Ultrafast, Non-Equilibrium Electron Transfer Reactions of Molecular Complexes in Solution

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Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmslaboratoriet, Lägerhyddsvägen 1, Uppsala, Friday, 19 December 2014 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Professor Antonín Vlček (Queen Mary University of London).

Abstract

Photoinduced electron transfer is a fundamentally interesting process; it occurs everywhere in the natural world. Studies on electron transfer shed light on questions about the interaction between molecules and how the dynamics of these can be utilized to steer the electron transfer processes to achieve a desired goal. The goal may be to get electrons to the electrode of a solar cell, or to make the electrons form an energy rich fuel such as hydrogen, and it may also be an input or output for molecular switches. The importance of electron transfer reactions will be highlighted in this thesis, however, the main motivation is to gain a better understanding of the fundamental processes that affect the rate and direction of the electron transfer.

A study of photoinduced electron transfer (ET) in a series of metallophorphyrin/bipyridinium complexes in aqueous solution provided fresh insight concerning the intimate relationship between vibrational relaxation and electron transfer. The forward electron transfer from porphyrin to bipyridinium as well as the following back electron transfer to the ground state could be observed by femtosecond transient absorption spectroscopy. Both the reactant and the product states of the ET processes were vibrationally unrelaxed, in contrary to what is assumed for most expressions of the ET rates. This could be understood from the observation of unrelaxed ground states. The excess energy given by the initial excitation of the porphyrin does not relax completely during the two steps of electron transfer. This is an unusual observation, not reported in the literature prior the studies presented in this thesis. This study also gave the first clear evidence of electronically excited radical pairs formed as products of intramolecular electron transfer. Signs of electronically excited radical pairs were seen in transient spectra, and were further verified by the observation that the rates followed a Marcus normal region behavior for all excitation wavelengths, despite the relatively large excess energy of the second excited state.

This thesis also concerns electron transfer in solar cell dyes and mixed valence complexes. In the ruthenium polypyridyl complex Ru(dcb)$_2$(NCS)$_2$, where dcb = 4,4’-dicarboxy-2,2’-bipyridine, inter-ligand electron transfer (ILET) in the 3MLCT state was followed by means of femtosecond transient absorption anisotropy that was probed in the mid-IR region. Unexpectedly, ILET was not observed because electron density was localized on the same bpy during the time-window allowed by the rotational lifetime.

Keywords: electron transfer, laser, spectroscopy, transient absorption, anisotropy, inter ligand electron transfer, dye sensitized solar cell, DSSC, vibrational relaxation, ultrafast dynamics, fs spectroscopy

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ISSN 1651-6214
urn:nbn:se:uu:diva-235461 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-235461)
Till Ruth & Henry
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


VI Julien Warnan, James Gardner, Loïc Le Pleux, Jonas Petersson, Yann Pellegrin, Errol Blart, Leif Hammarström, and Fabrice Odobel “Multichromophoric Sensitizers Based on Squaraine for NiO Based Dye-Sensitized Solar Cells” J. Phys. Chem. C 2014, 118, 103–113

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Contribution report

I  I did all of the experimental work and data analysis. I contributed significantly to the writing of the manuscript.

II  I did all the experimental work and data analysis. I am the main responsible for writing of the manuscript. I also took an active part in FSRS measurements and did all analysis of those.

III  I planned the study. I did all the experimental work, both the photophysical studies and the synthesis of the three viologens (DM 2I, 4,4’-Me-DM 2I, MVCN 2Br) I am the main responsible for writing of the manuscript.

IV  I did all the femtosecond spectroscopy and analysis. Synthesis and characterization was carried out by my collaborators. I am the main responsible for writing of the manuscript.

V  I planned the study. I took active part in the FSIR experiments, which were done in collaboration, and did all data analysis. I am main responsible for writing of the manuscript.

VI  I did the femtosecond spectroscopy measurements, and data analysis of that data. I contributed significantly to the writing of the manuscript.
Contents

1 Motivation and outline ........................................................................................................ 13
  1.1 Understanding electron transfer for controlling reactions ........................................ 14
    1.1.1 Photosynthesis; artificial and natural .................................................. 14
    1.1.2 Dye sensitized solar cells ....................................................................... 15
  1.2 Aim of the research .................................................................................................... 15
  1.3 Outline of the thesis .................................................................................................. 16

2 Theory .................................................................................................................................. 17
  2.1 Basic concepts of photophysics ............................................................................... 17
    2.1.1 Light-molecule interaction ....................................................................... 17
    2.1.2 Absorption and emission spectra ............................................................ 18
    2.1.3 Electronic vs. vibrational transitions ...................................................... 19
    2.1.4 Vibrational energy relaxation ................................................................... 19
    2.1.5 The fate of electronically excited states .................................................. 21
    2.1.6 Franck-Condon principle (vertical transitions) .......................................... 22
  2.2 Ultrafast and non-linear processes ......................................................................... 24
    2.2.1 Coherence and dephasing ......................................................................... 24
    2.2.2 Raman scattering ...................................................................................... 25
  2.3 Electron Transfer Theory ......................................................................................... 26
    2.3.1 Basic concepts of electron transfer ............................................................ 26
    2.3.2 The effects of nuclear tunneling in the inverted region .............................. 29
    2.3.3 The solvent controlled adiabatic limit ...................................................... 31
    2.3.4 Interplay between solvent dynamics and electron transfer ....................... 32
    2.3.5 Vibrational tunneling in competition with solvent relaxation .................. 36
    2.3.6 Electron transfer reactions from unrelaxed states ...................................... 37

3 Methods .......................................................................................................................... 39
  3.1 Lasers .......................................................................................................................... 39
  3.2 Pump-probe laser spectroscopy .............................................................................. 40
    3.2.1 Transient absorption ................................................................................. 40
    3.2.2 Spectroscopy with polarized light ............................................................. 42
    3.2.3 Stimulated Raman spectroscopy ............................................................... 44
  3.3 Data modeling (data analysis) .................................................................................. 45
    3.3.1 First order reactions ................................................................................... 45
    3.3.2 Response function ..................................................................................... 46
    3.3.3 Artifacts in transient absorption spectroscopy ......................................... 47
4 Interplay of relaxation dynamics and electron transfer (papers I-III) ... 51
  4.1 Porphyrin photophysics ................................................................. 53
    4.1.1 Absorption and emission spectra of porphyrins ..................... 53
    4.1.2 Excited state absorption of porphyrins .................................. 54
  4.2 Electron transfer to electronically excited radical pairs .............. 55
    4.2.1 Spectroscopy of radical ions ............................................... 56
  4.3 Electron transfer in competition with vibrational relaxation ...... 57
    4.3.1 Absorption spectra of unrelaxed states ................................... 58
    4.3.2 Stimulated Raman studies ..................................................... 60
  4.4 Concluding remarks, Electron transfer from higher excited states ... 62
    4.4.1 What is a direct spectroscopic observation? ............................ 63

5 Intra-molecular electron transfer dynamics in competition with inter-
molecular electron injection (paper IV–VI) ............................................. 65
  5.1 ILET – a rate determining step in charge injection? (paper V) ....... 67
    5.1.1 Transient absorption anisotropy as a tool to investigate ILET ... 68
    5.1.2 Structure of N712 and predicted anisotropy values .................. 69
    5.1.3 Unexpectedly slow rate of ILET ............................................. 70
    5.1.4 Initially delocalized state? ..................................................... 71
    5.1.5 Consequences for injection dynamics ..................................... 72
  5.2 Charge transfer to semi-conductors (paper VI) ............................. 72
    5.2.1 Increasing the DSSC efficiency by intra-molecular charge
    separation ....................................................................................... 73
  5.3 Mixed valence dynamics (paper IV) .............................................. 74
    5.3.1 Inter valence charge transfer in the mixed valence state .......... 75
    5.3.2 Towards time-resolved inter-valence charge transfer ............... 75
    5.3.3 Unrelaxed ground states as indicators of excited state
    dynamics ....................................................................................... 76

Svensk sammanfattning ........................................................................... 77

References ............................................................................................... 82
Abbreviations and symbols

UV Ultra violet
vis visible
IR infrared
IC Internal conversion
ISC Inter-system crossing
VR vibrational relaxation
VER Vibrational energy relaxation (same as VR)
IVR intramolecular vibrational energy redistribution
VC vibrational cooling
ET electron transfer
FET forward electron transfer
BET back electron transfer
CT charge transfer
CS charge separation ("CS state" reads charge separated state)
CR charge recombination
ILET inter-ligand electron transfer
IVCT inter-valence charge transfer
MLCT metal-to-ligand charge transfer
TA transient absorption
FSRS femtosecond stimulated Raman spectroscopy
DSSC dye-sensitized solar cell

Symbols in spectroscopy
\(\lambda\) wavelength
\(\tilde{\nu}\) wavenumber (= \(\lambda^{-1}\))
\(\epsilon\) molar extinction coefficient
\(k\) rate constant
\(\tau\) lifetime (for excited states)
\(\tau\) time-constant (for relaxation and transitions between states)

Symbols in electron transfer
D donor (molecule)
A Acceptor (molecule)
\(\lambda\) reorganizational energy
\(H_{RP}\) electronic coupling (between reactant and product state)
\(k_{ET}\) rate constant for electron transfer
$-\Delta G^0$  reaction free energy

$\omega$  angular frequency (for an average vibrational mode)
1 Motivation and outline

First I want to tell you the story of how I came into this field, the field of ultrafast electron transfer dynamics and laser spectroscopy. Let’s start at the beginning. As a kid I always liked to make things, put things together, and take things apart. Soccer goals, trash bins for small compartments, binoculars (could never put them together again), hi-fi amplifier (not that one either), sail rig for a wooden model sailboat, stuffed dragon, etc. Then when I got older and started high school the environmental impact that humans have on the planet also made its way into my mind. I started thinking of waste treatment and how we used our resources. Eventually I studied engineering physics at university to hopefully be able to come up with a new energy source, and again I came to think of the small parts in the world. I realized I wanted to take the world apart and look at it. So I went to CERN as a summer student to work with the giant synchrotron (Figure 1) and to look for the Higg’s boson. I then realized that fundamental particles were maybe a bit too much on the small scale of things. One day I walked past a door where it said that soon the department of photochemistry and molecular science will move in. That sounded perfect; I hardly knew anything about photosynthesis, laser spectroscopy, or electron transfer, but it did sound amazing. I could get to know the world on a very small scale and maybe it could be put together again for something useful (I still haven’t put it together though). Now I have come to realize that exactly what I’m studying is not the important part. The important part is that I get to study the very tiny parts of our world and maybe, hopefully, someday someone can use that knowledge for something good. If not, then at least we know a little more about the world.

Figure 1. A photo of me running in the LHC tunnel at CERN in July 2005.
So with that story in mind the honest answer to how this thesis has come together is that I want to do fundamental research. And why I want to do it is because I like to map out things and figure out how they work. Who knows what we would not have known today if people didn’t study all kinds of things also without defined purpose and usefulness. There are also cultural aspects of fundamental research. I think research is important for the development of our society very much like other arts.¹

1.1 Understanding electron transfer for controlling reactions

Having a vision can be quite helpful also for the scientist who is driven more by the fundamental aspects of research. While putting the research in context and make it more understandable for a general audience it can also be an important source of inspiration for research ideas.

Besides being a very interesting physical phenomenon in and of itself, electron transfer is also a key part in many important processes; in particular those processes that involve harvesting sunlight to produce energy. The electrons can be both the desired end result, such as for photovoltaic devices (solar cells), but also a crucial intermediate step such as in the natural and artificial photosynthesis the end product of which is an energy rich fuel. These types of reactions are those that have inspired my work the most, but the list of processes that involve electron transfer is nearly endless. So, understanding electron transfer can help powering the planet with clean energy, but it can also lead to something yet unpredicted. In the following paragraph I will describe the two mentioned areas where better understanding of electron transfer is desired. These are also the areas from where the research ideas in this thesis have sprung.

1.1.1 Photosynthesis; artificial and natural

The natural photosynthesis consists of multiple intricate reactions whose overall goal is to take the energy of the sunlight and produce a fuel that can be used for the growth of the plant. In these reactions electrons are taken from water (where oxygen is released) and transported via a chain of electron transfer reactions. In the end of this the electrons are used to produce carbohydrates, a fuel that plants use. The reactions are initiated by the absorption of sunlight in what is called photosystem (PS) I and II. Chromophores (light-absorbing molecules) that are arranged as an antenna system absorbs light and transfers the corresponding energy to the chlorophyll units (P₆₈₀ in PS II and P₇₀₀ in PS I) where the electron transfer chain starts. The first steps of both these electron transfer chains occur on the time-scale of
only a few picoseconds or even faster (1 ps = 10^{-12} s). The fast reactions are needed in order to prevent the electron to recombine with its initially oxidized \( P_{680} \) and \( P_{700} \).

Artificial photosynthesis aims to mimic certain parts of natural photosynthesis. A chromophore (dye molecule) absorbs light and this energy rich molecule can now oxidize water, \( 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \). In a following step the protons and electrons are combined to form molecular hydrogen, \( 2H^+ + 2e^- \rightarrow H_2 \), which can be stored and used as a fuel. To increase the efficiency of this process several intermediate electron transfer steps could be involved, just as in the natural photosynthesis. It is of interest to have a better understanding of factors that influence the electron transfer in order to optimize the process and convert as much as possible of the incoming sunlight to a useful fuel. The studies of ultrafast electron transfer presented in this thesis is highly relevant to the initial ultrafast electron transfer reactions in photosynthesis. The molecule that is used as a chromophore in most of these studies (paper I-IV) is a porphyrin and porphyrins are indeed structurally much related to the chlorophylls.

1.1.2 Dye sensitized solar cells

Just as in photosynthesis, a dye sensitized solar cell (DSSC) includes a dye molecule that absorbs the sunlight and utilizes the energy to drive electron transfer reactions. Also here the initial electron transfer is for many cases ultrafast, with timescales down to a few femtoseconds (1 fs = 10^{-15} s). However, rather than forming an energy rich fuel the solar cell produces electricity. A second crucial difference is that the DSSC is not a purely molecular system. The dye molecule is attached to a semiconductor that has a much higher density of acceptor states for the transferred electron and this enables a more efficient collection of the electrons. The electron transport in the semiconductor is very different from molecular electron transfer and allows for a more efficient charge separation. Charge recombination with the reduced dye is anyway a problem that has to be overcome, just as in photosynthesis. Better insight in electron transfer processes are therefore desired in order to modify the dye molecule to optimize the electron transfer processes.

1.2 Aim of the research

Both these areas of research contain many fundamentally interesting questions and have also been a great source of inspiration when I have set up to study electron transfer. Both the photosynthesis and the DSSCs can benefit from a better understanding of ultrafast electron transfer, and in this context the results presented in this thesis become relevant. The aim is to help the
research community get a better understanding of the following questions: how do different properties of the molecules affect the electron transfer; and can the dynamic properties of electron transfer be used for designing systems? One of the major findings presented in this thesis is the clear observations of electronically excited and vibrationally unrelaxed states that dramatically influence the electron transfer dynamics.

But to come back to what has been my main driving force during my time as a PhD student.

*Studying electron transfer is for me to get to know the world I live in a little better.*

1.3 Outline of the thesis

This thesis is based on the six papers (I–VI) that have been listed in the beginning, and are included at the end. In chapter 2 the main theories and fundamental concepts that are relevant for this work is presented. In chapter 3 the experimental methods are presented, both from a practical and a theoretical point-of-view. The results are presented in chapter 4 and 5, with a brief introduction and the most important results. For a more complete and detailed description of the experimental results the reader is referred to the individual papers. In chapter 4 the electron transfer itself is in focus, while in chapter 5 the dynamics of the electron transfer reactions are put in a somewhat broader context.
2 Theory

2.1 Basic concepts of photophysics

Spectroscopy - the tool that is used in this thesis – is the interaction between matter and radiated energy. Radiated energy can be viewed either as electromagnetic waves or as photons containing radiated energy. All radiated energy is in principle of the same nature, but how we perceive the radiation depends on the energy it contains. X-rays, visible light, infrared light, radiative heat and radio waves are all examples of radiated energy, and there are more. The name depends on both its origin and its energy. In this thesis it will simply be referred to as light, and the matter that it interacts with is molecules. The energy of the light is determined by its wavelength $\lambda$ according to $E = \hbar c / \lambda$ where $\hbar$ is Planck’s constant and $c$ is the speed of light. In the visible region wavelength is the common parameter to use, but for lower energies the wavenumber $\bar{\nu}$ is more common. The wavenumber is related to the wavelength by $\bar{\nu} = \lambda^{-1}$.\textsuperscript{14}

Photophysics is a concept that includes both the initial photoexcitation and the processes that take place from that excited state. Light is used both to initiate a reaction and to probe the changes; to have an understanding of how light interacts with molecules, and what kind of processes that takes place within a molecule when it has absorbed the light, is therefore vital. For a more extensive description of photophysics and spectroscopy, see e.g. textbooks by Parson\textsuperscript{15} and Atkins\textsuperscript{16}.

2.1.1 Light-molecule interaction

In order to understand how light interacts with molecules it is helpful to turn to quantum mechanics. In quantum mechanics the light can be described as both a particle (photon) and a wave. The properties of the molecule can be described by its wavefunction $\psi$. The wavefunction includes the properties of the system it describes, i.e. the electrons and nuclei. In the simplest case the molecule is viewed as an isolated system, but for a more complete description the wavefunction should also include the influence of the surrounding media (e.g. solvent). The wavefunction is obtained by solving the Schrödinger equation for the system it should describe. The different sets of properties of the wavefunction represent different states that the system (e.g. molecule) can be in, and each state is associated with a discrete energy. It is
these energy levels that give rise to the absorption and emission spectra of the molecule. When light interacts with a molecule it can either absorb or emit light with the same energy as the difference between two energy levels. Absorption of light is the result of photoexcitation that brings the molecule from one state to a higher excited state. Photoemission is the reverse process where the transition is from an excited state to a state lower in energy accompanied by the emission of a photon. The strength of the transition is determined by the transition dipole moment, which is a vector quantity that determines how strongly two states interact when they are effected by an electromagnetic field.\textsuperscript{15}

2.1.2 Absorption and emission spectra

The absorption spectrum of a molecule is determined by its different states and their properties. Empirically the absorption spectrum can be described by the Beer-Lambert law (equation 2.1). It relates the fraction of absorbed light ($I/I_0$) to the molar extinction coefficient $\varepsilon$. The extinction coefficient is in turn related to the transition dipole moment for the initial and final states that has energy levels such that their difference matches the wavelength of the absorbed light. The extinction coefficient therefore depends on the wavelength. The observed absorbance also depends on the number of molecules that the light encounters, i.e. the concentration of molecules ($c$) and the length ($l$) that the light travels through the medium.

$$A = -\log_{10} \frac{I}{I_0} = \varepsilon lc$$  \hspace{1cm} (2.1)

By scanning over the observed wavelengths an absorption spectrum is obtained. Another important aspect is that the absorbance is additive, i.e. the observed spectrum is the sum of the individual spectra for the molecules in the solution.

$$A_{tot} = l \sum_i \varepsilon_i c_i$$  \hspace{1cm} (2.2)

The intensity in the emission spectrum originates from transitions that occur from excited states to lower energy states. The emission intensity at each wavelength reflects the number of emitted photons of that wavelength per excited molecule, which is determined by its radiative rate constant. As will be seen in chapter 2.1.5 there are also other processes that take place from an excited state, which will then lead to lower emission intensity. Just as for absorption, the radiative rate constant is related to the transition dipole moment.\textsuperscript{15,16}
2.1.3 Electronic vs. vibrational transitions

A molecule is made up of atoms which in turn are made up of nuclei and electrons. The electrons in an atom can be divided in core electrons and valence electrons. While the nuclei and its core electrons in a molecule are usually described in classical terms the valence electrons are rather described as a charge density that is distributed over the molecule. If you like, the atoms are the skeleton of the molecule and the electrons are its soul. The different treatment of nuclei and electrons lead to the *Born-Oppenheimer approximation* which states that the nuclear wavefunction $\chi$ can be separated from the electronic wavefunction $\psi$. The total wavefunction $\psi$ is then obtained as $\psi(r, R) = \chi(R)\phi(r; R)$ where $r$ and $R$ are the electron and nuclear coordinates (see ref. 15 p. 163).

Depending on the energy of the absorbed light different types of transitions are involved. To induce changes in the electronic configuration of the molecule an energy corresponding to wavelengths in the visible region is generally required. That can however extend to the higher energy ultraviolet (UV) region and the lower energy infrared (IR) region.

Changes of the atomic positions can be divided in three types. The first is when the whole molecule moves through space, i.e. is translated. The more interesting motions from a spectroscopic point of view are when the molecule (or parts of it) rotates, or when the overall structure is intact but smaller changes in the relative positions are changed. The former is called rotations and the latter is called vibrations. Rotational transitions generally occur in the microwave region and vibrational transitions generally occur in the IR region. A molecule can be translated in three different directions and rotate in three different directions, but the number of *vibrational modes* can be many more; $3N - 6$ where $N$ is the number of atoms in the molecule.†

2.1.4 Vibrational energy relaxation

The decay of a vibrationally excited molecule in solution occurs via two different mechanisms, intramolecular vibrational redistribution (IVR) and vibrational cooling (VC). These are schematically depicted in Figure 2. IVR refers to the process where the initial vibrational energy of one or several modes is distributed over the lower energy levels of the same and other vibrational modes. When IVR is complete the molecule has reached thermal equilibrium and the different vibrational levels are populated according to the Boltzmann distribution. When the vibrational modes are treated as harmonic oscillators the vibrational temperature $T_{vib}$ can be related to the vibrational energy $E_{vib}$ according to equation 2.3 where the subscript $m$ stands for the vibrational modes and $k_B$ is the Boltzmann constant.16

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† $3N - 5$ for linear molecules.
VC refers to the process where vibrational energy of the molecule is transferred to the solvent. When less vibrational energy is stored in the molecule the vibrational temperature decreases. For energy to be transferred it requires energy matching of the transition in the molecule and the solvent. This requirement is met by the very high density of states made up of vibrations, rotations, and librations of the solvent. The transfer of energy from the molecule (solute) to the solvent is assumed to be fast, no longer than a few ps. A limiting step however is the transport of the heat from the first solvent shell to outer sphere solvent molecules (the bulk), and thus VC depends on the thermal diffusivity of the solvent. Timescales for VC are usually on the order of 1 – 50 ps.

\[ E_{vib} = \sum_{m}^{3N-6} h \nu_m \left( e^{\frac{h \nu_m}{k_B T_{vib}}} - 1 \right)^{-1} \]  

(2.3)

IVR is generally assumed to occur faster than VC. However, separation of the processes based only on the timescale is not always possible and VC might take place also from thermally unrelaxed molecules. There have been observations of IVR for large molecules in solution on timescales ranging three orders of magnitude; from tens of femtoseconds up to tens of picoseconds. When the exact relaxation mechanism is of minor importance the term vibrational relaxation (VR), or vibrational energy relaxation (VER), can be used.
2.1.5 The fate of electronically excited states

There are several processes that can occur from an electronically excited state of a molecule. Emission and vibrational relaxation has already been mentioned. When discussing possible decay mechanisms it is practical to refer to a Jablonski diagram\(^\dagger\) such as that in Figure 3. Electronic vs. vibrational transitions have been discussed in terms of the energy difference for the initial and final state. For electronic transitions it is also important to consider the electron spin. For each electron it can take the value +1/2 (“spin up”) or -1/2 (“spin down”) and the total spin of the molecule will determine its multiplicity. Photons have zero spin and in a photoexcitation transitions between states of different multiplicity is formally forbidden. Most organic molecules are singlets in their ground state with zero net spin, which then is denoted \(S_0\), and the initially photoexcited state will then also be a singlet. The lowest excited singlet state is called \(S_1\), the second \(S_2\), etc. A transition between states of same multiplicity is called internal conversion (IC) and a transition between states of different multiplicity is called intersystem crossing (ISC). ISC involves the change of spin corresponding to one electron, if the initial state is a singlet the final state will typically be a triplet with a net spin = 1 (e.g. \(S_1 \rightarrow T_1\)). The rate of ISC is generally slower than IC due to the formally forbidden transition. The presence of heavy nuclei such as Ru will however increase the rate of ISC. Both IC and ISC are radiationless transitions, i.e. they do not involve absorption or emission of a photon. The transition then has to occur between states of same energy and the product states will therefore be vibrationally excited.

In contrast, radiative transitions occur between states of different energies with energy difference matched by the absorbed or emitted photon. For emission the final state will be to the electronic ground state (\(S_0\) in Figure 3). In analogy to IC and ISC, emission corresponding to a transition between states of same multiplicity is called fluorescence and transitions between states of different multiplicity are called phosphorescence.

\(^\dagger\) named after Alexander Jabłoński
Quantum mechanics can predict the probability with which a transition occurs and for an ensemble of molecules this can be interpreted as the rate constant of the transition. What is observed in a spectroscopic measurement however are not the individual reaction rate constants but rather the lifetime of the excited state. That lifetime is determined by the sum of all rate constants $k_i$ for transitions depopulating the excited state. The lifetime of the $S_1$ excited state in Figure 3 is then determined as

$$
\tau^{-1} = k_{IC,S_1\rightarrow S_0} + k_{fl.,S_1\rightarrow S_0} + k_{ISC,S_1\rightarrow T_1} = k_{obs}
$$

(2.4)

There are more reactions that can occur from an excited state. When a second molecule is introduced the excited state can be quenched by e.g. energy- and/or electron transfer. Both of these reactions will lead to a shorter observed lifetime for the excited state.\cite{16,27}

2.1.6 Franck-Condon principle (vertical transitions)

The Franck-Condon principle relies on the Born-Oppenheimer approximation and states that the changes in electronic configuration occur much more rapidly than the changes in positions of the nuclei. This has the consequence that for electronic transitions the nuclear positions are the same immediately
before and after the transition. Since an electronic transition implies changes in electron density the nuclei in the excited state will also react on this different electrical field. Though the effect might sometimes be small, the excited state generally has a somewhat different nuclear configuration than in the ground state, and also somewhat different vibrational modes. The transition dipole moment depends on the overlap of the wavefunctions, and due to the Franck-Condon principle not all of the vibrational states of the electronically excited state can be reached by photoexcitation (Figure 4). The probability is determined by the Franck-Condon overlap, or Franck-Condon factor, given by equation 2.5 (see ref. 15 p. 165).

\[ FC_{m \rightarrow n} = \left| \langle \chi_i, m | \chi_f, n \rangle \right|^2 \]  

(2.5)

Here \( i \) and \( f \) stands for the initial and final state, \( m \) and \( n \) denote their respective vibrational states. Franck-Condon factors will be discussed more in relation to electron transfer in chapter 2.3.2.

For polar solvents such as water and alcohols the Franck-Condon principle also has another effect. Since an electronic transition generally includes a change in the permanent dipole moment the solvent molecules will be oriented in an unfavorable position relative to the exited molecule. Photoexcitation is therefore followed by solvent reorientation which lowers the overall energy of the system. While this has been discussed rather in terms of photoexcitation it also holds for electron transfer reactions (chapter 3).\(^{15,16}\)

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**Figure 4.** Illustration of Franck-Condon transitions. The ground- and excited states are represented by a parabolic free energy surface, where the difference between the two minima represents the electronic energy. The vibrational wavefunctions are calculated according to a harmonic oscillator for one vibrational mode, and are shown at their respective vibrational energy levels. The arrows represent absorption and emission between vibrational states with maximum overlap.
2.2 Ultrafast and non-linear processes

Lasers that have short pulses (temporally) also have the capability of high peak powers, i.e. many photons at the same time and place. This enables the observation of both ultrafast and non-linear processes. Many electron transfer reactions, in particular those studied in this work, occur on the femtosecond to picosecond time scale. Ultrafast non-linear spectroscopies offer the opportunity to observe events that would not be observed with slower spectroscopies. Coherence is one such phenomenon and will be described in chapter 2.2.1. Other phenomena that are not immediately related to a fast time resolution but rather high light intensities are the non-linear process. Two-photon absorption is one such event that however will not be discussed in this thesis. Another non-linear phenomenon is the event of Raman scattering, particularly stimulated Raman scattering. In chapter 2.2.2 the general concept of Raman scattering is introduced, and in the methods chapter 3.2.3 the technique of stimulated Raman will be discussed.

2.2.1 Coherence and dephasing

Two states that have the same energy level are called degenerate states. When an excitation can reach degenerate states the excited state can be described by a superposition of these states. This does not mean that the system is in both states simultaneously. It rather implies that if the system is studied, by e.g. absorption spectroscopy, there is a probability of finding the system in either state. If these two states have sufficient coupling the probability of finding the system in one particular state oscillates with a period depending on both the energy difference of the states and the coupling between them. If the system is initially in state 1, then there is a time-dependent probability that the system will be found in state 2 that can be described by equations 2.6 and 2.7.

\[ |C_2(t)|^2 = \frac{1}{2} \left( \frac{H_{21}}{\Omega} \right)^2 \left( 1 - \cos \left( \frac{2\Omega t}{\hbar} \right) \right) \]  
\[ \Omega = \frac{1}{2} \sqrt{(E_{21})^2 + 4(H_{21})^2} \]  

(2.6)  
(2.7)

The energy difference and coupling between state 1 and 2 is denoted \( E_{21} \) and \( H_{21} \). The probability of finding the system in state 2 \( (|C_2(t)|^2) \) will then oscillate with a period \( \hbar/2\Omega \). With \( E_{21} = 0 \) the system will at certain times be guaranteed to be in state 2 (the probability will oscillate between 0 and 1). The maximum probability for being in state 2 decreases as \( E_{21} \) increases. When a large ensemble of molecules is excited there is a distribution of excited states with different energy levels. Since the different relative energies imply a difference in oscillation frequency (eq. 2.7) these oscillations will
quickly get out of phase (on a sub ps timescale); the oscillating probability is
damped and reaches an average value. Vibrational relaxation will also cause
the energy difference to increase and damp the oscillations in a similar man-
ner.\textsuperscript{15,28}

With fast time resolution coherence effects might be seen as oscillations
in time resolved measurements.

In large molecules there are several vibrational states that are close in en-
ergy. The excited state, created by a photoexcitation with a (temporally)
short pulse, will then be a superposition of several vibrational states of the
electronically excited state. If this vibrational coherence has not dephased
prior to other reactions (e.g. electron transfer) the coherence will be trans-
ferred to the reactant state. For electron transfer this is particularly interest-
ing since it may provide information on promoting vibrations (chapter 2.3.2,
2.3.5-6).\textsuperscript{29} Coherence of electronic states might also have an effect on the
rates of processes that occur solely from either of the states 1 or 2.\textsuperscript{30} Examples
of molecules with degenerate excited states are porphyrins and Ru-
polypyrlyidyl complexes that are used extensively in this work. While there
are no clearly observed coherence effects for the ultrafast ET reactions from
porphyrins presented in chapter 4 (and papers I–IV), it can not be excluded
for the Ru-polypyrlyidyl dye that is presented in chapter 5 (paper V). Coher-
ence is an important concept for the theoretical description of Raman transi-
tions (chapter 2.2.2) and coherence can also have influence on the anisotro-
py, which will be discussed in chapter 5.14.

2.2.2 Raman scattering

Vibrational transitions can be accomplished by the absorption or emission of
infrared light (chapter 2.1.3). Vibrational transitions can however also be
accessed via Raman scattering induced by visible light. Raman scattering is
a non-linear process, the incoming light interacts with the molecule and is
scattered. In the scattering process the molecule either gains energy from the
light or gives away energy\textsuperscript{8}. The energy-difference between the scattered
light and the incident light corresponds to a vibrational transition in the mol-
cule according to equation 2.8.

\[ n\hbar v = h\frac{c}{\lambda R_P} \left( \frac{1}{\lambda R_P} - \frac{1}{\lambda} \right) \]  
(2.8)

Here \( n \) denotes the vibrational level and \( \lambda R_P \) denotes the wavelength of the
incoming light, supplied by the Raman pump.

Raman scattering is sometimes depicted as an initial photoexcitation to a
virtual state followed by emission to a vibrational level different than the

\textsuperscript{8} The elastic scattering where no net energy is transferred is called Rayleigh scattering.
initial state. While this serves as a simple visual picture it is not strictly correct. The Raman process is a scattering event where the intermediate state (virtual or not) is never populated. However, it involves coherence between the initial and intermediate state as well as between the intermediate and final state. IR transitions require that the vibration involve a change in the permanent dipole moment. Raman transitions require that the transition change the polarizability. Raman transitions can be greatly enhanced when the incident light is resonant or nearly resonant with an electronic transition. The resonance enhancement can be used to selectively enhance the vibrations of one particular molecule, which makes it especially useful for large complexes such as proteins where there are otherwise several vibrations that might overlap in the IR spectrum.\textsuperscript{15,16}

2.3 Electron Transfer Theory

Theories for electron transfer (ET) are often said to begin with the paper titled “On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I” published in the year 1956 by Rudolph Arthur Marcus.\textsuperscript{31} For this and following work he was given the Nobel Prize in chemistry 1992.\textsuperscript{32,33}

In the following sections theories by especially Sumi and Marcus, Zusman, Rips and Jortner, and Bixon will be presented. It should be noted that several important contributions to the development of electron transfer theory have been made also by others. However, the aim here is not to give a complete historic overview of the development of electron transfer theory, that can be found in e.g. Rips et al. 1987\textsuperscript{34} and Efrima et al. 1976\textsuperscript{35}, but rather present concepts and equations from ET theory that have been used for this work. Useful reviews are given in e.g. reviews by Newton and Sutin\textsuperscript{36}, Marcus and Sutin\textsuperscript{37}, and book chapters by Bolton and Archer\textsuperscript{38}, and Yoshihara\textsuperscript{39}.

2.3.1 Basic concepts of electron transfer

The electron transfer reactions in this work consist of a transfer of one electron from one molecule to another; the molecules are labelled donor (D) and acceptor (A) respectively.\textsuperscript{**} These molecules are linked to each other by some sort of static interaction, whether it is charge transfer interactions, covalent bonds or fixed as different ligands in the same complex. The overall ET reaction can be viewed as a transition from a reactant state (D/A) to a product state (D+/A\textsuperscript{-}), which in its simplest form can be represented by two free energy parabolas (more generally called free energy surfaces) as in Fig-

\textsuperscript{**} For transitions that are rather characterized by a redistribution of electron density the term charge transfer (CT) is preferred and ET is then an extreme case of CT.
Since the ET reaction is a dark reaction (no photons are absorbed or emitted) the transition from reactant to product has to occur at a configuration where both states have the same energy. This occurs most favorably at the crossing point between the two surfaces, i.e. the transition state. The probability of crossing depends on the electronic coupling ($H_{RP}$) between the two states (D/A and D+/A-). However, the overall rate of electron transfer $k_{ET}$ will not only depend on the electronic coupling but also on the rearrangement of solvent and nuclear positions of the molecules D and A that are needed in order to bring the system from the configuration of the reactant state to the product state, via the transition state. This rearrangement is connected to the reorganizational energy $\lambda$ which is described more below. In the one-dimensional representation of Figure 5 a generalized reaction coordinate Q is used that includes both solvent and nuclear coordinates and parameterizes the trajectory from reactant to product state. The equations for the reactant and product free energy are on the form given in equations 2.9 and 2.10.

$$V_r(Q) = \frac{Q^2}{4\lambda} + \Delta G^0$$  \hspace{1cm} (2.9)

$$V_p(Q) = \frac{(Q-2\lambda)^2}{4\lambda} + \Delta G^0$$  \hspace{1cm} (2.10)

Figure 5. Schematic representation of reactant and product free energy parabolas, $V_r$ and $V_p$, of the reactant and product states (D/A and D+/A-).

The solvent part of the reaction coordinate is especially large for polar solvents. Electron transfer reactions are associated with a change in dipole mo-
ment and reorientation of the solvent molecules is therefore needed to bring the system to the transition state and subsequently the product state.

With sufficiently strong electronic coupling $H_{AB}$ the two surfaces will split into a lower and an upper surface (diabatic states), the reaction will then proceed on the lower surface (always cross from reactant to product state) and the overall rate of ET will not depend on the electronic coupling but rather on the rate by which the system approaches the transition state. When the electronic coupling is strong the reactions are labelled adiabatic, and when the coupling is weak the reactions are labeled non-adiabatic.

The electron transfer reactions in this work are mostly discussed in terms of non-adiabatic electron transfer (i.e. relatively weak coupling). In the high temperature limit ($k_B T \gg \hbar \omega$, where $\omega$ is the average frequency of the vibrational modes) the Marcus type equation for the rate of electron transfer is:

$$k_{ET}^{NA} = \frac{2\pi \hbar^2}{h^2 \sqrt{\pi \lambda k_B T}} \exp \left( -\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right)$$

Here $\lambda$ denotes the reorganizational energy, $\Delta G^0$ the driving force (reaction free energy), $H_{RP}$ the electronic coupling between reactant and product states, and $T$ is the absolute temperature. It has the form of an Arrhenius equation where the activation energy is given by $E_a = (4\lambda)^{-1}(\Delta G^0 + \lambda)^2$. These properties can easily be obtained from equations 2.9 and 2.10 and also geometrically in Figure 5. The driving force is the difference of the minima for the product and reactant state and the reorganizational energy is obtained as the energy needed to bring the molecule to the configuration of the product state, without crossing to the product surface.

It is interesting to note what happens with the activation energy as the driving force is increased. With a relatively small driving force ($|\Delta G^0| < \lambda$) the activation energy is positive and eventually vanishes when the driving force is equal to the reorganizational energy ($E_a = 0$ when $-\Delta G^0 = \lambda$). However, a further increase of the driving force ($-\Delta G^0 > \lambda$) will cause the activation energy to increase again and slow down the electron transfer. This limit is called the inverted regime. These effects are a result of the quadratic dependence of the activation energy on the driving force, when plotting the logarithm of the ET rate versus driving force the characteristic bell shaped curve is obtained as seen in Figure 6. Marcus predicted the inverted regime, but it was not until 28 years later (1984) that is was clearly seen in experiments by Closs and Miller.42,43
2.3.2 The effects of nuclear tunneling in the inverted region

As was noted also in the experiments by Closs and Miller the inverted region effect did not have such a dramatic influence on the rates as expected from the classical Marcus theory (equation 2.11). This can be explained by the effects of nuclear tunneling from the ground state of the reactant state to a vibrationally excited product state; in the inverted region there is substantial overlap between the nuclear wavefunctions of the reactant state and higher vibrational states of the product state and the inclusion of these vibrational levels will lower the effective driving force and hence reduce the effect of the inverted region as already indicated in Figure 6.

Kestner\textsuperscript{44}, Ulstrup\textsuperscript{45} and Jortner\textsuperscript{46} as well as Bixon\textsuperscript{35,47} and others (see e.g. refs in Newton and Sutin\textsuperscript{36}) have explored the effects of high-frequency vibrational modes on the rates of electron transfer. In a general expression all vibrational modes of the reactant and product state is included. The coupling term should include the nuclear and electronic wavefunction overlap, which can be obtained by multiplying the term for the electronic coupling with the Franck-Condon overlap. The driving force should be the free energy of the vibrational transition. The total rate is then obtained by summing over all vibrational transitions.

However, to obtain a more comprehensible expression both Jortner and Bixon have presented alternate versions of the Marcus expression for non-adiabatic electron transfer where one average high-frequency mode \(\langle \omega \rangle\) is treated quantum mechanically and the other (slow) modes are treated classically. In this model it is assumed that the frequency \(\langle \omega \rangle\) is the same in the reactant and product state. It was also noted that unless the reaction is highly exergonic (\(\Delta G > \lambda\)) higher vibrational levels of the reactant state can be neglected. In the limit \(\hbar \langle \omega \rangle \gg k_B T\) for the high frequency mode and
\( h\omega \ll k_B T \) for the classical modes, the following expression is obtained for the total rate of non-adiabatic electron transfer:

\[
k_{ET}^{NA} = \sum_{n=0}^{\infty} k_{0-n}^{NA} = \frac{2\pi H_{RP}^2}{h} \exp(-S) \sum_{n=0}^{\infty} \frac{S^n}{n!} \exp\left(-\frac{(\Delta G^0 + \lambda_{cl} + n\hbar\omega))^2}{4\lambda_{cl}k_B T}\right)
\]

(2.12)

The Franck-Condon overlap between reactant ground state and vibrational level \( n \) of the product state \( \left| 0 \right| = e^{-\frac{S}{\hbar}} \left| 0 \right| / \sqrt{n!} \) is the Huang-Rhy’s factor. \( \lambda_{v} \) is the intramolecular reorganizational energy of the high frequency mode and \( \lambda_{cl} \) is the reorganizational energy of the remaining classical coordinates; \( \lambda_{v} + \lambda_{cl} = \lambda \). Note that with \( \hbar\omega \ll k_B T \) (207 cm\(^{-1}\) at 25ºC) the classical Marcus type expression (equation 2.11) is obtained. Figure 7 shows the effect of increasing frequency of the acceptor mode according to equation 2.12.

![Figure 7](image)

*Figure 7.* Rate of ET vs. driving force for different vibrational energy; \( H_{RP} = 50 \) cm\(^{-1}\), \( \lambda = 1.0 \) eV, and vibrational energy \( \hbar\omega_{v} = 200 \) cm\(^{-1}\), 1000 cm\(^{-1}\), 2000 cm\(^{-1}\). The lines are calculated from equation 2.12 with same displacement of the high frequency mode for all energies, i.e. \( S \) is constant. With \( S = 0.5 \lambda_{v} = 0.01 \) eV, 0.06 eV, and 0.12 eV for the respective vibrational modes. The lowest vibrational energy equals \( k_B T \) and the result then reduces to the classical limit.

In equation 2.12 the reaction is assumed to occur from the ground state of the reactant state. Bixon and co-workers\(^{35} \) however also derived explicit equations for reactions occurring from vibrationally excited reactant states. It was noted that the largest contribution was to the ground state of the product state and this has the most notable effect on very endothermic reactions (in analogy with the inverted region effect of excited product states). While vibrational relaxation generally is assumed to occur very fast (faster than ET reactions) the Porphyrin/Viologen experiments presented in this thesis (see chapter 4) showed that electron transfer can indeed proceed faster than vibra-
tional relaxation and hence must involve higher vibrational levels of the reactant state.

Kestner and Logan\textsuperscript{44} also noted on the possibility of not only having vibrationally excited but also electronically excited product states. Electronically excited product states were earlier suggested by Marcus as an effect of the inverted region and explanation for chemiluminescence.\textsuperscript{48} The coupling between reactant and product state would then also have influence on the relaxation of the electronically excited state. This was not included in the equations derived for the electron transfer rate, but is interesting to keep in mind for electron transfer reactions presented in chapter 4 and 5.

2.3.3 The solvent controlled adiabatic limit

The reorganization energy $\lambda$ can be divided into a solvent part and nuclear part $\lambda = \lambda_s + \lambda_p$, also referred to as outer and inner reorganizational energy, $\lambda = \lambda_o + \lambda_i$.\textsuperscript{36,37} So far we have only considered the solvent as a part of the reorganizational energy and neglected the dynamical properties of the solvent. As already mentioned, in order to bring the system to the transition state changes in both nuclear and solvent configuration may be necessary. Therefore the solvent dynamics are likely to have important effects on the electron transfer rates, especially in the case of strong electronic coupling. In the following paragraph theories by Rips and Jortner\textsuperscript{34,49}, Zusman\textsuperscript{50}, and by Sumi and Marcus\textsuperscript{51} will be summarized. For a more complete list of contributors to the field of solvent controlled reactions the reader is referred to the reviews already mentioned\textsuperscript{36,37} and also papers by Rips and Jortner\textsuperscript{34,49}

Theories of solvent controlled electron transfer was first developed by Zusman.\textsuperscript{52} They resulted in equations where the rate of ET was proportional to the inverse of the longitudinal dielectric relaxation time $\tau_L$ of the solvent, $k_{ET} \sim \tau_L^{-1} \exp(-\Delta G^F/k_B T)$. $\tau_L$ is related to the Debye relaxation time $\tau_D$ by $\tau_L = \tau_D \epsilon_0/\epsilon_s$. $\tau_D$ is the response of a dipole to an external electric field, the optical dielectric constant $\epsilon_0$ relates to the response of electrons to a high frequency field and the static dielectric constant $\epsilon_s$ relates to the slower response of atoms to a low-frequency field. Typical values of $\tau_L$ are 0.2 ps for water and acetonitrile, 3.3 ps for methanol, 9.8 ps for ethanol 42 ps for propanol.\textsuperscript{34,53,54} Rips and Jortner have used other methods and derived an expression that bridges the non-adiabatic and the solvent controlled adiabatic limits:

$$k_{ET} = k_{ET}^{NA}(1 + \kappa_A)^{-1}$$

(2.13)

Where $\kappa_A$ is the adiabactity parameter:

$$\kappa_A = \tau_s 4 \pi H_{RP}^2 (\hbar \lambda_s)^{-1}$$

(2.14)

31
A strong coupling and/or long solvent relaxation time will yield equation 2.15 where the rate is limited by the solvent relaxation time, and in the opposite limit the non-adiabatic expression (equation 2.11) is obtained. Figure 8 shows the ET rates as a function of the driving force for transition from the non-adiabatic to the solvent controlled adiabatic region, calculated with the adiabatic expression as compared to the non-adiabatic expression.

Figure 8. Rate of ET vs. driving force for different electronic coupling; $\lambda = 1.0 \text{ eV}$, $\tau_L = 0.2 \text{ ps}$, and the coupling $H_{RP} = 50 \text{ cm}^{-1}, 200 \text{ cm}^{-1}, 1000 \text{ cm}^{-1}$ (0.006 eV, 0.025 eV, 0.12 eV). Solid red lines are calculated with the non-adiabatic expression (eq. 2.11) and yellow dashed lines are calculated with the adiabatic expression (eq. 2.13) where $\kappa_A = 0.2, 2, \text{ and } 60$ for the respective couplings. For stronger coupling the adiabatic expression reaches the solvent controlled limit and the maximum rate equals $\tau_L^{-1}$.

However, in strongly associated hydrogen bonded solvents (e.g. water and alcohols) several relaxation times are present. This has been noted by Rips and Jortner$^{55}$ who made modified expressions to include a distribution of solvent relaxation frequencies. Zuzman however developed electron transfer theory to include two discrete relaxation times.$^{50}$ Zusman's theory for electron transfer also includes the contribution of intramolecular degrees of freedom on the reorganization energy and is more generalized than earlier work by Levic, Dogonadadze, and Lax.$^{56}$ The two relaxation times can be related to the slow rotation of solvent clusters and faster rotations of the polar group in the solvent molecule. Depending on the conditions, the rate may be limited either by the short or the slow relaxation time.

2.3.4 Interplay between solvent dynamics and electron transfer

The solvent-controlled adiabatic limit however only presents one other limiting situation of electron transfer. Sumi and Marcus have presented a twodimensional (2D) model where the solvent and nuclei are treated separately.$^{51}$ This serves as a good model for understanding of the interplay between the different relaxation dynamics of the solvent and the vibrational dynamics.
of the D/A molecule. It accounts for the fact that the population of reactant state is not necessarily in thermal equilibrium during the entire reaction. Some of the main concepts and results of this treatment will be outlined here.

Due to the separation of vibrational and solvent coordinates the one-dimensional free energy parabolas for the reactant and product states in Figure 5 are replaced by two-dimensional surfaces shown in Figure 9. The free energy, $V$, is given by equations 2.16 and 2.17 where $q$ is the nuclear (vibrational) coordinate and $X$ is the solvent coordinate (cf. $Q$ in equations 2.9 and 2.10).

$$
V_r(q,X) = \frac{1}{2}aq^2 + \frac{1}{2}X^2 \quad (2.16)
$$
$$
V_p(q,X) = \frac{1}{2}a(q-q_0)^2 + \frac{1}{2}(X-X_0)^2 + \Delta G^0 \quad (2.17)
$$

The equilibrium position of the reactant and product states are $(0,0)$ and $(q_0,X_0)$ respectively, and from these are related to the reorganization energy of the nuclei and solvent according to $\frac{1}{2}aq_0^2 = \lambda_v$ and $\frac{1}{2}X_0^2 = \lambda_s$. The relaxation for the vibrational motion is assumed to be fast and the electron transfer is then defined to occur along $q$ with a rate depending on $X$ (see Figure 9 right panel). The activation energy $\Delta G^\#$ as a function of $X$ is obtained by equating equations 2.16 and 2.17.

$$
\Delta G^\#(X) = \left(\frac{\Delta G^0 + \lambda - X\sqrt{2\lambda_s}}{4\lambda_v}\right)^2 \quad (2.18)
$$

The electron transfer then occurs at each $X$ with a rate $k(X) = \nu_q \exp\left(-\Delta G^\#(X)/k_B T\right)$ where $\nu_q$ is a frequency factor that describes the rate by which the system approaches the transition state. The overall ET reaction however is described by the depopulation of the product state and this will depend on the relative rates for solvent and vibrational relaxation. When these occur on similar time-scales the rate will be non-exponential, and a single (scalar) value for the rate cannot be obtained. In some limiting cases however relatively simple expressions for the rate of ET can be obtained.
The expressions derived by Sumi and Marcus assume that the initial population distribution of the reactant state is at equilibrium. For the ET reactions presented in this thesis however, the reactant state will not be in equilibrium.\textsuperscript{††} The value in understanding of ET from relaxed states can be extended to understanding ET also from unrelaxed states. Sumi and Marcus note four limiting situations (i–iv below) that depend on the relative values of the solvent relaxation ($\tau_L$), rate of electron transfer ($k(X)$) and reorganization energies ($\lambda_i$ and $\lambda_o$). Importantly these situations are not independent of each other, and consequently a general expression that accounts for all situations cannot be obtained.

(i) **Slow reaction limit (fast $\tau_L^{-1}$):** the reaction along the $q$-coordinate, \( k(X) \), is much slower than the reorientational motion of the solvent and the usual thermal equilibrium expressions for the rate constants are obtained (not dependent on $\tau_L$): \( k_{ET} = v \exp(-\Delta G^\# / k_B T) \) where and $\Delta G^\# = (\Delta G^0 + \lambda)^2 / 4\lambda$. In the adiabatic limit the electronic coupling is large enough not to limit the ET rate and the frequency factor $v$ is rather determined by the average phonon frequency $v = \left( \sum_j v_{jq}^2 \lambda_{jq} / \lambda \right)^{1/2}$ where the summation is over all vibrational modes. In the non-adiabatic limit the electronic coupling is small enough so that the surface crossing is the limiting step and hence the rate will be given by the classical non-adiabatic expression eq 2.11.

\textsuperscript{††} All reactions in this work are ultrafast (sub ps) and the reactant state is prepared far from equilibrium, either if it is a result of a photoexcitation or a product of an ultrafast reaction.
(ii) When the required reorientational energy of the nuclei is much larger than that of the solvent ($\lambda_i \gg \lambda_o$), then the rate $k(X)$ is similar for all values of $X$ and thus *independent of solvent relaxation time* $\tau_L$. The rate is then the same as for the slow limit, but the reorganizational energy $\lambda$ is dominated by $\lambda_i$.

(iii) In the other limit where $\lambda_i \ll \lambda_o$ a multi-exponential (though small) decay of the reactant state is obtained, and it may be dependent on the relaxation time $\tau_L$. This is because $k(X)$ has a sharp peak at $X = (\Delta G^0 + \lambda)^2 / \sqrt{2\lambda_o}$ and the limiting step might then be the motion of the solvent toward that $X$-value. When the solvent relaxation is slow and vibrational motion fast (in relation to the activation energy) the frequency factor is proportional to $\tau_L^{-1}$. However, when the solvent relaxation rate is sufficiently fast the reaction might still be limited by the same preexponential factors (adiabatic or non-adiabatic) as for the slow reaction limit, but with reorganizational energy $\lambda$ dominated by $\lambda_o$.

(iv) **Fast reaction limit (slow $\tau_L^{-1}$, non-diffusing limit):** Two cases may be envisioned here depending on the nature of the intrinsic ET step $k(X)$. The first is similar to (iii) but not necessarily with such a sharp peak of $k(X)$. The limiting step is then the solvent relaxation time $\tau_L$ and a rate similar to equation 2.15 is obtained, i.e. the solvent controlled adiabatic limit. The other situation, that is expected to be encountered relatively rarely according to Sumi and Marcus, is when the reaction $k(X)$ proceeds fast at all values of $X$ (the distribution of $X$-coordinates need not to be restored during the reaction). The decay of the reactant state is therefore a sum of exponential decays weighted by the initial (equilibrium) population and thus not dependent on the solvent relaxation time $\tau_L$.

Note that point (ii) and (iii) do not depend on whether the solvent relaxation is fast or slow. It is therefore not only important to look at the absolute value of the solvent relaxation rate $\tau_L$ but also necessary to account for the frequency factor and the activation energy. It is therefore too simple to say that an adiabatic reaction is always limited by the solvent dynamics. Adiabatic ET still requires the solvent relaxation rate to be slow enough to be rate limiting. Even with a slow solvent relaxation rate it may still be possible for reaction rates to exceed $\tau_L^{-1}$. Electron transfer reactions that occur from non-equilibrated reactant states will be of importance for the electron transfer reactions presented in this thesis (chapter 4 and 5).
2.3.5 Vibrational tunneling in competition with solvent relaxation

The Sumi-Marcus model described in previous section treats all coordinates classically. Nuclear tunneling to vibrationally excited acceptor states has been shown to have influence in the inverted region. A rather straightforward combination of equations 2.12 – 2.14 will yield the Jortner/Bixon model (eq. 2.19).  

\[
k_{ET} = \sum_{n=0}^{\infty} k_{NA}^{0\rightarrow n}(1 + \kappa_A^{0\rightarrow n})^{-1}
\]

(2.19)

The adiabacity factor \(\kappa_A\) depend on the coupling, and the coupling depend on the Franck-Condon overlap for the vibrational transitions. Hence, while the \(0 \rightarrow 0\) transition (ground state of reactant to ground state of product) might be in the solvent-controlled adiabatic limit, transitions to higher vibrational modes might still be in the non-adiabatic limit. In the adiabatic limit the rate is given by equation 2.12 and in the solvent-controlled adiabatic limit the rate is given by equation 2.20.

\[
k^{NA}_{ET} = \tau_L^{-1} \frac{\lambda_{cl}}{16\pi k_B T} \times \sum_{n=0}^{\infty} \exp \left( - \frac{(\Delta G^0 + \lambda_{cl} + nh(\omega))^2}{4\lambda_{cl} k_B T} \right)
\]

(2.20)

Inclusion of nuclear tunneling to vibrational acceptor modes in the rate expression has an important consequence, namely, rates can be faster than \(\tau_L^{-1}\). With a large coupling and high frequency acceptor mode the rate is not expected to vary as a function of \(\Delta G^0\) when \(-\Delta G^0 \approx \lambda\) (see Figure 10). This flat region can span more than 1 eV, depending on the coupling and vibrational energy in relation to \(\tau_L\).
Figure 10. Rate of ET vs. driving force; \( H_{ab} = 1000 \text{ cm}^{-1} \) (0.12 eV), \( \lambda = 1.0 \text{ eV} \), and \( \tau_L = 0.2 \text{ ps} \). The yellow dashed line is calculated with the adiabatic expression (eq. 2.13) where \( \kappa_A = 0.2 \). Solid red lines are calculated by equation 2.12 with \( \hbar \omega_v = 200 \text{ cm}^{-1}, 1000 \text{ cm}^{-1}, 2000 \text{ cm}^{-1} \) (same as in Figure 7 but with the stronger coupling). Orange dashed lines are calculated obtained from the by the Jortner/Bixon expression (eq. 2.19). Note that a rate higher than \( \tau_L^{-1} \) is reached in the region \( -\Delta G^0 \sim \lambda \).

2.3.6 Electron transfer reactions from unrelaxed states

In section 2.1.7 it was shown that the initially photoexcited state is generally not in equilibrium, both in respect to its internal coordinates and the surrounding media (solvent). With a sub picosecond laser pulses the initial relaxation processes can be observed. In order to describe ultrafast ET reactions faster than relaxation dynamics the initial condition cannot be the equilibrium position as has been the case for all expressions presented this far (equations 2.7–2.16). A combination of the Sumi-Marcus model for solvent dynamics and the Jortner/Bixon expression for vibrational tunneling has been presented by Barbara, referred to as the Barbara hybrid model.\(^{58,59}\) It was observed that electron transfer could occur faster than solvent dynamics, and also faster than what would be predicted with the Jortner/Bixon and Sumi/Marcus models (\( k_{\text{obs}}^{\text{ET}} > 1/(\tau_S) > k_{\text{JBR}}^{\text{ET}} > k_{\text{SM}}^{\text{ET}} \)). It was therefore reasoned as in the fast reaction (non-diffusing) limit (iv) of Sumi-Marcus theory that the intrinsic rate is very fast.\(^{60}\) It was also observed that the rates did not depend on the temperature, as would be predicted by a rate limited by the longitudinal relaxation time.\(^{61}\) With the initial population being displaced from the equilibrium position, in accordance with the Franck-Condon transitions from the ground state to upper excited state, the rate of ET could be well described. However, also in the Barbara hybrid model it is assumed that vibrational relaxation (not solvent relaxation) of the reactant state is faster than ET. That seems to be valid for the reactions observed Barbara and co-workers where the observed rates are lower than \( 2 \times 10^{-12} \text{ s}^{-1} \) (\( \tau_{\text{obs}} > 0.5 \text{ ps} \)). The results presented in this thesis however will show that not only can ET
reactions be faster than solvent relaxation, Et reactions can indeed also can be faster than vibrational relaxation.

The Barabara hybrid model have been used by several groups, in particular for studies of charge recombination of optically prepared charge separated states.\textsuperscript{62,63,64,65} Recently the group of Ivanov and co-workers have presented models for charge separation followed by charge recombination also from vibrationally unrelaxed states. This has the important distinction from the Barabara hybrid model in that the charge recombination occurs from excited high-frequency modes that are not necessarily in thermal equilibrium. The model accounts for the fact that electron transfer can be faster than vibrational relaxation of the high frequency modes and thus allow for the CS state to be re-populated during the time-course of vibrational relaxation.\textsuperscript{66} The results from this model, as well as the Barbara hybrid model, are necessarily non-exponential kinetics for the depopulation of the reactant state and therefore a comprehensible equation for the rate of electron transfer as in e.g. equations 2.11 and 2.20 is not obtained.
3 Methods

This chapter outlines the experimental techniques that have been used for the study of ET in this thesis. The first part deals more with the experimental apparatus and how they are used, the second part is more focused on data analysis.

3.1 Lasers

In order to study ultrafast reactions it is necessary to have ultra-short pulses that can initiate the reaction and equally short pulses that can monitor the dynamics. Ultra-short in this context means sub picosecond (\(< 10^{-12} \text{ s}\)). One way of realizing this is the pump-probe technique that was developed in the 1980’s, and this is the technique that enabled Ahmed Zewail to get the Nobel Prize in Chemistry 1999.

“for his studies of the transition states of chemical reactions using femto-second spectroscopy”\(^{67}\)

The experimental set-up in the studies presented here employ the same laser system to create the initial (fundamental) laser pulse. That laser system is made up of three essential parts; a seed laser, a pump laser, and an amplifier. The seed laser generates short pulses. The pump laser gives a continuous high power light. These two are then combined in an amplifier where the seed pulses are first stretched in time (positive chirp), then amplified in a Ti:sapphire medium which gets energy from the pump laser, and finally the high intensity pulses are compressed (negative chirp). The fundamental output from a Ti:sapphire laser system is typically 800 nm light with about 100 fs pulse width, 2.5 mJ pulse energy, and the time between pulses are 1 ms (1 kHz repetition rate).

Not all reactions can be initiated with 800 nm photons. Therefore it is necessary to be able to change the excitation wavelength. For the studies made here commercial optical parametric amplifiers (OPAs) are used to tune the wavelengths. These OPAs are based on non-linear processes that require high intensity light such as that obtained by lasers.
3.2 Pump-probe laser spectroscopy

Pump-probe spectroscopy is a technique that uses one light pulse to initiate a reaction and a second light pulse to monitor the changes. By varying the time delay between the pump and probe pulse a reaction can be followed as a function of time by probing the spectral changes taking place after the pump pulse. To achieve high time resolution two requirements must be met; 1) the pump and probe pulses must be short and 2) the time delay between pump and probe must be controlled with a high degree of accuracy. The best way to meet this requirement is to generate both pump and probe pulses from the same fundamental laser light pulse. Use of a beam splitter allows the pump and probe pulses to travel different trajectories. By letting the probe light travel a longer path than the pump light a time difference is obtained. Through piezoelectrics this can be controlled with sub micrometer precision allowing for femtosecond time-steps. This is seen in Figure 11 that describes the transient absorption set-up. The term pump-probe is mostly used for techniques where the probe directly monitors the reaction. Techniques exist however where the probe is not directly monitored but rather acts as a gate that allows a signal to be observed. An example of this is fluorescence up-conversion. There are also techniques where more than one probe is used, and one example of this is the stimulated Raman technique that will be presented in section 3.2.3.

3.2.1 Transient absorption

Transient absorption measurements monitor the change in absorbance as a function of time after the initial excitation. Figure 11 shows a schematic set-up of a pump-probe transient absorption experiment. In general not all of the molecules in a sample will be excited by the excitation light (pump light), so it is convenient to construct the difference absorption as in equation 3.1. This is easily obtained from the Beer-Lambert law (eq. 2.1). In this way the contribution from molecules unaffected by the pump light is eliminated. Experimentally this can be achieved by letting the pump light pass through a chopper-wheel that blocks every second pulse. The corresponding probe intensities are labeled “p/on” and “p/off” in equation 3.1.

\[
\Delta A = A_{p/on} - A_{p/off} = -\log_{10}\left(\frac{I_{p/on}}{I_{p/off}}\right) \approx -\log_{10}\left(\frac{I_{p/on}}{I_{p/off}}\right) (3.1)
\]

Since the reference light does not pass through the sample it is unaffected by the pump and thus cancel out in equation 3.1. Lasers are however not perfectly stable, so in order to correct for fluctuations in light intensity it is preferable to also measure the reference.
Contribution to observed $\Delta A$ signals
At negative delay times, when the probe arrives before pump, the $\Delta A$ signal should be zero, i.e. no change in absorbance. At positive delay times there are three main contributions to the observed $\Delta A$ signal: excited state absorption (ESA), ground state bleach (GSB), and stimulated emission (SE). Other contributions that arise from non-linear effects are in this context considered as artifacts. GSB gives a negative contribution to the observed $\Delta A$ since the ground state absorption ($A_{p/off}^p$) is subtracted. Stimulated emission is a transition from the excited state to a lower state that is induced by the probe light. This is accompanied by the emission of a photon in the same direction as the probe light. The increased intensity of the probe light then gives a negative contribution to the observed $\Delta A$. In principle spontaneous emission would also give a negative signal, but due to the geometry of the set-up only very little of that emitted light reaches the detector.

Probe light generation
Depending on the type of transitions that should be monitored different probe light is used. In the studies presented here UV-vis., NIR, and IR light has been used. The basic operational principles are the same for all wavelengths of detection but different optics may be required. The probe light
could either be monochromatic or a broad band pulse *i.e. white light continuum*. In principle white light is always preferred since it gives an absorption spectrum that allows for better determination of the processes. White light in the UV-vis. region is in this work generated by focusing the light on a CaF$_2$ crystal. CaF$_2$ is particularly useful to generate wavelengths shorter than 450 nm. When longer probe wavelengths are desired, including NIR light, a TiSapphire crystal is instead preferred. The longer wavelength mid-IR light is generated in an OPA.

### 3.2.2 Spectroscopy with polarized light

The laser light used in these studies is polarized, and this can be used in order to obtain orientational information of transitions that have otherwise identical absorbance. The transition dipole moment is a vector quantity, which means that is has both a magnitude and direction in space. The light will therefore most preferentially interact with molecules having transition dipole moment directed along the axis of polarization, see *Figure 12*.

*Figure 12*. Schematic picture of excitation with polarized light. On the left side all light has same direction polarization. On the right side the light is unpolarized, i.e. different polarization in several directions. The molecules are randomly (isotropic) oriented in the solvent, but the light selectively excites molecule that are aligned with its polarization. A polarized light therefore creates a polarized (anisotropic) population of excited molecules.

By measuring the difference absorbance both with probe light parallel ($\Delta A_\parallel$) and perpendicular ($\Delta A_\perp$) relative the pump light the anisotropy can be calculated according to equation 3.2. A schematic picture of the relative orientations is seen in *Figure 13*.

$$ r = \frac{\Delta A_\parallel - \Delta A_\perp}{\Delta A_\parallel + 2\Delta A_\perp} $$

(3.2)
The denominator in equation 3.2 is the isotropic signal (total absorbance), which is also obtained by having probe light polarized 54.7° relative to the pump. From the value of the anisotropy it is possible to obtain information on structural changes that are otherwise not seen. The simplest case is rotational dynamics, i.e. when the whole molecule rotates and hence changes orientation of the (all) transition dipole moment. Anisotropy is also applicable to different transitions of the same molecule, they might have different direction of their transition dipole moments and hence give different anisotropy values (see next chapter).

Figure 13. Relative orientations of pump and probe in the transient anisotropy measurements. The red block represent the sample. The dotted line is the pump and the solid line is the probe.

**Predicted values of anisotropy**

Values of the anisotropy can be predicted by the relative orientation of the transition dipole moments of the excitation and probe transitions. Let \( \mu_{exc} \) be the transition dipole moment for the ground state (GS) to excited state (ES) transition and \( \xi \) be the angle between \( \mu_{exc} \) and the polarization of the excitation light. Then the excited state population will depend on \( \cos^2 \xi \). Then let \( \mu_{pr} \) be the transition dipole moment of the transition from the excited state that is monitored with the probe light, and let \( \phi \) be the angle between \( \mu_{exc} \) and \( \mu_{pr} \). The expression for anisotropy given by equation 3.3.

\[
r = \frac{1}{5} \left( 3 \cos^2 \phi - 1 \right) = \frac{1}{5} \left( 3 \left( \mu_{exc} \cdot \mu_{pr} \right)^2 - 1 \right)
\]

(3.3)

This expression is independent of the technique used to monitor the reaction and is thus equally valid for transient absorption and time resolved emission. Different probed transitions have different values of the anisotropy and the observed anisotropy will therefore follow the decay dynamics just as in isotropic transient spectroscopy. Molecules in solution will however also rotate and this will cause the angle of the initially excited transition and the probed transition to change. When the sample is totally randomized the anisotropy will be zero. It is also seen from equation 3.3 that for parallel excitation and probe transition dipole moments the anisotropy is \( r = 0.4 \) and for perpendicular orientation \( r = -0.2 \), which are the classically limiting values of anisotropy for a single transition.27
Anisotropy values in transient absorption spectroscopy

As already mentioned, the observed transitions in transient absorption spectroscopy originate from excited state absorbance, ground state bleach as well as stimulated emission. Furthermore there are frequently several overlapping transitions that give rise to the observed $\Delta A$. The transient absorption anisotropy is then obtained as a weighted sum of all transitions

$$\tau_{\text{obs}} = \frac{\sum_i (\Delta A_{\text{ESA,}i}r_{\text{ESA,}i}^\text{r}) + \Delta A_{\text{GBS,}r}r_{\text{GBS}} + \Delta A_{\text{SSE}}r_{\text{SE}}}{\sum_i (\Delta A_{\text{ESA,}i}) + \Delta A_{\text{GBS}} + \Delta A_{\text{SE}}} \quad (3.4)$$

Since the $\Delta A$ signals can be both positive and negative, an observed anisotropy value may be both greater than 0.4 and less than 0.2. When two transitions have $\Delta A$ signals of opposite sign $\tau_{\text{obs}}$ can reach $\pm \infty$. To simplify analysis and reduce uncertainty it is preferable to probe regions with all $\Delta A$ contributions being either positive or all negative. This may be achieved if the probe light is in the mid-IR region. IR peaks are typically narrower than the broad absorption bands from electronic transition and it is then more likely that the observed $\Delta A$ originates from only one transition, without contribution from stimulated emission.

As will be discussed more in chapter 5 there are also effects that can give an anisotropy value higher than 0.4. Electronic coherence in the excited state may increase the anisotropy to 0.7, provided that the probe light brings the degenerate state to a common final state. Coherence usually decays on a femtosecond to (1) ps time-scale and thus requires ultrafast techniques to be observed.$^{15,28}$

3.2.3 Stimulated Raman spectroscopy

Stimulated Raman spectroscopy (FSRS) is a three-pulse pump-probe technique that probes vibrational transitions with both high temporal and spectral resolution. The relative timing of pulses is shown in Figure 14. A reaction is initiated by a laser pulse (actinic pump in Figure 14) and the Raman transition is then enabled by the narrow bandwidth Raman pump which is enhanced by the broadband Raman probe. A laser pulse can not be both ultra-short (temporally) and have a narrow spectral bandwith (due to the Heissenberg uncertainty principle). The simultaneous high temporal and spectral resolution in the FSRS experiments is made possible since the Raman transition is only observed when the Raman pump and probe overlap in time. Without the Raman pump the experiment would be identical to transient absorption. In practice the spectra are obtained as the difference in absorbance when the Raman pump is on and off. The Raman probe light gains intensity at the wavelengths of the Raman transitions. Though the process is quite different the observed effect is similar to stimulated emission. Effectively the Raman gain signals are seen as negative peaks of the transient
absorption spectrum. When the Raman pump is not chopped also the ground state Raman signal is observed throughout the transient spectra. Examples FSRS spectra are shown in chapter 4.3.2.

![Figure 14. Duration and relative timing of pulses in stimulated Raman spectroscopy. The Raman pump is temporally broad as a consequence of its very narrow (spectral) bandwidth. The Raman gain is only observed when the Raman pump and Raman probe overlaps in time, and the relative timing of Raman pump and Raman probe is kept fixed during the measurement.](image)

### 3.3 Data modeling (data analysis)

In order to extract information from the recorded absorbances the data needs to be compared with a suitable model where reaction rates and excited state spectra as well as yields of different reactions might be determined. All data analysis in this work has been done with MATLAB (The Math Works, Inc.). I constructed all the routines for reading data and wrote the code for desired fit-models. In transient absorption spectroscopy the traces (ΔA vs. time) are fitted. In transient IR and FSRS also the spectra are fitted to suitable line-shapes. For the actual fit a robust trust-region reflective Newton nonlinear-least-squares method has been utilized.

#### 3.3.1 First order reactions

Most of the reactions that are studied in this thesis are intramolecular reactions and they can be assumed to follow first order kinetics. These reactions are then characterized by the first order rate constants $k_{i\rightarrow j}$ for the reactions $x_i \rightarrow x_j$. They can be written on the form

$$\frac{d}{dt} x = K x$$

(3.5)

where $x$ is a vector containing each state $x_i$ and $K$ is a matrix containing all individual rates. The rate constant matrix $K$ then has the off-diagonal elements $K_{i,j} = k_{j\rightarrow i}$, and the diagonal elements $K_{i,i} = -\sum_{m\neq i} k_{i\rightarrow m}$. Each row
\( i \) in \( K \) has the negative observed decay rate constant of state \( x_i \) on the diagonal, and the individual rate constants for populating the state \( x_i \) on the off-diagonal. The difference absorbance is obtained from Lambert-Beer’s Law as \( \Delta A_i = \Delta \varepsilon_i \langle x_i \rangle \) where \( \Delta \varepsilon_i \) is the difference of the extinction coefficient for the excited state and the ground state. The general solution to equation 3.5 is \( x(t) = x_0 \exp Kt \). It will be shown in chapter 3.4.5 that this can be expressed as a sum of exponentials (eq. 3.6) where the lifetime \( \tau \) is the inverse of the sum of all rate constants leading from the excited state \( \tau_i = -K_{i,i}^{-1} \).

\[
\Delta A_{\text{reacn}}(t) = \sum_i c_i e^{-(t-t_0)/\tau_i} \quad (3.6)
\]

This is now the expression that is used to model the kinetic data. The amplitude \( c_i \) depends on the rate constants leading to and from the state, as well as the initial populations and the extinction coefficient. The term time-constant is commonly used to describe reaction rates and is defined by the inverse of the rate constant. It is somewhat misleadingly labeled \( \tau \) (\( \tau_{i \to j} = k_{i \to j}^{-1} \)) and should not be confused with the lifetime \( \tau_i = -K_{i,i}^{-1} = (\Sigma_j k_{i \to j})^{-1} \). As seen in equation 3.6, what is observed in a measurement is not the individual reaction rate constants but rather the effective lifetimes of each state. For consecutive reactions \( (x_1 \to x_2 \to \cdots \to x_N) \) however the inverse of the lifetime \( \tau_i \) is identical to the reaction rate constant \( k_{i \to i+1} \) and the numerical value of the time-constant is indeed identical to the lifetime.

### 3.3.2 Response function

Molecules are excited in the time-duration of the pump pulse, and the molecules are probed in the time-duration of the probe pulse. Combined this gives an overall temporal response width of the measurements that is seen experimentally as a rise of the initially excited state. The laser fundamental has a Gaussian shaped temporal profile and the total response will then also be Gaussian shaped as in equation 3.7.

\[
F_{\text{Gauss}}(t) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left(\frac{(t-t_0)^2}{2\sigma^2}\right) \quad (3.7)
\]

The parameter \( \sigma \) is related to the response width (fwhm; full width half maximum) by \( fwhm = \sigma \sqrt{2 \ln 2} \). Before comparing the reaction model with the data the model needs to be convoluted with the response (eq. 3.8). The convolution results in equation 3.9, which makes use of the error function (erf) to convolute the exponentials with the Gaussian.

\[
\Delta A_{\text{fit}}(t) = (\Delta A_{\text{reacn}} * F_{\text{Gauss}})(t) \quad (3.8)
\]
As will be discussed more in next chapter, there are processes that are nearly instantaneous and thus occurring only during the pump-probe overlap. These effects can be used to experimentally determine the response width.

\[
\Delta A_{\text{fit}}(t) = \frac{1}{2} \sum_i c_i \exp \left( -\frac{t-t_0}{\tau_i} \right) \exp \left( \frac{\sigma^2}{2 \tau_i^2} \right) \left( 1 - \text{erf} \left( \frac{\sigma}{(\tau_i - \sigma) \sqrt{2}} \right) \right) \tag{3.9}
\]

3.3.3 Artifacts in transient absorption spectroscopy

While the measured light intensity is interpreted as a change in absorbance of the sample there might be other effect that also causes a change in light intensity. The high power that is needed in order to excite enough molecules to get a detectable signal can also give rise to non-linear effects. One such effect is stimulated Raman where the pump acts as a Raman pump and the transition is enhanced by the probe. Another effect is the optical Kerr effect, which is a change in refractive index that is proportional to the square of the electric field.\(^6\)\(^9\) With a continuum probe there is also the possibility of cross phase modulation (xpm). The strong pump-pulse will modify the probe spectrum, without transferring any net energy to the probe. This effect is only observed when the probe is spectrally resolved.\(^7\)\(^0\)

In principle, if the transient absorption signal of the solvent alone is recorded under the exact same conditions as the real experiment, then these effects can be corrected for.\(^7\)\(^1\) This has however proven to be difficult in practice. Instead the xpm signals has been accounted for in the fit-model by adding a function (eq. 3.10) of the same form as that obtained by Kovalenko et al.\(^7\)\(^2\)

\[
\Delta A_{\text{artifact}} = c_\alpha e^{(t-t_0)^2/2\sigma^2} \sin(\delta - \beta(t - t_0 - \Delta t)^2) \tag{3.10}
\]

The parameters \(t, t_0\) and \(\sigma\) are the delay time, time zero, and Gaussian width; same as in equation 3.6 and 3.7. Parameters \(c_\alpha, \delta, \beta\) and \(\Delta t\) are used only as phenomenological parameters that however can be related to physical quantities.

Another non-linear process that does not give an artifact of the form as discussed above but rather contribute to the observed dynamics is two-photon absorption. With high pump intensities it is possible that two photons interact and excite the molecule to a level corresponding to the sum of the photon energies. In the present studies, laserpowers have been kept low enough to avoid two-photon absorption.
3.3.4 Chirp correction

Another optical effect from using a broadband probe is chirp. Different wavelengths travel through media with different speed. A broadband pulse therefore gets spread out in time, i.e. it gets chirped. When looking at individual traces ($\Delta A_{\lambda}$ vs. time) this has the effect that $\tau_0$ is shifted, but the dynamics are otherwise unaffected. In the UV-vis. transient absorption experiments presented here the red photons ($\lambda \sim 700$ nm) arrive at the sample ca. 1 ps after the blue photons ($\lambda \sim 350$ nm). When looking at spectra these will therefore be severely distorted during the first ca 10 ps. This can however be corrected for by shifting the data in time at each probe wavelength according to the chirp. The accuracy of this correction is for the spectra presented here usually $\pm 10$ fs.

![Figure 15. The effect of chirped white light probe on the observed time-zero. (left) The intense blue peak represents the pump pulse and the broad peak represents the spectrally chirped probe pulse. (right) The time-zero as a function of wavelength](image)

3.3.5 Global analysis

Global analysis is when two or more individual fits, e.g. $\Delta A(t)$ traces at different wavelengths, are fitted simultaneously with common parameters. This allows for more accurate determination of parameters. Global analysis can also be particularly useful for white light transient absorption spectroscopy where many processes could have both overlaying absorption spectra and kinetics with similar time-scales. With the help of decay associated spectra (DAS) and species associated spectra the processes might be distinguished so that the involved components (states) can be identified.

Here global analysis is discussed in terms of the transient absorption measurements presented in this thesis, but the idea and method of global analysis is applicable to time-resolved spectroscopies in general.

**Decay associated spectra**

For many reactions, except for vibrational relaxation, the time-constant $\tau_i$ should be same for all $\Delta A$ traces, i.e. independent on the observed wavelength. The coefficient $c_i$ that is seen in both equation 3.6 and 3.9 is related to the absorbance of the involved states and hence dependent on the wavelength ($c_i = c_i(\lambda)$). The time-constant $\tau_i$ can be connected to a state and the
corresponding coefficient $c_i$ will then form the decay associated spectrum for each time constant. The components of the DAS reflect on how the absorbance changes between the initial and final state of a reaction step.

**Species associated spectra**

When a suitable reaction scheme is determined it is also possible to use the DAS and time-constants to calculate the “species associated spectra”, i.e. the individual spectra of each state. As mentioned in chapter 3.3.1 the amplitude of the coefficient $c_i$ will not only depend on the absorbance of the involved states, but also on the kinetics of the reaction (i.e. the rates $k_{i\rightarrow j}$). When the reaction scheme has been determined (or at least assumed) it is possible to use the DAS to recalculate the individual extinction coefficients $\varepsilon_i$.

In order to obtain the expression for $c_i$ equation 3.5 has to be solved, which can be done by standard linear algebra. For textbooks on differential equations and linear algebra see e.g. 73,74,75. The solution to equation 3.5, $x(t) = x_0 \exp(Kt)$, only holds only when the matrix $K$ is diagonal. This can however be solved by a substitution of variables. By setting $x = Pu$ one gets $\frac{d}{dt}x = P \frac{d}{dt}u$. This gives $\frac{d}{dt}u = (P^{-1}K\varepsilon)u = DX$ where $D = P^{-1}K\varepsilon$. $P$ can now be chosen so that $D$ is diagonal; $D$ will then contain the eigenvalues to $K$ and $P$ will contain the corresponding eigenvectors. Each element in $D$ corresponds to the negative of the observed decay rates, i.e. $D_i = -\tau_i^{-1}$ (c.f. $K_{i,j}$ in chapter 3.4.1). This has the simple solution $u_i = q_i \exp(D_i t)$ where $q_i$ is a constant determined by the initial condition $x(t = 0) = x_0$. $x_0 = Pu_{t=0} = Pq$ which gives $q = P^{-1}x_0$. The solution to equation 3.5 then is $x(t) = P P^{-1}x_0 \exp Dt$. Hence, the problem is now reduced to finding the eigenvectors of the rate matrix $K$, which could be done by hand but more easily with a computational program such as MATLAB.

The difference absorbance can now be obtained as $\Delta A(t) = x(t)^T \Delta \varepsilon l$ where $\Delta \varepsilon$ is a vector with the extinction coefficients relative the ground state and $l$ is the pathlength. More correctly the concentration of $x_i$ should be used, i.e. $[x_i]$. That however directly corresponds to the population of state $x_i$ which will be used for simplicity. The final expression is then

$$\Delta A(t) = l \sum_i (\sum_j \Delta \varepsilon_j P_{j,i}) q_i \exp(D_i t)$$

(3.11)

where $D_i = K_{i,i} = -\tau_i^{-1}$ as already stated. By comparing equation 3.11 with 3.6 it is seen that the coefficients obtained from the fit can identified as $c_i = l q_i \sum_j \Delta \varepsilon_j P_{j,i}$. Thus, with some extra matrix algebra the individual absorption spectra of each state can be obtained.

To summarize; by solving the differential equation 3.5 with given reaction rates and initial condition an explicit expression for the amplitudes $c$ found in equation 3.6 can be obtained. Note that equation 3.5 is applicable to all
reactions that are of first order, it therefore includes reversible reactions and hence also equilibria.

This technique can also be useful for simulating transient signals in order to find out what the underlying process of a time resolved spectrum might be. These equations have been used to calculate species associated spectra in paper II and IV, which were important for identifying the intermediate reaction products and their relative yields.
Papers I-III show how a difference in initially excited state can influence the outcome of electron transfer (ET) reactions. Andersson et al. had previously shown that the rates of electron transfer from both the S2 and S1 excited states of a ZnTPPS4+/MV2+ complex were very similar and generated the radical pair\(^\dagger\) ZnTPPS\(^{3-}\)/MV\(^{2+}\) with a time constant \(\tau < 200\) fs, despite the ca. 0.9 eV difference in driving force for the two reactions. The following back reaction was also fast, \(\tau = 0.8\) ps. It was surprising that the rates of forward ET (FET) were seemingly identical for the two excitations; no signs of relaxation dynamics were seen in the back ET (BET) processes which indicated that the ca. 0.9 eV excess energy for the S2 reaction was dumped on a time-scale faster than the ET reactions. That study was done using a single color probe and the time-resolution of the experiment did not allow the FET to be observed. In papers I and II we try to resolve the FET and, if possible, quantify any difference in rates. The use of a white light probe also enabled us to identify possible differences in the intermediate spectra.

The results from these studies (I–II) showed that indeed the forward and back electron transfer rates are very similar \((\tau_\text{FET} \sim 180\) fs). We also observed that the BET produced unrelaxed ground state products that were dependent on the initial excitation. It could then be reasoned that the S2 FET produced a radical pair with excess energy that was not completely dissipated before BET. Unrelaxed ground states have been observed before in the literature, but this was a first demonstration of excess ground state energy being dependent on the excess energy of the excited state. Specifically, excitation to the ZnTPPS\(^{3+}\) S2 state gave higher observed yield of unrelaxed ZnTPPS\(^{4+}\) ground states S0\(^\dagger\) as compared with S1(v=1) excitation and in turn also higher yield than with S1(v=0) excitation. This could be envisioned using a Jablonski type diagram as in Figure 16.

\(\uparrow\) The term charge separated (CS) state is also found in the literature.
Figure 16. Schematic decay scheme of the observed processes in ZnTPPS\(^4^-/MV^{2+}\). D\(^+/A^- (S_0)\) indicates that the radical pair is dependent on the initial excitation. Higher initial excitation leads to higher excited radical pairs that do not completely relax before BET. Figure obtained from II (Figure 10).

In a third paper (III) we studied a series of porphyrin/viologen complexes (Figure 17) and demonstrated that the S\(_2\) FET produced an electronically excited radical pair. Electronically excited charge separated states have been assumed to play a role in charge separation reactions before, but this is the first report that gives clear evidence of their existence in intramolecular electron transfer. Electronically excited charge separated states were also presented in Paper II, where differences between radical pair spectra for the S\(_2\) and S\(_1(\nu=0)\) excitation matched the difference spectrum for the electronically excited methyl viologen that had been reported previously.\(^{77}\)

The observation of unrelaxed ground states and their dependence on both the initial excitation and the driving force for electron transfer revealed a rich interplay of electron transfer and relaxation dynamics. Kasha’s rule states that all emission occurs from the lowest excited state, and was then generalized to other photophysical processes.\(^{78}\) In general, for large molecules in solution the higher excited states have a lifetime of less than 10 ps and the fluorescence rate constant is less than 1\(\cdot\)10\(^9\) s\(^{-1}\). However, as is clearly seen in this thesis, electron transfer reactions can in many cases be faster than 1\(\cdot\)10\(^9\) s\(^{-1}\). Kasha’s rule was postulated before pump probe techniques enabled the studies of ultrafast reactions, reactions faster than excited state relaxation could not be observed. In the last decades the higher excited states of porphyrins has received an increasing amount of attention, and there have been many reports of electron transfer directly from the S\(_2\) excited state.\(^{76,79,80,81,82,83}\)

In the following sections will elaborate on the concepts and results from Papers II-IV. The results from paper I-III can also be used to understand the dynamics in paper IV that will be discussed further in Chapter 5.
4.1 Porphyrin photophysics

Porphyrins are important building blocks in many natural and artificial electron transfer processes and have been used both as important components in devices such as photovoltaics and pressure cells as well as tools for understanding more fundamental aspects of photophysics and photochemistry.\textsuperscript{84,85} With the development of ultrafast spectroscopies also the higher excited states of porphyrins have received increasing attention\textsuperscript{86} An unusual feature of porphyrins is the relatively long lifetime of the second electronically excited state $S_2$ that is on the order of a few ps. An even more extreme case is the phthalocyanines that have been observed to have a lifetime of up to 5 ns for the second excited state.\textsuperscript{87,88}

The porphyrins and viologens that have been used for the study of electron transfer in paper III is shown in Figure 17.

![Figure 17. The viologens and porphyrins used in paper III.](image)

4.1.1 Absorption and emission spectra of porphyrins

Figure 18 shows the absorption and emission spectrum for ZnTPPS\textsuperscript{4−}, which is typical for a metalloporphyrin. The most intense peak (425 nm in Figure 18) is the Soret band that corresponds to an $S_2 \rightarrow S_0$ transition. The lower intensity bands in the 500 – 600 nm region are the Q-bands, which correspond to an $S_1 \rightarrow S_0$ transition. Transitions between different vibrational levels are resolved in the spectra, and these are labelled with the vibrational level of the excited and ground state respectively. Absorption of 555 nm light puts the ZnTPPS\textsuperscript{4−} in the first vibrational level of the $S_1$ state, which in this thesis will be labeled $S_1(v=1)$ and the lowest $S_1$ state will correspondingly be labeled $S_1(v=0)$. 
As seen in Figure 18, emission also from the higher excited $S_2$ state can be observed in a steady state measurement. This observation is enabled due to an unusually high quantum yield for $S_2$ emission which is a unique property for many porphyrins ($\phi_{fl}(S_2\to S_0) = 0.0018$ for ZnTPP in EtOH).  

It has also been shown that the Soret band consists of several (two or more) overlapping absorption bands. This was first reported by Zewail and co-workers and later by Steer and co-workers and others. A presence of several overlapping absorption bands could in principle have an effect on the ET rates that would depend on the excitation wavelength within the Soret-band. Different states can give a different coupling for the ET reaction, and could also provide a parallel relaxation pathway for the decay of the $S_2$ state. No clear excitation wavelength dependence of the ET for different excitation wavelength within the Soret-band is observed in the porphyrin/viologen complexes, but should be kept in mind when analyzing sub ps kinetics of $S_2$ excited porphyrins.

4.1.2 Excited state absorption of porphyrins

While the excited state absorbance is remarkably similar for the $S_1$, $S_2$ and $T_1$ excited state of porphyrins, there are features by which the different states may be differentiated in transient absorption difference spectra (Figure 19). For the singlet states the most characteristic feature is the stimulated emission band that occurs at the same wavelengths as the corresponding steady state emission (see chapter 3.2.1). This can be seen when comparing the transient absorption (TA) spectra with the emission spectra in Figure 19.
A global analysis of the time resolved spectra for ZnTPPS$^{4-}$ in aqueous solution revealed a $\tau_{S_{2}} = 1.3$ ps lifetime for the $S_{2}$ state, in agreement with the earlier report. The $S_{2} \rightarrow S_{1}$ IC forms a vibrationally excited $S_{1}$ state ($S_{1}^{'v}$) that relaxes with $\tau = 5$ ps. There are only small observable differences in the absorption spectra for the $S_{1}^{'v}$ and $S_{1}$ state, where the 5 ps component is needed in order to accurately fit the traces at all wavelengths. The lifetime of the $S_{1}$ state has previously been reported to be 1.7 ns, while the $T_{1}$ state has a 1.4 ms lifetime.

4.2 Electron transfer to electronically excited radical pairs

The porphyrin and viologen form a ground state complex with absorption spectrum which is similar to the free porphyrin; the Soret band is red-shifted by ca. 5 nm, while the Q-bands are less affected (see III). The reduced viologen and oxidized porphyrin have strong absorbances at ca 390 and 405 nm, respectively, that allows the FET and BET processes to be followed spectroscopically. The rate of FET vs. driving force for the porphyrin/viologen complexes (Figure 17) is shown in Figure 20. The overall rate of FET increases with increasing driving for both the $S_{1}$ and $S_{2}$ reactions, which means that the electron transfer reactions of the porphyrin/viologen systems investigated are in the normal region where $|\Delta G^0| < \lambda$. They can then be analyzed with the classical expression for non-adiabatic electron transfer (eq. 2.7). What cannot be discerned from Figure 4 is whether the $S_{1}(v=0)$ and $S_{1}(v=1)$ sets of reactions should be treated separately or not, i.e. be fitted with same pa-
rameters for the rate equation. Figure 20 shows that the $S_2$ and $S_1$ reactions lie on different Marcus parabolas (purple and light green, respectively) meaning that different electronic states are involved for the two sets of reactions. While fit of the $S_{1(v=0)}$ reactions yield a reasonable reorganizational energy ($\lambda$) of 0.9 eV the fit of the $S_2$ reactions yield an unrealistically high $\lambda$ of 1.9 eV. $S_2$ FET reactions, therefore, do not progress to the ground state of the radical pair but rather to an electronically excited radical pair. The $S_2$ FET should have same $\lambda$ as the $S_1$ FET reactions. This condition can be met if the driving force can be varied. The best fit of the $S_2$ data with $\lambda = 0.9$ eV is obtained if the $\Delta G^0$ values are shifted 0.9 eV (see paper III figure 7). We could conclude that the product state for $S_2$ FET reactions corresponds to an electronically excited radical pair state that lie ca. 0.9 eV higher in energy than its ground state. This is indeed reasonable, as both porphyrin and viologen radicals have low lying states.

![Figure 20. $k_{ET}$ vs. $\Delta G^0$ for the porphyrin viologen complexes in Figure 17. The lines are a fit of eq. 2.11 to each set $S_2$, $S_{1(v=1)}$, and $S_{1(v=0)}$. Colors of data points refer to the color of the viologens in Figure 17. See paper III Figure 6 for details.](image)

4.2.1 Spectroscopy of radical ions

Of interest was to see where the excess energy was localized: on the porphyrin or the viologen. The observed transient spectra look similar for both $S_2$ and $S_1$ reactions, but when calculating the species associated spectra some differences became apparent. This was done for the ZnTPPS$^{4-}$/MV$^{2+}$ complex (II), where differences in the radical pair spectra for the different excitations matched fairly well with reported difference spectrum for the excited viologen radical (see Figure 21). This is an indication that at least part of the excess energy is located on the viologen in the radical pair state.
Radical ions are not easy to detect spectroscopically due to their often short lifetime. The reported time constants for the D₁ excited MV⁺⁺ in acetonitrile are 700 fs and 16 ps, which was attributed to D₁ → D₀ IC and vibrational relaxation respectively. Verlet and co-workers have studied the excited states of reduced benzo-quinones and related molecules using photoelectron spectroscopy. They observed that the electronically excited state D₀ decays on a sub 40 fs time-scale via several low lying states.

4.3 Electron transfer in competition with vibrational relaxation

Unrelaxed ground states (S₀⁺) are observed as products of the ET in the porphyrin/viologen complexes, and the yield of S₀⁺ depends on the initially excited states S₂, S₁(v=1), and S₁(v=0). As is seen in Figure 22 the BET reactions take place in the inverted region (−ΔG° > λ). In this regime nuclear tunneling to vibrationally excited product states are also expected to occur from the relaxed reactant state. The similar rate of BET for all excitations however suggests that the driving force for BET is similar for regardless of initial excitation. It can then be concluded that the relaxation of the radical pair is not complete prior to BET. Excess energy that survives two steps of electron transfer, and also depends on the initially excited state, is an unusual observation not previously reported in the literature prior to Paper I.
Figure 22. $k_{BET}$ vs. $\Delta G^0$ for the porphyrin/viologen complexes. The lines are a fit of eq. 2.11 (dotted) and 2.12 (solid) to the BET rates for all excitations. Colors of data points correspond to the color of the viologens in Figure 17. See paper III Figure 6 for details.

That the yield of $S_0^\nu$ did not only depend on the initial excitation, but also on the driving forces of electron transfer, showed the rich interplay of relaxation and electron transfer that can occur for ultrafast electron transfer of large molecules in solution. The coupling between higher excited vibrational modes of both reactant and product state can indeed be strong enough, to allow electron transfer to be faster than vibrational relaxation. This is discussed in more detail in Paper III.

4.3.1 Absorption spectra of unrelaxed states

The observation of unrelaxed ground states is important for a full description of electron transfer from unrelaxed states. From the amount of unrelaxed ground state products we can deduce information about the dynamics of the excited states. For a vibrationally excited state the electronic transitions to higher electronic excited states will be the same as for the relaxed state, but the energy gap will be smaller. A vibrationally excited state will then have a similar spectrum to that of the ground state, but shifted to longer wavelengths. The difference spectrum ($\Delta A$) that is seen in a transient absorption (TA) spectrum will have a derivative shape as seen in Figure 23.
Figure 23. Difference spectrum ($\Delta A_{vib}$) for a vibrationally unrelaxed state (yellow line). The absorption spectrum of the relaxed state (red line) is here represented by a Gaussian. The unrelaxed state (green) is a Gaussian of same width but shifted to lower energies. Note that the simulation is made on an wavenumber scale, while the plot is made on a wavelength scale.

We have used the term unrelaxed state rather than hot since hot implies that the vibrationally excited state is in thermal equilibrium (see eq. 2.3). A hot state would not only have one shift but rather a Boltzman weighted distribution of shifts. This could not be seen in the spectra of the unrelaxed ground states in paper I-IV, and they were therefore analyzed with a single shift ($\bar{\nu}_{shift}$) and an amplitude ($\alpha$) according to equation 4.1.

$$\Delta A_{vib} = \alpha \times \left( A_{GS}(\bar{\nu} + \bar{\nu}_{shift}) - A_{GS}(\bar{\nu}) \right)$$

(4.1)

Here $A_{GS}$ stands for the absorbance of the ground state, and $A_{GS}(\bar{\nu} + \bar{\nu}_{shift})$ is then the ground state spectrum shifted by $\bar{\nu}_{shift}$ wavenumbers. The amplitude $\alpha$ was included to account for the fraction of molecules that were already in the ground state, either by a fast vibrational relaxation or a parallel pathway to the ground state. We did not attempt to distinguish an IVR process from VC, and instead used the more general term vibrational relaxation (VR). It is interesting to note that for the ZnTPPS$^{4-}$/MV$^{2+}$ complex (I–II) the decay of the unrelaxed ground state did not only involve a decrease of $\bar{\nu}_{shift}$ but also a decrease of $\alpha$. This is seen both in the raw data (Figure 24) and in the species associated spectra (paper II Figure S10). The good agreement with a single shift suggests that there is only one acceptor mode, or a narrow set of acceptor modes, that are involved in the electron transfer.
Figure 24. Transient absorption spectra at different probe times for ZnTPPS$^{4-}$/MV$^{2+}$ excited at 426 nm. The spectra correspond to unrelaxed ground state ($S_0^\nu$) and are fitted according to eq. 4.1. The amplitude is relative that of the 2.5 ps spectrum.

Unrelaxed ground states (here denoted $S_0^\nu$ for the porphyrin) are likely to be an important reaction product in many ET reactions. However in order to observe their signature in a transient absorption the ground state absorption peak needs to be sharp. This criterion is met by the Soret-band which makes porphyrins an excellent probe for unrelaxed ground states in the visible spectra.

4.3.2 Stimulated Raman studies

The unrelaxed ground state provided indirect information of the relaxation dynamics of the radical pair state, as indicated from the difference of the intermediate spectra (Figure 19). Vibrational spectroscopy could possibly give more direct information of which modes that are coupled to the electron transfer. The transient absorption experiments in the visible region were done in H$_2$O, however, water is not a suitable solvent for IR measurements due to its intense vibrational features. The replacement of water by organic
solvents was not feasible due to low solubility of porphyrin/viologen complexes in those media. Raman spectroscopy is a vibrational spectroscopy where the light is in the visible region (see chapters 2.2.2 3.2.3). Water is transparent to visible light and the Raman spectrum is weaker than the IR spectrum. It might then be possible to study the vibrational dynamics of the electron transfer reactions using time resolved Raman techniques. In cooperation with Michael R. Wasielewski and Dick Co at Northwestern University, we set out to study the ZnTPPS$^+/MV^{2+}$ complex with stimulated Raman spectroscopy (FSRS).$^{99,100}$

Several different Raman pump wavelengths ranging from 480 nm to 660 nm were tested. The most promising result was obtained with Raman pump 660 nm (Figure 25), which lies at the red end of the Q(1,0) ground state absorption band. Two transient peaks at wavenumbers 1360 cm$^{-1}$ and 1560 cm$^{-1}$ were resolved which correspond well with MV$^+$.$^{101}$ The dynamics ($\tau = 0.16$ ps rise and 0.8 ps decay) matched the rise and decay of the radical pair seen in the TA spectra. However, no signs of excited porphyrin could be seen. Despite the vast use of porphyrins in many fields there has, to the best of my knowledge, not been any report of excited states of porphyrins studied with FSRS (note that the transient spectra in Figure 25 are from the viologen and not the porphyrin). That seems likely that the porphyrin does not have a sufficient cross-section for stimulated Raman transitions.
Figure 25. FSRS spectra of ZnTPPS$^{4-}$/MV$^{2+}$ in H$_2$O (2mM phosphate buffer) with Raman pump at 630 nm. The baseline at each delay time and the ground state spectrum (obtained from negative delay times) are subtracted from the spectra. Top panel shows the ground state spectrum.

4.4 Concluding remarks, Electron transfer from higher excited states

The observed dynamics of the porphyrin/viologen complexes can be rationalized with the free energy parabolas seen in Figure 26. The solvent reorganization is believed to be very fast and most of the reaction coordinate is from low frequency internal modes of the D/A complex. The dynamics that is reported by Wallin et al.\textsuperscript{102} can be related to the kinetic competition between electron transfer and vibrational relaxation seen here. There it was seen that FET from porphyrin excited to the $S_2$ state produced a charge separated state (CS) that quickly recombined to the $S_1$ state where a second FET again produced CS state ($S_2 \rightarrow \text{CS}^{\text{hot}} \rightarrow S_1 \rightarrow \text{CS}$). Similar observation in another
porphyrin diimide dyad has been observed by Robotham et al. In paper IV we observed a similar kinetics where the unrelaxed CS state recombined both directly to unrelaxed ground states and in parallel also to the porphyrin T₁ state, where a further FET to the relaxed CS state occurred. Both these examples show the dramatic effect excited charge separated states can have on the reaction pathways.

![Figure 26](image.png)

*Figure 26.* Schematic free energy parabolas for the states involved in the electron transfer of the porphyrin/viologen complexes. The radical pair is denoted D⁺/A⁻. The energy level of the D⁺/A⁻ state is between the solid and dashed lie depending on the redox potentials of the porphyrin and viologen.

The electron transfer theories, including the Barbara hybrid model, presented in chapter 2.3 all assume thermal equilibrium in the reactant state. This is clearly not directly applicable for the electron transfer observed here. Ivanov and co-workers however have used a model similar to the Sumi-Marcus and Barbara models that treats the solvent dynamics with a distribution of relaxation times and also uses a more complete quantum mechanical description for all internal vibrations. They could then accurately reconstruct the kinetics observed by Wallin et al. and also simulate kinetics similar to what is observed here for the porphyrin/viologen complexes.

4.4.1 What is a direct spectroscopic observation?

Marcus explained the observation of chemiluminescence with the presence of electronically excited states as product states of electron transfer in the inverted region already in the 1960’s. In the later years there have also been many reports of photoinduced electron transfer from the porphyrin
S$_2$ state that discuss the possibility of an excited (vibrationally and/or electronically) charge separated state based on a unexpectedly fast rate of ET.$^{76,110,111}$ More “direct” observations has been made for charge recombination reactions; Following charge separation from the porphyrin S$_2$ state, recombination could be concluded to occur to the porphyrin S$_1$ state which indeed is an electronically excited state.$^{82,102,103,112,113}$

Koch et al. recently reported on a series of electron donor and acceptor molecules where the unrelaxed ground state of the acceptor could be observed with IR spectroscopy. Based on the estimated temperature of the unrelaxed ground state it was reasoned that for some DA pairs an electronically charge separated state was involved in the process.$^{114}$

I would argue that the spectra seen in Figure 21 is the first direct observation of electronically excited radical pairs (or charge separated state), not simply clear evidence, in photoinduced intramolecular charge separation, where the results from Figure 20 provide further evidence for our direct observation.
5 Intra-molecular electron transfer dynamics in competition with inter-molecular electron injection (paper IV–VI)

This chapter will deal with the competition between different electron transfer processes. Rather than studying how properties of a system affects the individual electron transfer rate, here we show how the dynamics of electron transfer might affect other processes.

Paper V concerns the photosensitizer Ru(4,4’-dicarboxylate-2,2’-bipyridine)₂cis(NCS)₂ that is extensively used in dye sensitized solar cells (DSSC), mainly as the tetrabutylammonium salt. The dynamics of its metal-to-ligand charge transfer (MLCT) excited state is fundamentally very interesting and also has relevance to the electron injection dynamics, i.e. the electron transfer from dye to semiconductor in a DCCS or related devices.

In paper VI the stabilization of the charge separated state in a p-type DSSC is studied through a series of three dye molecules that are designed to increase the distance of the electron-hole pair. Paper IV has already been discussed in terms of electron transfer from unrelaxed states (Chapter 4) but can further be put in relation to paper VI in the way that the charge separated states are delocalized in both cases.

Even though the three studies from papers IV–VI involve different types of electron transfer dynamics, the overall theme describes how dynamics and character of the charge separated state influences charge separation and recombination. This connection is represented in Figure 27.
Inter ligand electron transfer (ILET) in the MLCT state is the subject of paper V. Depending on the binding of the photosensitizer molecule to TiO$_2$ the rate of ILET might be a limiting step in the electron injection dynamics. While this has direct connection to VI that deals with DSSCs it could also be put in perspective of the mixed valence dynamics studied in paper IV. Both the ILET in the N712 molecule and the mixed valence of the Ru$_3$O-pz-Ru$_3$O dimers are isoenergetic electron transfers. The MLCT state of the photosensitizer molecule might also be delocalized which would make it similar to the inter-valence charge transfer (IVCT) in the mixed valence state of the Ru$_3$O-pz-Ru$_3$O dimers. In both cases it seems that any degree of localization, if there were any at all, is lost on a very fast time scale.

The study presented in VI concerns a photosensitizer made up of three individual subunits, hence the name “triad dye” in Figure 27. This dye was designed to give a more long-lived charge separated state by virtue of an increased electron-hole-pair distance. While most of the recombination occurred on a very fast (ps) time-scale, the overall trends where the desired, i.e. dyes that increased the distance also gave the longest lifetime and highest efficiencies of the DSSC. The following the three studies (IV,V,VI) will be presented separately.
5.1 ILET – a rate determining step in charge injection? (paper V)

The Ru-polypyridyl molecule N3 has been extensively used in the dye sensitized solar cells. It has four carboxylic acid groups (see Figure 28), the half and fully deprotonated version of N3 is called N719 and N712. The deprotonation causes a blueshift of the visible absorption spectrum.\(^{115}\)

![Figure 28. Structure of N3, N719, and N712. N719 and N712 are used in the form of tetrabutylammonium salts.](image)

The \(^1\)MLCT state has a very short lifetime and converts to the \(^3\)MLCT state in 10 – 100 fs.\(^{116}\) Whether the electron injection from dye to the TiO\(_2\) in a DSSC occurs from the \(^1\)MLCT or \(^3\)MLCT depends on the competition between electron transfer and relaxation (ISC). Electron transfer on the order of a few fs is not unlikely due to the high density of acceptor states in the TiO\(_2\) that, just as high frequency acceptor modes in the inverted region (see chapter 2.3.2), facilitate the ET.\(^{13b,29,117}\) Still, a substantial part of the injection may also take place from the \(^3\)MLCT state. The dynamics of the injection from dye to the TiO\(_2\) is the center of an ongoing debate. While many studies have demonstrated ultrafast (100 fs, 10 fs or even faster) injection into TiO\(_2\) from attached dyes, there is a controversy around the injection timescale for the real device, i.e. with the most efficient dyes and electrolytes.\(^{10,118,119,120}\) A recent report by Antilla et al. showed that both fs and slower injection dynamics can be observed and that this depends on solvent and electrolyte conditions.\(^{121}\)

The initial excitation to the \(^1\)MLCT state is described as an electron transfer from the Ru to one of the bipyridine (bpy) ligands.\(^{122,123}\) The MLCT state is then localized mainly on one bpy and the ruthenium (with some backbonding to the NCS ligand).\(^{124}\) The two bpy ligands are structurally identical, and the MLCT state where the electron density is instead localized on the other bpy has exactly same energy level and absorption spectrum. A transfer between the two MLCT states can be viewed as an electron transfer between
the two bpy ligands, i.e. inter-ligand electron transfer (ILET). ILET in general can also occur between two different ligands,\textsuperscript{125,126} but when they are close in energy the electron may hop back again leading to an electron transfer equilibrium

This ILET process is not only fundamentally interesting; it also might limit injection dynamics to the TiO\textsubscript{2} in the DSSC. If only one of the bpy ligands bind to TiO\textsubscript{2} then, for molecules in the MLCT state where the electron is localized on the unbound ligand, the electron will have to hop to the bound ligand from which electron injection can occur. ILET mostly refers to the hopping between relaxed MLCT states. As described in the previous chapter, electron transfer can indeed take place also from unrelaxed states. In this case the ILET might then be initially very fast, either in the \textsuperscript{1}MLCT state or the vibrationally unrelaxed \textsuperscript{3}MLCT state, and slow down as the molecule and surrounding solvent relaxes to a state where the barrier for ET could be higher.

Two previous reports show completely different results for ILET in the N3 dye. Kelley and co-workers\textsuperscript{127} report a ILET time-constant of 3 ns while Sundström and co-workers\textsuperscript{128} report a time constant of ca. 20 ps. For the related molecule Ru(bpy)\textsubscript{3}\textsuperscript{2+} the ILET occur on a sub ps time-scale where the initial state is delocalized over both bpy ligands.\textsuperscript{129,130,131} It is surprising that the rate of ILET seemingly is very different in N3 and Ru(bpy)\textsubscript{3}\textsuperscript{2+}. A more detailed discussion about the conflicting results for N3 is given in \textit{V}.

5.1.1 Transient absorption anisotropy as a tool to investigate ILET

A complicating factor for direct measurements of the ILET process is that both bpy ligands are structurally identical and will therefore have same absorption spectra. This is indicated in Figure 29 As already mentioned in chapter 3.2.2 the two ligands can be distinguished with polarized spectroscopy due to the different directions of their transition dipole moments. Both the previous measurements on N3 were made with transient absorption anisotropy and probed the electronic transitions in the visible region. That can be problematic since several overlapping absorption bands are present (see chapter 3.2.2). We therefore set out to measure the ILET with transient absorption spectroscopy where the probe light is in the mid-IR region.
Figure 29. Schematic diagram of $^3$MLCT decay. The rate of ILET cannot be determined from isotropic (magic angle) absorption spectroscopy that only depends on the magnitude of the transition dipole moment. Therefore absorption anisotropy is needed. Anisotropy is dependent on the direction of the dipole moment, which is different for the carboxylates on the two bpy ligands. The labels 1-2 and 3-4 refers to the carboxylates, see Figure 30.

5.1.2 Structure of N712 and predicted anisotropy values

It is assumed that extra electron density on the bpy will have an effect also on the carboxylate vibrations and lead to a downshift of the vibrational frequency of the MLCT state. We have chosen to study the N712 molecule due to the favourable direction of the transition dipole moments for the vibrations. The carboxylate (−COO$^-$) has two strong spectral peaks in the IR region at ca. 1624 cm$^{-1}$ and 1348 cm$^{-1}$ belonging to the asymmetric and symmetric stretch, respectively. The direction of the IR transition dipole moment relative to the phenyl-carboxylate axis is denoted by the angle $\theta$ (see Figure 30). In the C$_{2v}$ structure of the carboxylate the symmetric stretch corresponds to an angle $\theta = 0^\circ$ and the asymmetric stretch $\theta = 90^\circ$. The electronic excitation can be viewed as a Ru $\rightarrow$ bpy CT transition that is directed from the Ru to the center of the bpy, as indicated in Figure 30.
Figure 30. Schematic picture of the Structure of the N712 molecule. The transition dipole moment for the electronic excitation is labeled $\mu_{el}$ and the vibrational transition (that is probed) is labeled $\mu_{vib}$. The carboxylate group is assumed to freely rotate around the $q$-axis. The symmetric stretch symmetric stretch has $\theta = 0^\circ$ and the asymmetric stretch has $\theta = 90^\circ$. The molecule can be assumed to have mainly octahedral symmetry, but deviations from this are included in the calculation of expected anisotropies. Especially, a $\sim 10^\circ$ contraction of the N-Ru-N angle of the bipyridines is expected (corresponding to $\alpha = 5^\circ$) which will have a small but noticeable effect on the calculated anisotropy.

Expected anisotropy values can be calculated by equation 3.3. The directions of the transition dipole moments for the electronic excitation $\mu_{el}$ and the probed vibration $\mu_{vib}$ are given in Figure 30. The expected anisotropies for the localized and randomized state are $r_{loc} = 0.1$ and $r_{rand} = 0.025$ for the symmetric stretch, and $r_{loc} = 0.05$, $r_{rand} = 0.0125$ for the asymmetric stretch. In the calculation the carboxylate is assumed to freely rotate around its principal axis (denoted $q$ in Figure 30) and the anisotropy will then be an average of all angles. The above-mentioned anisotropies are for an ideal octahedral structure. A more realistic structure includes a contraction of the N-Ru-N angle ($2\alpha$ in Figure 30) of about 10$^\circ$. An expression for the anisotropies that depends on both the direction of the IR transition dipole moment and the contraction of the N-Ru-N angle is derived in paper V. Further distortions caused by a bending of the carboxylates out of the bpy plane leads to only a small decrease of the calculated anisotropies. The expected anisotropies should then be rather robust with respect to structural distortions. The method of probing the vibrational transitions rather than the electronic transitions should be a promising way to proceed.

5.1.3 Unexpectedly slow rate of ILET

Though there were some overlapping absorption bands also in the transient IR spectra the carboxylate stretches were distinct enough to allow the symmetric stretch to be observed. The anisotropy decay for the symmetric stretch is seen in Figure 31. The time-constant for the slow decay is 400 ps which is in agreement with the results from Kelley an co-workers. The aniso-
sotropy of 0.1 is in agreement with a localized state and the results then show that ILET is at least slower than rotational diffusion, which is expected to be on the 400 ps time-scale.\textsuperscript{127}

Figure 31. Anisotropy trace of the symmetric stretch in N712 excited at 650 nm. The absorption is probed at 1332 cm\textsuperscript{-1} where the contributions from other excited states and ground state bleach is negligible. The trace is fitted with time constants 1.5 ps and 400 ps. When the decay is treated as a consecutive reaction the corresponding anisotropies for the initial and intermediate state are 0.05 and 0.09 respectively.

5.1.4 Initially delocalized state?
The initial rise of the anisotropy with a time-constant of 1.5 ps is an interesting observation. The total absorbance is constant on this time-scale and there are no peak shifts of the spectra. The initial anisotropy of 0.05 corresponds to the anisotropy value expected for a randomized state, which could also be interpreted as a delocalized state.

Coherence effects on the observed anisotropy
The two structurally identical bpy ligands will result in two degenerate MLCT states of N712. As shown in chapter 2.2.1 these degenerate states could give rise to coherence effects provided that the states have sufficiently large coupling to each other. It was also mentioned that degenerate state might have an impact on the anisotropy (chapter 2.2.1). This is however only valid when probing electronic transitions from a coherent state to the same end state, as for stimulated emission.\textsuperscript{28} This is certainly not the case here; the excitation and relevant coherence is electronic while the observed (probe) transition is vibrational. Furthermore, it is not expected that the vibrational
transitions of the separate bpy ligands have sufficient coupling to result in a coherence of the vibrational states.

The electronic coherence of the excited MLCT state might manifest itself as a delocalized state with excess electronic density affecting the vibrations of all COO⁻ groups. A delocalized state can be expected to have the same anisotropy as a randomized state. That is indeed what is observed; the initial anisotropy starts at \( r = 0.05 \), then increases with a time-constant of ca. 1.5 ps to an anisotropy of \( r = 0.09 \) which corresponds to a localized state. We do note that it is an unexpected long decay time for the coherence dephasing. Hochstrasser has reported dephasing of coherence in MgTPP with a 1.6 ps time-constant and this dephasing was argued to be driven by vibrational relaxation.\(^{28}\) At the present stage of analysis, we tentatively suggest this explanation for the observed initial rise of the anisotropy.

### 5.1.5 Consequences for injection dynamics

It is then interesting to come back to the topic of injection dynamics for the dye on TiO₂. A slow ILET could be a limiting step in the injection dynamics provided that only carboxylates from one of the bipyridines are involved in the binding to the TiO₂ surface. It is reasonable to assume that the symmetry for N712 is not conserved when bound to TiO₂. Both the TiO₂ and the disrupted solvent environment will likely have an effect on the relative energies of the two ligands. This is indicated from the results of Olsen et al. that studied ILET in the N3 dye on Zirconia.\(^{133}\) Anisotropy measurements from this group showed that within the 120 ps time-window allowed by the experiment, no difference in anisotropy was observed. This suggests that the electron is trapped on the bpy ligand that is lowest in energy.

### 5.2 Charge transfer to semi-conductors (paper VI)

There is an important difference between charge transfer to molecules and charge transfer to semiconductors; semiconductors have a much higher density of states than do molecules. In Chapter 5.1 electron injection into the TiO₂ conduction band was mentioned. The NiO semiconductor, that is used in paper VI, however is not an electron acceptor but rather an electron donor. The electron transfer from the NiO valence band to the excited dye can also be viewed as a hole transfer from the dye to NiO.
5.2.1 Increasing the DSSC efficiency by intra-molecular charge separation

The dyes studied in paper VI were designed to both increase the total absorption cross-section and also increase the distance between the electron and the hole injected to NiO. The dye is made up of three sub-units: a squarine (SQ), a perylene monoimide (PMI), and a naphtalene-diimide (see structure in Figure 32). The different chromophore units could, in principal, work as an antenna that transfers excitation energy to the squarine subunit nearest to NiO where hole injection could take place. This proposed energy transfer pathway was outcompeted by a very fast (τ ~100 - 400 fs) intramolecular charge separation (see reaction scheme Figure 32). A further electron shift between subunits did result in hole injection and a more long lived charge separated state as compared to the squarine/NiO system. The electron shift reactions of the initial charge separated state occurred, however, they were in competition with very rapid (τ ~100 ps) charge recombination. Nevertheless the net result was positive: the use of the triad resulted in a more long lived charge separated state and a greater efficiency of the complete DSSC as compared with the dyad and squarine monomer.

This study highlighted the need for tighter control of the very fast charge recombination in order to achieve the full potential of intramolecular charge separation. This can be achieved through improved molecular design.
5.3 Mixed valence dynamics (paper IV)

The original concept behind paper IV was to investigate time resolved dynamics in a series of mixed valence complexes exhibiting a high degree of electronic coupling. What was most appealing about this proposed study was its potential to provide entirely new information concerning the timescale and possible dynamics of the evolution of a delocalized (mixed valence) state. A delocalization of the electron density in the reduced dimer can be viewed as an increase in the electron-hole-pair distance. The increased distance has the net effect of reducing the electronic coupling for the charge...
recombination and hence make a more long-lived charge separated state, in a very similar manner as described in paper VI (and section 5.2)

5.3.1 Inter valence charge transfer in the mixed valence state

Mixed valence states have traditionally been characterized by the energy, shape and solvent dependence of their corresponding inter valence charge transfer (IVCT) bands.\textsuperscript{134,135,136} IVCT in a symmetric dimer can be viewed as an electron transfer between the individual monomer units (in analogy with the ILET between the two bpy ligands, chapter 5.1). The coupling that indicated in Figure 5 is in this context relatively weak. For more strongly coupled systems the transition state will be significantly lowered and the free energy surfaces will also be stabilized in energy. For a completely delocalized mixed valence system the coupling is so large that a single-well surface is predicted.\textsuperscript{134} The charge transfer (CT) bands in the absorption spectrum, which are vertical (Franck-Condon) transitions from the reactant state to the final state, can be related to the coupling and reorganizational of the electron transfer between the monomers. It is fundamentally interesting to investigate whether mixed valency can be viewed as a very fast electron transfer or a delocalized electron density. In either picture, the degree of delocalization or rate of electron transfer will be influenced by the electronic coupling.

Figure 33. Structure of the ZnTPPpy-(Ru3O-pz-Ru3O) dyads and decay scheme for the observed reactions. Reaction rates were somewhat different for the different complexes, the difference in ET rates agreed with variation in driving force. The numbers in the figure indicate average values.

5.3.2 Towards time-resolved inter-valence charge transfer

The time-resolution needed to study the evolution of delocalized mixed valence states will likely need to be very fast, i.e. less than 10 ps.\textsuperscript{137} It was necessary to covalently link an electron donating porphyrin to the, such that a
photoinduced electron transfer from the porphyrin to the ruthenium dimers could be followed by pump-probe transient absorption spectroscopy. Following dynamics in the mixed valence state requires that the initial electron transfer that produces them must be fast. The synthesis and characterization of the dyads has been reported by Henderson et al.\textsuperscript{138} The excited state energies and electrochemical potentials of the dyads are such that electron transfer from the porphyrin S\textsubscript{1} state has approximately 0.5 eV driving force, and the charge transfer state (oxidized porphyrin + reduced Ruthenium-dimer) lies just below the porphyrin Triplet state in energy. This means that excitation of the porphyrin should lead to an intramolecular electron transfer to the dimer portion of the dyad and produce the mixed valence state.

5.3.3 Unrelaxed ground states as indicators of excited state dynamics

The charge separation in the porphyrin-ruthenium dyads was indeed fast, with \( \tau \approx 0.6 \) ps. However, the sub ps charge recombination from the reduced dimer to the porphyrin prevented direct spectroscopic observation of the inter-valence charge transfer bands. Rather than being a story of mixed valence dynamics, the results of the study revealed the fascinating competition of electron transfer and vibrational relaxation. The charge separation formed unrelaxed charge transfer states, that recombined to unrelaxed ground states. A sub ps spin change of the radical pair was also observed as the porphyrin triplet state was formed from unrelaxed charge separated states. Even though the charge separated state was never observed in the spectra, the reaction pathway could be determined based on the observation of unrelaxed porphyrin ground states. The unrelaxed ground states were shown to be formed by charge recombination. Furthermore, based on the relative yield of these intermediate products for two different complexes it could be speculated that at least part of the expected delocalization occurs on timescales faster than 100 fs. This is indeed the first indication of delocalization dynamics based on time resolved measurements. Slowing recombination kinetics should lengthen the time window for the study of mixed valence generation dynamics. This next phase of this investigation will likely require structural changes to the porphyrin linker.
Svensk sammanfattning

Denna avhandling behandlar två grundläggande processer; interaktionen mellan ljus och molekyler och överföring av elektroner mellan molekyler, hur elektroner ”förs över” från en molekyl till en annan. Att studera elektronöverföring är intressant ur ett fundamentalt perspektiv. Det visar på grundläggande interaktioner mellan molekyler. Elektronöverföring är även en viktig process i både naturligt förekommande system samt system gjorda av människor. Fotosyntesen är exempel på ett naturligt system. Det är via fotosyntesen som växter kan ta upp energi från solljus och skapa de kolhydrater de behöver för att växa. Dessutom frigörs syre som djur behöver för att andas. En av de första reaktionerna i fotosyntesen är just elektronöverföring, och de allra första stegen i elektronöverföringskedjan går väldigt fort (tidskonstant på ca 1 ps = 10⁻¹² s). Ytterligare exempel är konstgjord fotosyntes och solceller. I båda systemen absorberas ljus, och energin från ljuset omvandlas med hjälp av elektronöverföring till en mer användbar form av energi. Från solcellen fås el, som kan användas direkt eller lagras i ett batteri. Den konstgjorda fotosyntesen syftar till att med hjälp av solenergi ta fram ett bränsle som kan lagras och användas vid ett senare tillfälle. T.ex. skulle vatten kunna oxideras (precis som i naturligt förekommande fotosyntesen), elektronerna som tagits från vatten kan då användas för att tillsammans med protoner bilda vätgas. Vätgas kan lagras, och när det används som bränsle är vatten den enda biprodukten. Även i dessa artificiella system, framförallt för solceller där i vissa fall elektronöverföringsreaktionshastigheterna antas ha en tidskonstant på endast 1 fs (1 fs = 10⁻¹⁵ s). Detta motsvarar 1 000 000 000 000 000 reaktioner per sekund.

Ett viktigt verktyg för att studera dessa snabba processer är spektroskopi. Spektroskopi låter oss studera växelverkan mellan strålningenergi och materia, vilket i denna avhandling innefattar växelverkan mellan ljus och molekyler. Ljus används här i ett vitt begrepp och kan innebära både ljus i det synliga området – det vi uppfattar som färg – och i det infraröda området – det vi uppfattar som värme. Energin i ljuset beror på dess våglängd genom förhållandet \( E = hc/\lambda \), där \( h \) är Plancks konstant, \( c \) är ljusets hastighet, och \( \lambda \) är våglängden. Ljus av olika energi kan interagera med molekyler och om ljuset tas upp av molekylen ger det upphov till ett spektrum. Ett spektrum som de flesta har upplevt är regnbågen. Solljuset färdas genom vattendropparna med olika fart beroende på dess våglängd. Det innebär att ljuset reflek-
teras olika i vattendroppen. En ytterligare interaktion mellan ljus och materia sker i våra ögon. Ögat reagerar olika på ljus av olika våglängd vilket ger upphov till vårat färgseende. Detta innebär att ljuset som färdas genom vattendropparna kommer visa sig som en regnbåge – ett spektrum.

Spektrumen som behandlas i denna avhandling kommer från att ljus har absorberats av en molekyl. Ljus absorberas olika mycket beroende på vilken våglängd det har och hur molekylen ser ut. Absorbansen beror också på vad som händer i molekylen, i vilket tillstånd den befinner sig i.

**Figur 1: Schematisk uppställning av spektroskopi.** Ljusstrålen (som kommer från vänster) reflekteras på ett gitter där det delas upp i dess olika våglängder. Strålen samlas sedan med en lins och ljusintensiteten mätts med en detektor (inte med i bilden). Den nedre ljusstrålen har färdats genom en prov som skall studeras. Vissa våglängder har absorberats av molekylerna som studeras (i detta fallet porfyriner). Ljuset med dessa våglängder är då svagare, och kommer synas som toppar i ett absorptionsspektrum (se rutan till höger).

För att en kemisk reaktion skall ske krävs att sluttilstståndet har lägre energi än starttillståndet. Energiskillnaden mellan start- och slutttillstånd kallas för drivkraft. Samtidigt som reaktionen sker kommer denna energi att omvandlas till vibrationer i molekylen; molekylen blir varm. Denna värme kommer så småningom sprida sig till omgivningen genom en process som kallas *vibrationsrelaxation*. I denna avhandling studeras just dynamiken mellan vibrationsrelaxation och *elektronöverföring*.

Reaktionerna som studerats i denna avhandling har en karakteristisk tid på ca 100 femtosekunder, vilket innebär att det sker 10 000 000 000 000 stycken reaktionssteg varje sekund. Detta kan jämföras med biofilm som filmas med 24 bilder per sekund. Det krävs alltså en ofattbart snabb kamera för att filma elektronöverföringsreaktionerna. Sättet det görs på är genom att använda sig av det snabbaste som finns, ljus. Korta ljuspulser kan skapas i ett lasersystem. Dessa ljuspulser kan sedan användas för att både starta reaktionen och

Att förstå elektronöverföring är därför av stor nytta. I denna avhandling har jag dels studerat de fundamentala processerna och även tillämpat kunskapen vid studier av solceller och färgämnen. Jag har visat på hur relaxationsprocesser och överskottsenergi kan påverka reaktionsmekanismen vilket är viktigt att ta hänsyn till när system designas.

Framförallt har elektroniskt existerande elektronöverföringsprodukter observert. Detta är något som antagits under lång tid, men aldrig tidigare har så tydliga bevis lagts fram.
Acknowledgements

First I would like to thank my two supervisors Prof. Leif Hammarström and Prof. Jan Davidsson. Thank you Leif! For your generosity, for your support and always open door. Thank you Jan For your help in the laser lab and for entrusting me to teach chemistry.

I want to thank Mattias Eklund for being my first unofficial supervisor. And I'm also grateful to Dr. Hans-Christian Becker for being the unofficial supervisor to everyone.

I would also like to thank my collaborators abroad. Mike Wasielewski: for always welcoming me to your lab, over and over again. Dick Co: You are a big inspiration to me. Ann Woys: For your fantastic IR measurements. Jane Hendersson: For sending your molecules to Uppsala and for the good work we did on the manuscript.

And off course friends and co-workers at the department that have been and are still.

And an extra thanks to
Todd Markle: You made work much more fun! And thanks for all help with synthesis questions and NMR recordings.
Starla Glover: For your invaluable help with proofreading the thesis, and for being a nice person in general
Maria Abrahamson: Du är en förebild, och vet att inte alltid lära ut som du lever.
Susanne Karlsson: För att du var först på kontoret nästan varje dag.
Daniel Karlsson: Du var en stor hjälp i laserlabbet under mina första år som doktorand, och ditt sätt att arbeta inspirerade mig under mina första år som doktorand.
Allison Michelle: For being a talented laser spectroscopist and a good friend
Jens Föhlinger: För din hjälp med IR mätningarna och sällskap i Chicago

And to everyone else, you ae all valuable for me in your own ways
Självklart också ett stort tack till vänner och familj!

**Störst tack av alla**

Elina: Du berikar mitt liv!

Ruth and Henry: Ni är de mest fantastiska personer som finns!
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Acta Universitatis Upsaliensis

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Editor: The Dean of the Faculty of Science and Technology

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