)$ signal (b).

processes:

- 1. Excited state absorption (ESA). This process is a positive contribution to ΔA arising from an increased absorption from the excited species, $I_{on} < I_{off}$. It takes place when optically allowed transitions exist for the transient population generated by the pump at the probed wavelength.
- 2. Stimulated emission (SE). A negative contribution to ΔA can be observed when the number of photons in the probe beam increases by photons being emitted from the sample producing $I_{on} > I_{off}$. This process takes place when a photon stimulates an excited species and triggers the emission of an additional photon with the same energy and momentum. This process occurs for radiative allowed transitions and follows the general pattern of the fluorescence spectrum.⁸
- 3. Ground state bleach (GSB). This process is the second negative contribution. It arises again for $I_{on} > I_{off}$ but this time the cause is not the emission of photons but rather a decrease in the number of them being absorbed by the sample. This contribution is observable when the number of species in the ground state is reduced by the pump. It is usually detected where steady state absorption bands are present.
- 4. Product absorption (PA). This contribution arises from absorption originated from new species formed after the excitation pulse. These new products can be produced by photoinitiated chemical reactions, electron transfer or energy

⁸ Under a second quantization formalism, fluorescence is nothing else than stimulated emission by virtual photons originated from fluctuations of the quantized electromagnetic field.

transfer processes. The contribution is observed as a positive signal and by a not-recovering ground state bleach.

5. Contributions external to the model. Under certain conditions, transient absorption signals will have contributions arising from non-linear interactions between the light pulses and the probed medium. Thus, they are usually seen on fast timescales and depend on the spectral and temporal characteristics of the pumpprobe pair of pulses. Under the theoretical description presented in section 3.2 these contributions are fairly well understood and can in principle be considered in the analysis. However, from an experimental point of view, it is a challenging task to deal with them because its description requires a high level of characterization of both pulses and the medium being probed. Given this, under the phenomenological approach here presented, all contributions outside the four previously mentioned that do not represent population dynamics, are treated under the term "coherent artifacts". From an experimental perspective is always important to minimize the contribution of this type of signals.

3.3.1 Femtosecond Absorption Spectrometer

Transient absorption spectrometers are relatively well-stablished tools, and several commercial systems are available. However, our study demands to have a setup that allows measuring systems in solution, solid-state samples, and samples under high vacuum conditions. Additionally, the flexibility of fine adjustment of the time resolution of the instrument as well as the wavelength range of operation made a home built system a better choice for this study. Briefly, our setup employs the tunable output of the NOPA as the pump beam and a supercontinuum (450-720 nm) generated in a sapphire plate as the probe beam. The cross-correlation of pump and probe beam was taken as the instrument response function (IRF) and was kept below 30 fs by using a prism pulse compressor. A single wavelength detection scheme was implemented using a monochromator (Oriel Cornerstone-260 74125), a biased Si photodiode (Thorlabs DET10A), and a lock-in amplifier (Signal Recovery 7230 DSP). A detailed description of the system is given next.

As can be seen in Figure 3.4, transient absorption spectrometers can be divided into four parts: supercontinuum stage, pump delay line, sample chamber, and signal detector. In the following, each component will be described in detail.



Figure 3.4: Schematic of the transient absorption spectrometer.PB: Parabolic mirror, SP: Sapphire plate, BS: Beam splitter, DL: Delay line, MCM: Monochromator, PD: Photo diode.

Supercontinuum probe. The instrument in question used a supercontinuum probe generated by focusing 0.1 μ J in a 3 mm thick sapphire window with a 50 mm focal length fused silica lens. To achieve a single-filament, stable supercontinuum with the desired spectral components, a careful control of the focusing parameters is necessary. In this setup, the numerical aperture, position of the focus within the crystal, and power of the incoming beam was finely tuned by an iris, a reflective neutral density filter, and a translation stage. Optimizing these three parameters is a challenging task due to the high order nonlinear mechanisms involved in the continuum generation process. Thus, fine adjustment requires some hands-on experience on the setup. Several studies on the relation between the different parameters and the supercontinuum output have been done by the Riedle group and are summarized in Bradler's dissertation. [119] Their results were a useful starting point to generate an optimal supercontinuum in the transient spectrometer as well as in the NOPA. After generation, the continuum was collimated with a 90° off-axis parabolic silver mirror with an effective focal length of 50 mm. The use of this mirror minimizes spherical, and chromatic aberrations in the broadband pulse. Afterward, the broadband pulses were sent into a compressor composed of a pair of BK7 prisms. This design allows a high resolution of the experiment at a single wavelength compared to transient absorption spectrometers that use an uncompressed probe beam to allow multichannel detection over the whole continuum spectrum. [117, 120, 121] The compressor design was chosen for two reasons: first, a time resolution below 50 fs was necessary, second, a multichannel detector capable of operating at 10 kHz was not available in the laboratory at the time. Nonetheless, the prism compressor in the setup proved to be the most challenging part to maintain and operate. Along the course of this work, the design saw various improvements. Finally, the compressor was set to function in three distinct configuration modes depending on the system under study. The first of these setting gave the best possible time resolution attainable with our setup (IRF < 20 fs); it was used when a high-resolution kinetic trace at a single wavelength was required. When operating in this mode, the distance between prisms and the amount of glass in the beam path was adjusted following standard procedures to minimize the IRF at the desired wavelength. [122] The second mode of operation was used when several kinetic traces, or a spectrum scan (generated by a stepwise scan of the monochromator), was required without the need of high temporal resolution. For this configuration, the distance between prisms was adjusted to minimize the cross-correlation between the pump and the central wavelength of the desired spectra. Finally, the third configuration gave the best compromise between time resolution and automatized multiple wavelength scans. To do this we start from the second configuration, then the amount of glass in the beam path is changed by translating the prism transversely to the incoming beam with a stepper motor. For this configuration to work, a calibration curve is required. This curve relates to each wavelength a position of the stepper motor that produces the smallest possible IRF. It is worth mentioning that in all the above procedures, adjusting the prism distances to minimize the IRF is a long and iterative process. Given this, it is important to perform a rough adjustment of the distance first. This adjustment is achieved, by maximizing the second harmonic signal of the spectral component in question.

Pump delay line. The pump beam coming from the NOPA is first focused

through the blades of a chopper wheel. The chopper modulates the signal for the Lock-In amplifier. Then, the beam is brought close to recollimation with a lens mounted on a translation stage. This adjustment allows making slight changes in the beam diameter of the pump beam when it hits the sample. Next, it crosses a half wave plate that allows changing the relative polarization between probe and pump beams. Finally, the beam is delayed from the probe beam by hitting a corner-cube aluminum retroreflector (PLX Inc) mounted on a DC-servo motorized stage (PI M410.DG).

Sample chamber. Pump and probe beams were focused onto the sample using the same off-axis parabolic silver mirror with a 200 mm effective focal length. This geometry results in an intersecting angle around 3.5° and a spot diameter of 350 μ m for the pump. The probe beam diameter was always below 100 μ m. The beam diameters were regularly checked because they can introduce artifacts in the measurement by a partial overlap of the beams. To do this, the knife-edge method was used for the intense pump beam. However, this technique proved to be inappropriate for the low intensity of probe beam. To measure the spot diameter of the probe a set of pinholes with different aperture sizes were used. As mentioned before, an advantage of our setup is the capability to measure different sample types. For samples in solution, a quartz (Spectrosil) 1 mm path cuvette (Starna Cells) was mounted on a fixture capable of x-y-z positioning plus two orthogonal rotations around the axes perpendicular to the incoming beam. The degrees of freedom allow an accurate adjustment of the position of the overlap and the angle between the cuvette window and the incoming beams. Measurements on the sensitized semiconductor electrodes were done in a high vacuum chamber. The setup can accommodate a home-modified microscopy cryostat (CRYO RC102-CFM) used as a vacuum chamber. The chamber has a pair of 0.5 mm fused silica windows, and was kept at 10^{-7} mbar by a turbomolecular pump (Pfeiffer Vacuum HiPace80). The same degrees of freedom can be adjusted in the vacuum chamber.

Signal detection. After the sample, the probe beam was spatially filtered, collimated, and focused onto the slit of a monochromator. The grating (Newport 74072) used inside the monochromator for the experiments was blazed at 475 nm

and had 300 l/mm. At the monochromator's output, a biased Si photodiode (Thorlabs DET10A) collects the signal. The photodiode's signal was sent to the Lock-In amplifier together with the reference signal of the chopper, which frequency was set to 337 Hz. Finally, the phase of the lock-in was adjusted by setting the signal to be positive using a known sample with a strong positive signature like ZnTPP.

3.3.2 Measurement Procedure and Acquisition Software

After the description of the transient absorption spectrometer used in this study, it is important to clarify the process followed to get the TA data. The steps followed are:

- 1. The first step in a measurement consists in the tuning and alignment of the NOPA. This assures that the pump beam has the right power and wavelength.
- 2. Similarly, the aperture and focus geometry that generates the probe beam should be adjusted. The aim is to obtain a stable white light filament. This optimization was carried by minimizing the noise of the white light measured by displaying the output of a photodiode in an oscilloscope.
- 3. Once the pump and probe beam satisfy the requirements, the beams are spatially overlapped on a 100 μ m pinhole. At this point, it is also useful to measure the spot size of each beam at the focal point. The spot size of the pump beam can be adjusted by the translation of a collimating lens after the SHG stage.
- 4. After having a good spatial overlap, the temporal overlap can be found in two ways. One is by finding the sharp TA signal of a strongly absorbing molecule like ZnTPP. The second one is by looking for the frequency mixing signal obtained by placing a non-linear BBO crystal at the sample's position.
- 5. At this point, it is important to measure the cross-correlation (CC) signal of pump and probe beams. This signal will determine the IRF of the experiment. To minimize the IRF it is important to fine tune the prism compressor at the output of the NOPA. To account for the glass in the cuvette, the CC should be measured and minimized after 1 mm of quartz.
- 6. Once the spatial and temporal overlap have been checked, a strong absorbing sample with a known transient spectra is placed in the holder. To find the TA signal, the delay between pump and probe is set to several ps. After this, the sample should be translated to the point where it maximizes the TA signal. This is done for the following reasons: First, the position of the overlap changes as a consequence of diffraction from the cuvette. In addition, the time zero point also

changes as a result of the previous adjustments. And most important, aligning on artifacts at early times should be avoided.

- 7. Once the TA signal is maximized, the waveplate in the pump beam is adjusted to get the desired polarization. Most of the measurements were carried at the so-called magic angle polarization, which is the angle that averages out the contribution of selective excitation. Then the phase in the lock-in should be adjusted based on a known spectra.
- 8. At this point, minor adjustments should be done to maximize the signal. Depending on the strength of the TA signal, the scale and integration time of the lock-in amplifier should be adjusted (usually 20 to 200 ms).
- 9. Finally, the parameters for the scan can be set in the home-developed LabVIEW aquisition software and the measurement can be started.

The acquisition software requires the following parameters: an array of wavelengths to measure, and an array of time delays to scan. For a quick scan, the delays can be set to be uniformly distributed between an initial and final range. However, for systems with relaxation dynamics spanning different time scales, a non-uniform step scan is faster and advantageous. In this case, the time steps were distributed in a quasi-exponential way. This gives a constant time step size between -1 and 1 ps and the rest of steps increase according to

$$\Delta t(i) = \begin{cases} -1 + \frac{2i}{N} & \text{for } i = 0 \dots N - 1, \\ 1^{-1 + i/N} & \text{for } i = N \dots M. \end{cases}$$
(3.26)

In the above equation, N stands for the number of points between -1 and 1 ps and M is the maximum delay time calculated as

$$M = N(1 + \log \Delta t_{max}) \tag{3.27}$$

The initially linear scan is helpful for the correction of the continuum chirp, while the exponential sampling minimizes the measurement time. This time scale has been proved useful because it generates the same number of delay points from -1 to 1 ps as between 1 and 10 ps, 10 and 100 ps and so on. [117] Hence, if a fitting routine is applied to such a data set, the dynamics on every time scale will have equal weight. For a proper data representation and a clear analysis of the baseline of the measurement, additional, uniform distribution points are added before time zero.

Once the array of delay steps are feed into the acquisition software, the acquisition software moves the spectrometer to the desired wavelength. Then a scan is initiated by moving the delay stage to the desire time delay position and the lock-in amplifier collects data for a time given by four times the integration constant of the instrument. Finally several scans will be taken and averaged to get the final transient absorption kinetic trace.

3.3.3 Data Analysis

Spectroscopic data provides an indirect measurement of the intrinsic properties of the system in question. Thus, every spectroscopic experiment needs to be analyzed based on a suitable model. Nevertheless, every model carries assumptions and approximations that should be clearly stated and understood. From first principles, it is possible to describe a pump-probe experiment as a light-matter interaction using Liouville's formalism introduced in section 3.2. This formalism describes the time evolution of the density matrix operator in quantum mechanics. Namely,

$$\dot{\boldsymbol{\rho}} = -\frac{i}{\hbar} \left[H_0 + V(t), \boldsymbol{\rho} \right] - \Gamma \boldsymbol{\rho}.$$
(3.28)

If the potential term V(t) originates from the interaction between the electric field Eand the samples dipole moment μ as

$$V(t) = \boldsymbol{\mu} \cdot \boldsymbol{E}(t), \qquad (3.29)$$

the Liouvillevon Neumann equation leads, under the dipole and rotating-wave approximation, to the so-called optical-Block equations (OBE). [123]
In theory, one could solve the OBE equations to find the corresponding elements of the density matrix. However, a simpler model, based on linear rate equations can be applied. From a mathematical perspective, the rate equation approach has been proved to be asymptotically equivalent to the OBE if the dynamics of the system are slower than the decoherece time. [124] In the following, the rate equation model will be discussed in detail. The physical basis of the model is: from a theoretical point of view, the Einstein rate model for photoexcited transitions, and from an experimental one the Beer-Lambert law. For the two-level system depicted in Figure 3.5 the Einstein coefficients will give rise to the following linear rate equations.

$$\dot{N}_{1}(t) = I_{0}I_{pump}(t) - \frac{1}{\tau_{inj}}N_{1}(t)$$

$$\dot{N}_{2}(t) = \frac{1}{\tau_{inj}}N_{1}(t) - \frac{1}{\tau_{rec}}N_{2}(t)$$
(3.30)

where $I_{pump}(t)$ denotes the intensity of the pump pulse and I_0 is a constant prefactor. The source term, $I_{pump}(t)$, is proportional to the square of the envelope of the pump electric field. Referring to the previous model, the measured transient absorption signal at a delay time τ , $S_{N_2}(\tau)$, is calculated as the convolution of the probe pulse and the population of the N_2 state,

$$\mathcal{S}_{N_2}(\tau) = \int_{-\infty}^{\infty} I_{probe}(t-\tau) N_2(t) dt.$$
(3.31)

If the envelope of the pump pulse $I_{pump}(t)$ is considered to be Gaussian, the solution for $N_2(t)$ will be expressed in terms of the error function an can be cumbersome. To avoid this, it is convenient to exploit the fact that there is only one source term in equations 3.30. Hence, the solution can be written again as the following convolution:

$$N_2(t) = \int_{-\infty}^{\infty} I_{pump}(t') \tilde{N}_2(t-t') dt', \qquad (3.32)$$

where the tilded quantity refers to the solution of the homogeneous case of the set of

equations 3.30. Mainly,

$$\tilde{N}_1(t) = N_0 \exp\left(-\frac{t}{\tau_{inj}}\right) \tag{3.33}$$

$$\tilde{N}_2(t) = N_0 \frac{\tau_{rec}}{\tau_{rec} - \tau_{inj}} \left[\exp\left(-\frac{t}{\tau_{rec}}\right) - \exp\left(-\frac{t}{\tau_{inj}}\right) \right]$$
(3.34)

Inserting equation 3.32 into equation 3.31 and interchanging the order of convolutions using the commutation of integrals gives the following result:

$$\mathcal{S}_{N_2}(\tau) = \int_{-\infty}^{\infty} \tilde{N}_2(t') \int_{-\infty}^{\infty} I_{pump}(t-t') I_{probe}(t-\tau) dt dt'.$$
(3.35)

The second integral term in the last equation corresponds to the experimentally measure cross-correlation of the pump and probe pulses, i.e., the instrument response function (IRF). Thus, lifetimes from the different states can be extracted through a deconvolution procedure with the measured IRF. The previous description represents the simplest data fitting method for pump-probe signals. However, this description only works under the assumption that there are not coherent terms in the OBE. The question regarding the point at which the rate equation model is not accurate anymore has been addressed by several authors. [97, 125, 126]. In particular, Ernstorfer [97] compared simulations of HET processes up to injection times of 15 fs. He concluded that the main difference between the two approaches was a temporal shift of the signals maximum. If the temporal position of the maximum of the signal, also called timezero, is left as a free parameter in the fitting procedure, the rate equation model reproduces the OBE signal quite reasonable. In this study, this was the approach followed regarding the fitting procedure.

Now, to generalize the rate model for more than two levels, and allow the inclusion of non-radiative transitions, additional independent pathways, must be included. These additional relaxation channels are not known a priori and their integration pose the following inverse problem: recover the appropriate relaxation scheme, in addition to the spectroscopic and kinetic parameters from the observed signal $\Delta A(\lambda, t)$.



Figure 3.5: Sequential relaxation pathway in a two-level system.

The earlier studies using transient absorption experiments did not face this challenge because they were characterized by the relatively small amount of data. These studies mostly focused on fitting few kinetic traces with a minimum number of exponential decays. Nowadays, the availability of multichannel detectors, high repetition lasers and an overall improvement in laser stability, have contributed to the production of large amounts of data that requires a more careful analysis. Because of this, the approach based on multivariate data analysis techniques, and the nomenclature introduced by van Stokkum et al. is now commonly found in the literature. [127]

This multivariate analysis scheme builds on the following assumptions:

- Homogeneity. The system is assumed to be homogeneous because the observed dynamics of the ensemble can be ascribed to individual members. Thus the system can be described with a discrete set of parameters.
- Separability. The transient absorption signals can be thought to be originated from a set of emitting and absorbing states. Hence, the signal can be modeled as a superposition of the spectroscopic properties of each state weighted by their concentration. This assumption is nothing else than the Beer-Lambert law.⁹ The

 $^{^9}$ The law is named after August Beer and Johann Heinrich Lambert, and consist of two experimental observations. The first one states that absorbance of a material sample is directly proportional to

transient absorption signal is separated as

$$S_{\lambda} = \sum_{i=0}^{n} A_i^{\lambda} N_i(t), \qquad (3.36)$$

where A_i^{λ} is the independent amplitude at each wavelength, and $N_i(t)$ is the population of each state.

• Stochastics. The measurements are assumed to contain additive Gaussian distributed noise.

The *n* terms involved in equation (3.36) represent the states participating in the relaxation process. The idea of the fitting procedure is to keep the number nat the minimum that allows fitting the signals at all wavelengths, using the same number of states, without a systematic deviation of the residuals. Thus, the signal at a given wavelength has a weighted contribution from the population of each state. The time-dependent population of each can now be obtained by solving a set of linear rate equations that allow parallel and sequential decays. In the absence of a priori knowledge on the relaxation model, it is useful to consider an entirely parallel and sequential model. For the case of an entirely parallel model, the population dynamics of each state is independent of each other. And the set of coefficients A_i^{λ} constitute what is called the decay associated difference spectra (DADS). If the model is assumed to be unbranched, and all states are connected in series, the dynamics of each state is given by a linear combination of decays. In this sequential case, the A_i^{λ} coefficients are known as the evolution associated difference spectra (EADS). On the other hand, a model inspired by scientific hypotheses and assumptions that can potentially include parallel and sequential decays is called a target model. With a target model, the associated spectral coefficients are called species associated difference spectra (SADS).

In this work, thanks to the fairly well-understood photophysics of the tetrapyrrole systems, a target analysis was implemented. Thus, the set of equations representing

its thickness. The second one states that absorbance is proportional to the concentrations of the attenuating species.

the imposed relaxation model were:

$$\dot{N}_{0}(t) = -Bg(t) + \sum_{j} \frac{1}{\tau_{j}} N_{j}(t),$$

$$\dot{N}_{1}(t) = Bg(t) - \sum_{k} \frac{1}{\tau_{k}} N_{1}(t),$$

$$\dot{N}_{i}(t) = \sum_{j} \frac{1}{\tau_{j}} N_{j}(t) - \sum_{k} \frac{1}{\tau_{k}} N_{i}(t).$$

(3.37)

In the last set of equations τ_j are the time constants associated to the $N_j \to N_i$ population transitions, whereas τ_k represent the $N_i \to N_k$ depopulation constants. The term Bg(t) in equations 3.37 acts as a source term that represents the pump pulse and is composed of the amplitude B and the Gaussian envelope

$$g(t) = \exp\left[-4\ln(2)\left(\frac{t-t_0}{W_{IRF}}\right)^2\right].$$
(3.38)

This function takes into account W_{IRF} as the width at half maximum of the IRF. Therefore, the fitting procedure aims to find a set of parameters $\{A_i^{\lambda}, \tau_i\}$ that produce the best global fit and represent the lifetime and signal amplitude of each species.

3.4 Additional Instrumentation

3.4.1 Prism Based Spectrograph

In the late stage of the project, an improvement in the transient absorption spectrometer was the design and construction of multiple wave detection capability using a CCD camera. The data discussed in this dissertation was not acquired with this setup. Similar multiple wave detection setups have been successfully used in transient absorption spectrometers. [117] The advantages of a prism spectrometer over a grating spectrometer are: the high transmission throughout a large spectral range when used at Brewster angle configuration, and the absence of higher order diffraction.

A schematic of the setup is displayed in Figure 3.6. It consists of an adjustable mechanical slit (Thorlabs VA100), a collimating silver spherical mirror (R=-400 mm),



Figure 3.6: Schematic of the home-built prism spectrometer.

a silver turning mirror, a BK7 Pellin-Broca prism (Thorlabs ADB-10), a focusing silver mirror (R=-500 mm), a silver turning mirror, and a high-speed line scan camera (e2V EV71YEM1GE1014-BA9). The camera is the core of the design and allows a single shot spectra aquisition at 10kHz. The choice of all reflective optics reduces chromatic aberrations. The small angle of reflection of the spherical mirrors and the double reflection geometry from two spherical mirrors reduces spherical aberrations. The selection of the collimating mirror gives the instrument a 200 mm focal length. The focal length and the height of the dispersing prism (10 mm) gives the device an optical acceptance cone of f/20. The Pellin-Broca prism was chosen because of its 90° deflection that simplifies the optical design. The focusing spherical mirror was selected from commercially available mirrors to produce a spectral range in the 420-760 nm range on the CCD array. A consequence of the non-linear dispersion introduced by the prism is that the focal plane is tilted and slightly curved. These aberrations were characterized during the design process by adding bandpass filters and finding the position of the focus for different wavelengths. The focal tilt can be compensated by tilting the detector at angle $\theta \sim 59^{\circ}$ as shown in Figure 3.6. Contrary, correction of the curvature of the focal plane is not an easy task, and the aberration was accepted. It was previously determined that the error introduced by this effect was below the Raleigh resolution criteria for the device.

The spectrometer, being a home-built instrument, allows for a relatively easy change of the spectral range, alignment, calibration, and future improvements. All optical elements are mounted on adjustable optical holders, and the focusing spherical mirror is mounted on a translation stage for fine tuning of the focal length. The alignment procedure was done by placing a bright commercial fluorescent lamp as close as possible to the adjustable slit. The slit was closed as much as possible while still having an acceptable signal on the detector. The distance between the focusing mirror and the fixed sensor is critical to allow the resolution of the spectral peaks from the fluorescent lamp. So, if the instrument is completely misaligned this must be the first step to do. Next, an iterative process must be implemented to optimize the resolution. The iteration process consists of performing a two-dimensional optimization (walking the beam) to put the desired part of the spectrum on the 1024 pixels CCD array while trying to keep the tilt angle ($\theta = 59^{\circ}$) unchanged, followed by adjustment of the focal distance using the micrometer translation stage. Figure 3.7 shows a comparison of the performance of the home-built instrument against a commercial fiber spectrometer when recording the spectra of a common fluorescence lamp.

The CCD camera is capable of acquiring 12 bit spectral lines at the native 10 kHz repetition rate of our laser system. Because of this, particular attention is required in the implementation of the acquisition software to be able to handle the data at the same rate. This was done by implementing a producer-consumer software architecture in LabVIEW®. This software architecture relies on separating and balance the hardware resources in charge of the acquisition and processing of the data. A subroutine of the software is interfacing with the camera and reads the array of pixels, calculates the logarithm of the array and assigns a tag depending on the state of the pump beam. The state of the pump can be on or off depending on the position of a synchronized chopper



Figure 3.7: Comparison of the fluorescent lamp spectra recorded with a commercial fiber spectrometer and the home-built setup herein described.

wheel. The producer subroutine then stores the data in a queue that is available to the consumer subroutine. The consumer subroutine calculates the difference in absorption by subtracting signals with different pump state tags.

Chapter 4

ENERGY LEVEL ALIGNMENT WITH DIFFERENT ELECTRONIC STATES

This chapter presents addresses the first objective, measures the electron transfer rate for two different energy level alignments. These different alignments were obtained by exciting electrons into two different electronic states. The measurements were done by using the phlorin, $3H(Phl^F)$ molecular system described in section 2.2. The results of the relaxation dynamics of the phlorin system in solution are presented and discussed first. Afterward, the results of the HET rates from the S₁ and S₂ states of $3H(Phl^{CO_2H})$ into TiO₂ are explained and discussed using the previous knowledge of the dynamics in solution. Finally, at the end of the chapter the results and conclusions obtained by this experimental design are summarized.¹

4.1 Phlorin System in Solution

4.1.1 Spectral properties

As mentioned before, to disentangle the HET rates it is important to have a thorough understanding of the intra-molecular relaxation process. With this intention, the transient absorption spectra of $3H(Phl^F)$ was measured in toluene. The transient

¹ The results discussed in this chapter were published in 2015 and can be found in reference [128]. The author of this dissertation is the first author of the cited publication. This chapter is mainly a slightly modified reprint of the mentioned article. The images and text herein shown are reprinted with permission from RSC Publishing as stated in their policy: "You do not need to request permission to reuse your own figures, diagrams, etc, that were originally published in a Royal Society of Chemistry publication. However, permission should be requested for use of the whole article or chapter except if reusing it in a thesis. If you are including an article or book chapter published by us in your thesis please ensure that your co-authors are aware of this. Reuse of material that was published originally by the Royal Society of Chemistry must be accompanied by the appropriate acknowledgement of the publication". [129]



Figure 4.1: Normalized absorbance difference spectra at different delay times following Soret band excitation. Dashed lines show the wavelengths at which kinetic traces were measured.

spectra after excitation of the Soret band are shown in Figure 4.1. There are several features in these spectra that can be noted. First, there is a positive peak with a maximum around 510 nm assigned to a mixture of two contributions. The first of these contributors is the early singlet excited state absorption (ESA) $S_1 \rightarrow S_n$, similarly observed in previous porphyrin studies. [130–133] Second, the previously mentioned peak evolves into a weak absorption plateau after ~50 ps which is assigned to the absorption of the triplet state $T_1 \rightarrow T_n$. This triplet ESA feature was assigned given the similar absorption signatures from triplet states reported in theoretical and experimental studies. [133–135] Third, there exists an isosbestic point at 590 nm separating the absorption signal from a peak with negative signal centered at 650 nm. Finally,



Figure 4.2: Comparison of the relaxation dynamics of $3H(Phl^F)$ for different solvents. Solid lines represent the fit.

the negative signal at 650 nm is a mixed contribution of ground state bleach (GSB) and stimulated emission (SE). Consequently, the short wavelength part of the negative peak is mainly attributed to the bleach of the $S_0 \rightarrow S_1$ transition, in agreement with by the steady state spectrum. At wavelengths longer than 650 nm the negative signal is expected to show the predominantly contribution from SE, which generally follows the steady-state emission spectra.

An additional spectral feature was observed for the case of Soret excitation of $3H(Phl^F)$ in a polar solvent; a long-lived contribution at 720 nm (Figure 4.2). An unambiguous assignment of this solvent-dependent signal is a challenging task and requires further investigation. However, its absence in non-polar solvents, after Q band excitation, and in measurements on $3H(Phl^{CO_2H})$ suggests that it is connected to an excited state that is localized primarily on the fluorinated phenyl groups and stabilized by polar solvents. The rest of the spectral components were solvent polarity independent. For this reason, measurements in toluene are taken as the standard throughout this work except for Figure 4.3c where cyclohexane was used for 720 nm detection wavelength. Since HET measurements are the primary goal of our study, and these experiments were performed in vacuum conditions, measurements with a



Figure 4.3: Normalized kinetic traces of 3H(Phl^F) in toluene (panel a and b) and cyclohexane (panel c) after Soret excitation. The insets show the long term behavior of the signal. Solid lines represent the fit and the contribution of each state to it.

non-polar solvent were conducted for comparison. Kinetic traces were measured at the probe wavelengths indicated as dashed lines in Figure 4.1. Namely, 540 nm to monitor the S_1 and T_1 ESA, 650 nm to track the GSB and SE, and 720 nm to follow the SE. These traces are shown in Figure 4.3 following Soret excitation. Likewise, Figure 4.4 shows the traces after Q band excitation. For the latter case, traces at 650 nm were not taken due to the strong signal arising from scattered pump light.



Figure 4.4: Normalized kinetic traces of $3H(Phl^F)$ in toluene following Q band excitation. The insets show the long term behavior of the signal. Solid lines represent the fit and the contribution of each state to it.

Besides the previously mentioned long-lived contribution no significant difference between $3H(Phl^F)$ and $3H(Phl^{CO_2H})$ was found. Particularly, during the first 9 ps, the traces are indistinguishable from each other (Figure 4.5). Thus, the same relaxation model, shown in the Jablonski diagram in Figure 4.6, was used for both phlorin derivatives.

4.1.2 Relaxation dynamics.

To reproduce the relaxation dynamics after excitation of the Soret band; a target analysis was used. A model with five consecutive decay process between six states was required to fit all the measured traces globally. In contrast, following Q band excitation, only the last four process, connecting five of the previously identified



Figure 4.5: Comparison of the relaxation dynamics between 3H(Phl^F) and 3H(Phl^{CO₂H}) in toluene. Both systems were successfully fit with the same model.

states contribute to our signal. The assignment of the signals to individual states will be discussed next. The global fit parameters for Figure 4.3 and Figure 4.4 are summarized in Table 4.1.

The first population has a lifetime of ~150 fs. Following Soret excitation, the lifetime of this state is observed as a rise at 540, 650, and 720 nm. This time constant is not observed at any wavelength following excitation of the Q band, where the S_1 state is populated directly. The early dynamics following excitation in the individual states are shown in Figure 4.7. This state is thus identified as S_2 , which is populated instantaneously during Soret band excitation. Its lifetime is observed as a rise time after Soret excitation in the S_1^{hot} population (see below). The measured lifetime agrees with previously reported results for free base porphyrins in solution, [131, 136] as well as gas phase measurements. [137, 138] The ultrafast relaxation from S_2 to S_1 indicates relaxation through a conical intersection. [137]

The second state is identified as a vibrational hot S_1 species, denoted S_1^{hot} , with a lifetime of $\tau_2 \sim 180$ fs after Soret excitation. This time-constant is only observed in the SE signal $S_1 \rightarrow S_0$ as a decay. In contrast, the $S_1 \rightarrow S_n$ transition can in principle always access a corresponding vibrational level in the upper excited state S_n . Thus, the



Figure 4.6: Relaxation model for the phlorins after Soret and Q band excitation.

dynamics of the S_1^{hot} relaxation process is not observed at 540 nm. This is indicated in Figure 4.6 by the green and maroon arrows. The dynamics associated with the S_1^{hot} state appear as a decay with a small amplitude at 650 nm on top of the bleach signal, along with a decay at 720 nm (green line in Figure 4.3 and Figure 4.4). The lifetime of this state after Q band excitation is $\tau'_2 \sim 90$ nm, shown in Figure 4.7. The reduced lifetime after Q band excitation can be attributed to the reduced amount of excess vibrational energy. This time constant is similar to those assigned to vibrational cooling processes within the Q bands of other porphyrins. [131, 136]



Figure 4.7: Early dynamics after excitation of the Q and Soret bands of $3H(Phl^F)$ in toluene.



Figure 4.8: Calculated molecular orbitals for the HOMO, LUMO, and LUMO+1 of 3H(Phl^F) and proposed change in the conformation around the meso carbon. Notice the missing bridging orbital across the sp³ hybridized *meso*-carbon in the LUMO.

The third state, with a lifetime around 6 ps, is assigned to an intermediate step in the relaxation of the Q band. This state dominates the dynamics of the SE signal at 720 nm (orange line in Figure 4.3 and Figure 4.4). The lifetime of this state was not affected by changing the excitation wavelength, and hence conventional vibrational cooling can be excluded. Processes with similar dynamics have been observed in other porphyrins [131, 136, 139, 140] and have been assigned to either solvent-induced vibrational energy redistribution, [136] or conformational changes in the relaxation pathway of non-planar porphyrins. [139, 140] It is known that conformational relaxations can be sensitive to solvent polarity [141] due to the difference in polarity between the two states. A change of ~40% in the lifetime of the state was measured when using protic (methanol) as well as aprotic (DMF) polar solvents when compared to non-polar solvents (cyclohexane). In addition, molecular orbital calculations of $3H(Phl^F)$, depicted in Figure 4.8, show that the S₁ state has a node at the sp³ hybridized *meso*-carbon in contrast to the S₀ and S₂ states. This together with the measured buckling at the *meso*-carbon in the phlorin ground state, suggests that the geometry of the S₁ state differs from that of the S_0 and S_2 states. Therefore, a conformational relaxation process consisting of the flattening of the macrocycle in the S_1 state is proposed. This process is thus assigned to a conformational change in the macrocycle of the phlorin, and the corresponding state is labeled S_1^{buckled} .

The fourth state corresponds to the vibrationally cold S_1 band and has a lifetime of 32 to 44 ps depending on the solvent. This lifetime is assigned to $S_1 \rightarrow T_1$ intersystem crossing (ISC), and agrees with the fluorescence lifetime of the molecule. Similar lifetimes for ISC have been previously observed in free base porphyrins as a consequence of the heavy-atom effect. [142, 143] Besides, the time constant is in agreement with previously reported fluorescence lifetime measurements of $3H(Phl^F)$ by picosecond transient fluorescence measurements. [78] The population of this state appears as an absorption at 550 nm, as well as a negative signal at 650 and 720 nm. The contribution of this state to the fits is indicated by the red line in Figure 4.3 and Figure 4.4.

Finally, the fifth state is assigned to the triplet state T_1 with a lifetime longer than 120 ps. Thus, this process exceeds the temporal detection window of our experiment. This state is assumed to decay to the ground state with a time constant corresponding to the phosphorescence lifetime, which in the case of free base

transient absorption kinetics of $3H(Pin)$ in non-polar solvent.								
Excited Band	Probe	A_1^{λ}	A_2^{λ}	A_3^{λ}	A_4^{λ}	A_5^{λ}	A_0^{λ}	
	[nm]	S_2	$\mathrm{S}_1^{\mathrm{hot}}$	$\mathbf{S}_1^{\mathrm{buckled}}$	S_1	T_1	S_{0}	
	540	0	0.26	0.33	0.32	0.09	0	
Soret	650	0	-0.44	-0.23	-0.25	0	0.08	
	720	0	-0.56	-0.32	-0.12	0	0	
Q	540	0	0.33	0.30	0.30	0.07	0	
	720	0	-0.62	-0.30	-0.08	0	0	
Time [ps]]	$ au_1$	$ au_2^a$	$ au_3$	$ au_4$	$ au_5$	b	
constants	3	0.15	0.18	5	44	>120		

Table 4.1: Summary of time constants (τ_i) and amplitudes (A_i^{λ}) corresponding to the transient absorption kinetics of $3H(Phl^F)$ in non-polar solvent.

^{*a*}This time constant is reduced to 0.09 ps for Q band excitation.

^bThe ground state is repopulated with the triplet lifetime.



Figure 4.9: Band alignment of anatase TiO_2 and $3\text{H}(\text{Phl}^{\text{CO}_2\text{H}})$. All energies are given in eV. The dark gray area represents the calculated DOS for anatase (101) reproduced from Ref. [95].

porphyrins is characterized by a very low quantum yield. [142–144] Population of this state is observed as an absorption at 540 nm, and its lifetime governs the GSB recovery at 650 nm. This is in agreement with reported triplet state absorption in porphyrins. [134, 135] Its contribution to the fits is indicated as the blue line in Figure 4.3 and Figure 4.4.

4.2 Phlorin System on TiO₂ Films

4.2.1 Level alignment.

Before the discussion of the electron injection process, it is important to know the energy band alignment between $3H(Phl^{CO_2H})$ and the TiO_2 film. The position of the HOMO was calculated from the work function of anatase of 5.1 eV [145, 146] and the ionization potential of free-base porphyrin of 6.4 eV [147]. Following a proposed universal level alignment [31] a HOMO to Fermi level offset of 1.65 eV can be expected. It has been shown that the Fermi level is very close to the conduction band



Figure 4.10: Kinetic traces of TiO_2 sensitized with $3\text{H}(\text{Phl}^{\text{CO}_2\text{H}})$ after Q and Soret excitation.

edge in colloidal anatase. [148] Assuming an offset of 50 meV results in a HOMO to valence band edge offset of 1.5 eV when using the well-established anatase band gap of 3.2 eV. This value agrees well with experimental results for Zn-porphyrin bound to rutile TiO₂. [83] It should be noted that the level alignment for porphyrins does not change significantly upon substitution of side groups, [83] or removal of the central metal atom. [149] Therefore, we assume a HOMO offset of 1.65 eV for our system and deduce the position of the S₁ and S₂ state from the respective optical gaps. This results in the level alignment shown in Figure 4.9 that includes a difference of 0.9 eV between the first and second excited states of the phlorin. The proposed alignment has to be taken with care since changes in the surface composition can lead to significant shifts. The calculated density of states (DOS) for the defect-free anatase (101) surface is shown in dark gray (reproduced from Ref. [95]). It is important to note that due to the very narrow maximum of the DOS, the DOS that is resonant with the S_1 and S_2 state differs strongly regardless of a systematic energy shift between the molecular states and the TiO₂ DOS. Assuming that the full width of the electron transfer spectrum can be accommodated inside the conduction band and that the electronic coupling between excited molecular state and TiO₂ acceptor states is constant over the whole energy range, it can be expected that the ET rate is proportional to the density of acceptor states. Thus, a significant difference for HET times from both states is expected from elementary considerations. It is the aim of this work to test this assumption for the 0.9 eV difference in the energy level alignment.

4.2.2 Spectroscopic properties.

Steady state absorption of the sensitized TiO_2 film resembles the absorption spectrum of 3H(Phl^{CO₂H}) depicted in Figure 2.6. The only observed difference was a reduction in the Q band absorption. The absorption spectrum was measured before and after the transient absorption experiment and no noticeable changes were observed. Kinetic traces at 550, 650, and 710 nm were measured after excitation of the Soret band, and at 550, and 750 nm after Q band excitation. All kinetic traces show a 50 ± 10 fs contribution. This contribution appears as the rise time of all measurements after Soret excitation, as can be seen in Figure 4.10b, Figure 4.13 and Figure 4.14b, and is significantly faster than the $S_2 \rightarrow S_1$ transition observed in solution. After Q band excitation, the signals measured at 550 nm (S_1 absorption band) show a rise with the IRF followed by a fast 50 fs decay (Figure 4.10a and Figure 4.12). The same time constant is observed as a rise at 750 nm, identical to the dynamics measured after Soret excitation. This behavior can be explained by the knowledge of the lack of ESA from the second excited state. In this way, the 50 fs decay observed after Q band excitation corresponds to electrons being injected, and the 50 fs rise time after Soret excitation corresponds to the rise of the cationic absorption. The 50 fs process is on the same time scale as previously reported injection times for other porphyrins, [132, 133, 150, 151] and



Figure 4.11: Injection model of TiO_2 sensitized with $3\text{H}(\text{Phl}^{\text{CO}_2\text{H}})$. The injection rate was found to be the same for Soret and Q band excitation.

is assigned to HET.

At later times, excited traces after Soret or Q band excitation can be fit with the same time constants throughout the whole probe spectrum using the target model shown in Figure 4.11. These processes have lifetimes of 0.5, 3.8 and >300 ps, and were attributed to cation relaxation based on the similar process measured for the intra-molecular relaxation and electron recombination for the expected long cation lifetime. [133] The diagram showing the corresponding injection model is depicted in Figure 4.11, and a summary of the parameters used for the fits is shown in Table 4.2. The assignment of the different contributions to the signals is supported by the

		-	(/		<u> </u>	
	in Figure 4.10	0, Figure 4.1	3, and Figur	re 4.14			
	Excitation Dand	Probe	A_1^{λ}	A_2^{λ}	A_3^{λ}	A_4^{λ}	
Excitation 1	Excitation Dand	[nm]	S_1	PI_1	PI_2	PI_3	
		550	0	0.74	0.24	0.02	
	Soret	650	0	0.49	0.34	0.17	
		710	0	0.42	0.37	0.21	
	O hand	550	0.79	0.11	0.07	0.03	-
Q Dalid	Q Danu	750	0	0.50	0.33	0.17	
	Time		$ au_1$	$ au_2$	$ au_3$	$ au_4$	
	constants [ps]		0.05	0.5	3.8	>300	

Table 4.2: Summary of time constants (τ_i) and amplitudes (A_i^{λ}) corresponding to the transient absorption kinetics of $3H(Phl^{CO_2H})$ attached to TiO_2 displayed in Figure 4.10. Figure 4.13, and Figure 4.14



Figure 4.12: Early dynamics of electron injection process for Q and Soret excitation. The intensity is scaled at long delay times. The Soret signal can be fitted with only the contribution of post-injection species generated after Q excitation. The decay after Q band excitation (red) resembles the rise after Soret excitation (blue).

following. First, the clear correlation between the 50 fs decay and rise time of the signals after Q and Soret excitation, as well as the similarity of the dynamics after the injection process for both excitations. This can be seen in Figure 4.12. Second, no negative signal associated with $S_1 \rightarrow S_0$ SE was detected after Soret excitation, indicating that the S_1 state is not significantly populated. This is shown in Figure 4.13 and Figure 4.14b. Also, traces obtained at 750 and 710 nm show the same 50 fs rise



Figure 4.13: Kinetics of the sensitized film probed at 650 nm after Soret excitation.



Figure 4.14: Kinetics of the sensitized film probed outside the S_1 absorption band. Notice the similarity of the signals after both excitations.

time and very similar decay dynamics after Q and Soret excitation, as can be seen in Figure 4.14. The latter suggests that the two signals arise from the same post-injection processes as expected from the cation being formed independently of the excited band. Finally, the slow relaxation dynamics of the post-injection processes PI_1 , PI_2 , and PI_3 detected throughout the probe spectrum agree well with absorption characteristic of the cation. Cation absorption spectra have been reported for free base [152] and metal [132] porphyrins, and show a broad flat absorption between 500 nm and 750 nm. Also, long cation lifetimes up to several nanoseconds have been reported [133] in agreement with the long-lived PI_3 contribution in our signal that can not be resolved within our temporal detection window. These measurements show that HET proceeds with a 50 fs time constant from both states regardless of the large difference in DOS. It should be noted, that this time scale can be easily resolved with our instrument and that it is clearly different from the time constants measured for intramolecular dynamics in solution. Figure 4.15 shows a comparison of the measured electron transfer rates against the predicted rates assuming the steady state surface density of states shown in Figure 2.9. The expected rates were calculated using two assumptions. First, the WBL condition is satisfied; hence, HET rates are given by equation 1.10. Second, the electronic coupling factor (V_{DA}) is assumed constant and was fixed to generate a 50 fs injection time for a driving force of $|E - E_{fermi}|=0.25$ eV.



Figure 4.15: Comparison of the measured HET rates from phlorin into TiO_2 against the predicted rates considering a steady state density of states

4.3 Conclusions

The ultrafast excited state dynamics in a phlorin molecule was investigated after S_1 and S_2 excitation. The overall dynamics is comparable to those reported earlier for other porphyrin derivatives. In addition to the $S_2 \rightarrow S_1$ internal conversion and initial vibrational relaxation, both occurring in the sub-200 fs time scale, a reorganization of the phlorin macrocycle was observed. The reorganizational relaxation of the macrocycle involves the phlorin sp³ hybridized meso-carbon, and can be ascribed to bending motions. This leads to a buckling of the porphyrin ring in the 5 ps time scale. The observed intersystem crossing $S_1 \rightarrow T_1$ in this strongly fluorinated phlorin is very efficient when compared to unsubstituted porphyrins due to the heavy atom effect of the fluorine atoms.

The intra-molecular dynamics measured in the solvent environment changed dramatically when the phlorin molecule was attached to colloidal TiO_2 via a carboxylic acid anchor group. HET with a time constant around 50 fs competes with intramolecular relaxation pathways and results in the formation of the phlorin cation.

In contrast to the expected significant change in HET dynamics between the S_1 and S_2 state due to the difference in DOS, identical dynamics for electron transfer from both states were observed. This observation can be explained either by assuming that the DOS does not have a major influence on HET, or that the assumption that the coupling between donor and acceptor state is energy independent is wrong. In the latter case, the difference in DOS could in principle be compensated by stronger coupling for the S_2 state. However, since this explanation would require a fine balance between two uncorrelated quantities, it is less likely. HET dynamics that is independent of DOS, on the other hand, would suggest that the first step of ET, *i.e.* the formation of the cation, involves states that are different from the surface DOS for bare TiO_2 . The involvement of such intermediate states has been proposed recently, mostly with regard to defect states. However, the very high efficiency of initial injection quantum yield in molecule/TiO₂ systems used for DSSC [153] suggests that these intermediate states are inherently present in the system and may better be characterized as transition states that are not observed in the DOS obtained from calculations or steady state measurements. Transient spectra of the molecular molecular data of an HET system do not give the full picture for charge separation in HET. Two-photon photoelectron spectroscopy would be one way to perform complementary measurements that allow for the dynamics of electrons after HET in the conduction band to be elucidated. [154]

Chapter 5

ENERGY LEVEL ALIGNMENT WITH DIPOLE-BRIDGE GROUPS

This chapter presents the results corresponding to the second approach to change the level alignment. Namely, the level alignment was modified by the introduction of dipole groups in a ZnTPP porphyrin. Specific details on the molecule can be found in section 2.2. HET rates were measured from three different molecules looking for a correlation between the injection rates and the energy position of the excited state. Similarly to the previous chapter, the results corresponding to the relaxation of the molecules in solution are presented first. The measurements of the HET rates into colloidal TiO₂ are discussed afterward. The chapter ends by summarizing the results and conclusions of the experiments.¹

5.1 ZnTPP systems in Solution

Photophysics of ZnTPP chromophores has been extensively investigated in the past. [90–92, 131, 157–160] For comparison, femtosecond transient absorption spectroscopy (TA) was measured in solution to reproduce the reported dynamics for commercial ZnTPP.

Figure 5.1 shows TA traces for compounds 1-3 at the indicated probe wavelength after excitation of the Soret band at 420 nm. Transients have been measured at three different wavelengths to monitor the dynamics of the S_2 and S_1 excited state absorption

¹ The results discussed in this chapter were published in 2016 and can be found in reference [155]. The author of this dissertation is the first author of the cited publication. This chapter is mainly a slightly modified reprint of the mentioned article. The images and text herein shown are reprinted with permission from ACS Publications as stated in their policy: "Authors may re use all or part of the submitted, accepted or published work in a thesis or dissertation that the author writes and is required to submit to satisfy the criteria of degree-granting institutions. Such reuse is permitted subject to the ACS Ethical Guidelines to Publication of Chemical Research". [156]



Figure 5.1: Transient absorption at the indicated wavelength of the three compounds in ether after Soret excitation. The global fit and its decomposition into contributions from individual states is indicated. The difference in dynamics between the compounds 1 and 3 and compound 2 is indicated for 520 nm probe wavelength by the blue shaded area.

(ESA), the stimulated emission (SE) and the ground state bleach (GSB). Global fitting to a rate model at these wavelength allows extracting lifetimes for the individual states. Two different relaxation models were used. The first one is the sequential model applied to the relaxation processes for commercial ZnTPP and **2** shown in Figure 5.2. The extracted time constants for this model are given in Table 5.1 and the corresponding amplitudes are shown in Table 5.2. Briefly, after Soret excitation the negative signal at 550 nm appears within our IRF; it is attributed to GSB in accordance with the steady-state spectrum of the Q band. The positive signals at 520 nm and 655 nm



Figure 5.2: Jablonski diagram showing the well-known intramolecular photodynamics of ZnTPP. The relaxation times for ZnTPP and **2** are given in Table 5.1.

show rise times between 100 fs and 120 fs. These time constants are considered to originate from vibrational relaxation within the S₂ state. This assignment was still debated [91, 161] at the time the data was taken for this dissertation. However, recent studies from our research group, using four wave-mixing spectroscopy, have resolved the doubts and assigned it to a vibrational process. [162] The blue dashed line in Figure 5.1 includes relaxation processes in the S₂ state. The femtosecond relaxation is followed by internal conversion (IC) from S₂ to S₁ in about $\tau_2 = 1.5 \pm 0.1$ ps. This process appears as a positive contribution at all wavelengths assigned to ESA (red dashed line in Figure 5.1). At 655 nm a 10 ps relaxation component followed by a slow relaxation (>500 ps) is observed. Measurements at 550 nm show a 100 ps component followed

Table 5.1: Summary of time constants (τ_i) of the absorption kinetics of the studied compounds. Amplitudes can be found in Table 5.2.

System	$\tau_1(\mathrm{fs})$	$\tau_D(\mathrm{ps})^a$	$\tau_2(ps)$	$\tau_3(ps)$	$\tau_4(ps)$	$\tau_5(ns)$
ZnTPP	120		1.8	10	100	1.8
2	120		1.5	10	100	1.8
$\mathbf{1/3}$	110	3.5	1.5	10	100	1.8

^{*a*} The energy transfer process (τ_D) is present only in **1** and **3**, cf. Figure 5.4.

by a >500 ps process. At 520 nm only the slow process (>500 ps) is observed. The 10 ps and 100 ps processes have been assigned to vibrational relaxation (VR) within the S_1 state and are the subject of ongoing research. [91, 163] The slowest component in our model was set to 1.8 ns, corresponding to the fluorescence lifetime. For clarity, the relaxation processes within the S_1 band were combined in the red dotted line of Figure 5.1.

As discussed above, ZnTPP and **2** shows overall the same dynamics. This is in agreement with studies showing that the photo-physics of Zn-porphyrins was not affected by functionalization of one of the meso-phenyl groups. [80, 83] On the other hand, compounds **1** and **3** showed different dynamics at 520 nm and 550 nm (Figure 5.1 blue shaded area at 520 nm) while the dynamics at 655 nm was almost identical to **2**. The wavelength dependence indicates that the respective process is coupled to the S_2 excited state since at 655 nm predominantly S_2 population is probed. This is also supported by TA measurements in solution after Q band excitation that

System	Probe	Amplitudes					
(= +]= = = =)	$\lambda \ (nm)$	A_0^{λ}	A_1^{λ}	A_2^{λ}	A_3^{λ}	A_4^{λ}	A_5^{λ}
(ether)		S_{0}	$\mathrm{S}_2^{\mathrm{hot}}$	S_2	$\mathbf{S}_1^{\mathrm{hot}-1}$	S_1^{hot-2}	S_1
	520	0	0	0.17	0.24	0.29	0.30
Zn-TPP	550	-0.26	0.02	0.09	0.22	0.23	0.18
	655	0	0.50	0.35	0.07	0.03	0.05
	520	0	0	0.22	0.29	0.25	0.24
1	550	-0.23	0.01	0.22	0.21	0.16	0.17
	655	0	0.47	0.23	0.14	0.08	0.08
	520	0	0	0.20	0.26	0.27	0.27
2	550	-0.23	0.03	0.11	0.22	0.22	0.19
	655	0	0.50	0.27	0.08	0.07	0.08
	520	0	0	0.20	10.28	0.27	0.25
3	550	-0.22	< 0.01	0.23	0.19	0.21	0.15
	655	0	0.56	0.17	0.11	0.08	0.08

Table 5.2: Summary of amplitudes (A_i^{λ}) of the global fits applied on the studied compounds.



Figure 5.3: Transient absorption of the studied compounds after Q band excitation.



Figure 5.4: Molar absorptivity of the nitroaniline linker and S_2 fluorescence of ZnTPP.

show identical dynamics for all three compounds at 520 nm (Figure 5.3). The UV-vis spectrum indicates that direct excitation of the nitroaniline group is very weak and not likely to be the reason for the change in dynamics. To confirm this, we performed TA measurements under identical conditions on the bridge group alone (diphenyl-N,N-dimethyl-4-nitroaniline). The weak absorption around 420 nm (Figure 5.4) required 15 times higher concentration for achieving a comparable TA signal at 550 nm probe wavelength.

Therefore, direct excitation cannot account for the additional signal from 1 and 3 in Figure 5.1. As a side note, the dynamics of the weak TA signal from the nitroaniline group is similar to dynamics reported earlier for p-nitroaniline. [164] The next



Figure 5.5: Comparison of the S_1 fluorescence QY of the studied compounds after Soret band excitation (a), and after Q band excitation (b). The fluorescence quenching only takes place after Soret band excitation. This is in agreement with an energy transfer process from the S_2 state.

possible explanation is energy transfer from the Zn-porphryin chromophore S_2 state to the excited state of the nitroaniline group. The spectral overlap shown in Figure 5.4 is favorable for energy transfer. Energy transfer from Zn-porphyrin should result in quenching of the fluorescence from the S_1 state. Steady-state fluorescence quantum yield (QY) measurements comparing QY from the three compounds showed that fluorescence is indeed quenched by 20% in **1** and **3** when compared to **2** (Figure 5.5). Fluorescence lifetime measurements confirmed that the lifetime of the S_1 state was not affected by the nitroaniline group (Figure 5.7). At the same time, no difference in QY was detected after Q band excitation. The 20% loss in QY corresponds to an energy transfer time of around 6 ps from the S_2 state to the bridge group. Energy transfer adds another pathway for de-exciting the S_2 state that is indicated as τ_D in Figure 5.6.

By applying the branched relaxation model shown in Figure 5.6, the photodynamics of 1 and 3 can be fit globally by assuming an energy transfer time constant



Figure 5.6: Jablonski diagram including energy transfer from the S_2 state of ZnTPP to the nitroaniline group.

 τ_D =3.5 ps, a value that is in overall agreement with the fluorescence QY measurements. For the fit, all time constants were kept constant while small adjustments to the amplitudes were necessary to account for changes in spectral weight. Fit parameters are summarized in Table 5.1 and Table 5.2. This confirms that energy transfer accounts for the difference in intramolecular photodynamics. To distinguish between Förster and Dexter energy transfer, the expected Förster energy transfer was calculated from the distance between chromophore and semiconductor surface and the overlap integral. [165] The resulting 200 ps are much longer than the observed 3-6 ps and indicate that Dexter energy transfer is the prevailing mechanism.

5.2 ZnTPP Systems on TiO₂ Nanoparticles

HET in the film can in principle occur from the S_1 and S_2 state. Energy transfer to the nitroaniline group is not expected to influence HET from the S_1 state. UPS measurements of the ground state level alignment combined with UV-Vis spectra indicated that the S_1 excited state is located around the Fermi level about 100 meV below the conduction band edge when absorbed on ZnO. Intrinsically n-doped ZnO single crystals and TiO₂ nanoparticles have similar band gap energies and Fermi level alignment. Hence, a similar molecular level alignment can be expected. Accordingly, no signature of fast HET can be observed in TA measurements after excitation of the



Figure 5.7: S_1 fluorescence lifetimes of the studied compounds after Soret band excitation (a), and after Q band excitation (b). The deconvoluted lifetimes (1.8 ns) were identical for both cases. This is in agreement with an energy transfer process taking place from the S_2 state.

Q band. The fastest time constant for the decay of the S_1 state is around 9 ps (Figure 5.8a). This decay is at least one order of magnitude slower than expected when compared to systems with similar bridge groups [22, 133, 166]. Therefore, we conclude that the S_1 excited state is located below the conduction band edge at the TiO₂ interface and the slow decay is likely governed by injection into defect trap states [56]. Several TA measurements on similar systems found fast HET by evaluating the rise time of the probe signal around 600 nm. [22, 133] This assumption appears to be unreasonable in our case because the rise time resembles our instrument response function of 28 fs (Figure 5.8b). Sub-20 fs ET would be very fast considering the length of the linker group. [57] It should be noted that the previously published measurements were performed in a solvent environment while our measurements were performed in vacuum. Energy level alignment deduced from electrochemical measurements in solvent environment was different for these measurements when compared to level alignment measured by the Bartynski group via UPS in UHV. [88]



Figure 5.8: Transient absorption signal from solution (a) offset for visibility and from the film for compound 2 (b) after Q band excitation. The 9 ps fit to the decay is included in (a). Rising edge of the signal together with the instrument response function (IRF) and a fit with 20 fs rise time.

Comparison between the three compounds on the TiO₂ film after Soret excitation is complicated by the interaction between the ZnTPP chromophore and the nitroaniline group because it cannot be excluded that the excited state of the nitroaniline group is involved in the HET process for **1** and **3**. Indeed, TA traces for the three compounds at 520 nm and 620 nm when attached to colloidal anatase TiO₂ show that the dynamics of **2** differs slightly from that of **1** and **3** (Figure 5.11, and 5.12) while **1** and **3** show almost identical dynamics. A fit with a model that includes the HET process shown in Figure 5.9 results in an initial decay of 80 ± 7 fs for all three compounds (Figure 5.10, 5.11, and 5.12). Fit parameters for **1** and **3** are given in Table 5.3. The fast decay of the excited state absorption is assigned to electron injection into TiO₂. This is also supported by photocurrent measurements that clearly show electron injection from **1**, **2**, and **3** into TiO₂, [167] and by efficient fluorescence quenching. [80] This injection time agrees well with measurements on similar systems. [22, 166] It is clearly



Figure 5.9: Relaxation diagram for 1 and 3 on the TiO_2 film including HET. The energy axis is not to scale.

faster than the 1.5 ps S_2 - S_1 IC measured in solution (cf. Figure 5.1). The decaying signal on the ps time scale has previously been attributed to transient absorption from the cation for compounds similar to 2 and can be fitted with similar time constants that have been reported previously. [22,133] The difference in the ps dynamics between 1/3 and 2 is not easy to explain. The energy transfer on the 3.5 ps time scale should be negligible when competing with 80 fs HET. On the other hand, the LUMO of the

System	Probe	Amplitudes					
	$\left(nm\right)$	A_0^{λ}	A_1^{λ}	A_2^{λ}	A_3^{λ}	A_4^{λ}	
	λ (IIII)	S_0	S_2	\mathbf{P}_1	\mathbf{P}_2	P_3	
1	520	0	0.65	0.21	0.09	0.05	
	620	0	0.74	0.16	0.07	0.03	
3	520	0	0.65	0.21	0.11	0.03	
	620	0	0.75	0.15	0.07	0.03	
System	Probo	Time constants (ps)					
	11006		$ au_1$	$ au_2$	$ au_3$	$ au_4$	
1 and 3	520,620		0.08	2.7	25	>100	

Table 5.3: Summary of amplitudes (A_i^{λ}) and time constants (τ_i) of the global fits applied on **1** and **3** attached to TiO₂. The time constants were fixed for both systems at all wavelengths.



Figure 5.10: Transient absorption signal from the film after Soret-band excitation for two different time intervals.

nitroaniline group is near resonance with the excited state and can influence coupling to the electrode. The cation spectrum and dynamics of the di-phenyl nitroaniline group are not known and are hard to measure because of the weak transition dipole moment and since the concentration of the chromophore in the film can not easily be increased. Therefore, the discussion is focused on the comparison between the compounds **1** and **3** that show the largest difference in level alignment (200 meV) and at the same time identical HET dynamics. It should be noted that the dipole induced level shift of 200 meV was measured on a ZnO single crystal surface while our time-resolved measurements were performed on colloidal TiO₂. The binding geometry of the molecule on the surface is another important aspect that can influence the injection pathway and the projection of the dipole moment. IR-spectroscopy suggests a chelating or bidentate bond of the anchor group to TiO₂ that would support an upright binding geometry. [80]


Figure 5.11: TA signal at 520 nm of 1, 2, and 3 on TiO_2 after Soret band excitation. The curves are normalized at longer times.

In addition, previous measurements showed that through-space electron injection, in general, is slow and does not compete with through-bond injection in systems with injection times below 100 fs. [133,166,168] Therefore, is assumed that electron transfer occurs predominantly through the bond. Under this assumption, the relevant parameter is the dipole moment projected onto the molecular axis which is independent of the binding angle of the molecule. The independence of HET dynamics on level alignment is the main result of this experiment. The simple approximation for non-adiabatic HET rates k_{ET} is given by a Fermi-Golden rule expression:

$$k_{ET} = \frac{2\pi}{\hbar} \left| V_{DA} \right|^2 \mathcal{F}$$
(5.1)

The Frank-Condon weighted density of states \mathcal{F} is a sum over all possible donoracceptor combinations weighted by the respective Franck-Condon factor. In the socalled wide-band-limit the band of acceptor states in the semiconductor is wide enough, and the donor level is sufficiently above the lower band edge such that the whole ET spectrum can be accommodated. In this case, the FCWD is reduced to a pure DOS. Ramakrishna, Willig, and May developed a parametrized fully quantum mechanical model for HET that includes an electronic-vibrational quasi-continuum and allows to



Figure 5.12: TA signal at 620 nm of 1, 2, and 3 on TiO₂ after Soret band excitation.

compare HET dynamics as a function of crucial parameters like level alignment, reorganization energy, and electronic coupling V_{DA} . [169] Two of the cases that were compared in their work used parameters that are very close to systems 1 and 3 investigated here. The excited states were located 0.5 eV and 0.7 eV above the edge of a 1.4 eV wide band of acceptor states with constant DOS. A reorganization energy of 200 meV and a constant electronic coupling that gave rise to an electron transfer time of 84 fs in the wide band limit were assumed. Their calculations showed that even in the case of constant DOS and constant coupling strength HET times differ by about 18 fs, between 90 fs for 0.7 eV and 108 fs for 0.5 eV (fits to Figure 3 in Ref. 169). Comparison of fits with fixed injection times (62 fs and 98 fs) show that even in this case an energy dependent injection time can be resolved by our measurement (Figure 5.13). This difference would increase if one of the parameters showed energy dependence. It is known that the DOS of the TiO_2 anatase (101) surface shows a steep rise close to the CB edge. [58] On the other hand, calculations suggest that the coupling strength does not depend strongly on the energy. [60] The particular case where the energy dependence of the coupling is assumed to compensate the change in DOS exactly can not be excluded. However, considering our previous results this situation is not very likely. [128]



Figure 5.13: Close in of the TA signal at 620 nm of 1 and 3 on TiO_2 after Soret band excitation (symbols). The black line shows the best fit, it includes an electron injection (ET) component of 80 fs. The blue line includes a 65 fs ET time, and the red line includes a 95 fs component.

The fact that the measurements show identical HET times for both molecules can be explained by assuming a strong modulation of electronic coupling that favors acceptor states in resonance with the donor state or a strongly modulated transient DOS that is much narrower than the steady-state surface density of states. Both cases result in the same situation where the donor state only couples to a narrow band of acceptor states that makes HET virtually independent of level alignment. The distribution or density of these active acceptor states has not been observed in any steady-state measurements or calculations. It can be assumed to be governed by the formation of the excited state that leads to a transient electronic configuration. This electronic configuration determines the density of active acceptor states. However, restricting the donor-acceptor coupling to only a few states contradicts the non-adiabatic picture of HET because narrowing the band of acceptor states would require increasing the electronic coupling to keep the HET time constant. The electronic coupling in the example mentioned above was already around 8 meV. A considerably narrower band would require a much stronger electronic coupling, leading to a higher Landau-Zenner transition probability and, consequently, render the application of a non-adiabatic model questionable. It is interesting to note that the results coincide with recent measurements of inter- and intra-molecular photoinduced charge transfer reactions in molecular systems that show ET rates that are independent of the driving force in the inverted region. [170, 171]

From the measurements, it is concluded that the distribution of acceptor states cannot be deduced from parameters like the surface density of states and the electronic coupling alone. The discrepancy can be explained by the formation of a transient transition state during the first tens of femtosecond of the reaction that is different from the permanent surface or defect states found from equilibrium calculations. This short lived configuration is generated by the strong perturbation due to the excitation of the electron, and governs the density of acceptor states and consequently HET dynamics. These conclusions are supported by previous measurements from our group [128], and by other recent experiments. For example, Racke et al. found a new hybridized interfacial density of states that fundamentally alters carrier dynamics and changes the electronic structure [172]. While Siefermann et al. used femtosecond XPS to study HET and found strong indications for the formation of a transient electronic configuration. [173]

5.3 Conclusions

The photodynamics and electron transfer dynamics of a set of Zn-TPP derivatives with a variable dipole moment in the bridge group have been investigated. As expected, the intramolecular photodynamics resembled the well-known dynamics of the Zn-TPP chromophore. However, the dipole carrying nitroaniline group gave rise to Dexter energy transfer from the excited state of the Zn-porphryin chromophore.

Surprisingly, after comparing the measurements on the film, the two derivatives with oppositely oriented dipole moments that resulted in a shift of 200 meV in level alignment showed identical HET dynamics. The HET dynamics were compared with a previously published quantum mechanical model for non-adiabatic HET. This comparison gave a strong indication that the dye's excited state couples to a much smaller subset of acceptor states than expected from the electrode's surface density of states. Future work involving different chromophores, various dipole groups with possibly stronger dipole moments, and different semiconductor substrates will show if this is a general property of HET systems or specific to the combination that was herein investigated.

Chapter 6 SUMMARY

The heterogeneous electron transfer rates from various tetrapyrroles into colloidal anatase TiO_2 films were measured. These measurements were done using femtosecond transient absorption spectroscopy in a high vacuum environment. The objective of our measurements was to compare the electron transfer rates as a function of the energy level alignment. Two different experimental strategies were implemented to change the energy level alignment. Both strategies made use of novel synthesized molecules from collaborators.

The experimental setup required for this investigation was built as part of this research work. This work included the construction of a non-collinear parametric amplifier and a homebuilt transient spectrometer. The femtosecond spectrometer generated single wavelength kinetic traces and was able to resolve sub 30 fs components.

The first experimental strategy was the change of the energy level alignment by the excitation of two different electronic states of a phlorin. This approach exploits the fact that the two different excited states of the phlorin have a similar absorption strength and are both located above the conduction band minimum of TiO_2 . Similar previous experiments that attempted to compare the injection rates were forced to make the comparison on either different molecules or different electrodes. Thus, our experiments provide a better comparison.

The relaxation dynamics of the phlorin and its acid form were studied in solution as a prerequisite to elucidate the electron transfer rates. This relaxation dynamics was found to be similar to standard porphyrins, and an all sequential model was successfully applied. The identified sequential relaxation time constants were: a fast internal conversion of 150 fs between the second and first excited states, two internal vibrational relaxation processes of 180 fs and ~ 5.5 ps were identified in the singlet state, this is followed by a 33-44 ps intersystem crossing and a long >120 ps ground state recovery. Two of the identified processes separate the phlorin from standard porphyrins. The unusual fast and efficient intersystem crossing, and the picosecond internal relaxation process assigned to a reconfiguration of the nonplanar macrocycle.

Measurements of the phlorin when attached to TiO_2 produced two very different signals for the case of exciting the first or second excited state. Nevertheless, using the knowledge of the relaxation and spectroscopic properties of the phlorin, an electron transfer time of 80 fs was extracted from the signals. This contribution appeared as the decay time of the excited state absorption after excitation of the singlet state, and as the rise time of the cation absorption after excitation of the second excited state. The nature of these observed results arises from the fact that the phlorin does not show excited state absorption from the second excited state. The fact that the \sim 900 meV difference between the excited states of the phlorin shows the same electron transfer rate within our time resolution was unexpected from the common assumption that predicted a faster electron injection for the higher energy state.

The previously described strategy compared the HET rates from two different excited states, which in principle can have different coupling parameters (V_{DA}) . Hence, it was important to perform a comparison of electron injection rates originated from the same electronic state. This additional comparison was made by exploiting the recently proposed idea of varying the energy level alignment by the introduction of dipole groups within the dye molecules. The idea was successfully proved by collaborators, and three molecules were synthesized that allow tuning of the energy level alignment by up to 200 meV. The molecules in question were composed of a Zn-porphyrin as the chromophore with a nitroaniline group as the dipole in the bridge between the chromophore and the anchor group attached to the TiO₂ surface. The introduction of the dipole group did not produce major changes in the static spectroscopic properties of the compounds. However, transient absorption experiments in solution showed different relaxation dynamics when compared to the unsubstituted Zn-porphyrin. The measurements in solution of the two compounds including the mentioned dipole groups showed an ~ 3.5 ps relaxation component non identified in the unsubstituted molecules. This contribution was assigned to a Dexter energy transfer process in parallel to the intersystem crossing from the second excited state. This attribution was supported by fluorescence quantum yield and fluorescence lifetime measurements. Despite the presence of this unexpected process, the HET rates were extracted from measurements of the dyes attached to colloidal TiO_2 . This extraction was possible mainly because the injection transfer rates were found to occur on a femtosecond time scale, making the Dexter transfer process very inefficient. Thus, in a similar fashion to the experiments with the phlorin molecule, the same HET rates of 80 fs were measured for the case of a 200 meV difference in the energy level alignment. These measurements were compared with a theoretical model that predicted an 18 fs difference for a case with similar parameters. This small predicted difference lies at the limit of the quantitative resolution of our instrument, however, a qualitative comparison between the two extreme cases supports the conclusion of having injection rates independent of the energy level alignment.

The results obtained in this research are in agreement with each other. This work provides strong evidence against the commonly used assumption of the effect of the availability of acceptor states in the HET rates. The question initially posed by this dissertation, regarding the relation between the HET rate and the energy level alignment, can be answered in the following way:

- The HET reaction, in general, is not mediated by the bulk or surface steady states of the semiconductive electrode. The process is more likely to take place between the molecular excited state and a different subset of acceptor states than the steady state usually measured or calculated.
- This subset of transition states must be generated after the strong electronic redistribution at the interface produced by the light absorption process and their lifetime must be below the few femtosecond timescale.

• The nature and signature of this intermediate transient states still need to be elucidated and unequivocally detected.

The implications of the results herein presented have the following consequences for applications: the design of chromophores with desired spectroscopic properties can be done independently of the energy level alignment, and the presence of this transition states may generate bottleneck situations for apparently well-designed HET systems.

Extension of the present research work can be done in different directions. First, measurements on a different semiconductor substrates, ZnO for example, could help to understand the poor performance of energy conversion devices using this electrode despite some of its advantageous electronic properties. Second, once the dipole group strategy has been prooved successful to study HET, the introduction of different groups leading to a larger difference in the energy alignment could bring a stronger support to our experiments. Finally, various spectroscopic techniques, like two-photon photoelectron spectroscopy to monitor HET from the conduction band side, and four-wave mixing spectroscopies that allow tracking vibrational wave packet motions, could bring light into the research field.

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