Ultrafast Investigation of Light-Driven Electron Proton Transfer in Intermolecular Model Systems

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Abstract

Brittany Cole Westlake: Ultrafast Investigation of Light-Driven Electron Proton Transfer in Intermolecular Model Systems
(Under the direction of John M. Papanikolas)

This dissertation investigates Electron-Proton Transfer (EPT) and other excited state reaction kinetics in organic molecule systems. This work was done with the goal of gaining a better understanding of the interrelated motions of electrons and protons in excited state molecular systems. Ultrafast spectroscopy techniques were used to monitor the excited state dynamics on the time scale they are occurring. Chapter 1 provides an introduction to EPT, the research, and the important chemical properties that affect these excited state dynamics. A review of recent literature on proton coupled electron transfer and electron proton transfer is included in Chapter 2. Chapter 3 describes the experimental techniques used for the experiments in this dissertation.

Chapter 4 presents the spectroscopic evidence for photo-EPT in nitrophenyl-phenol. Femtosecond transient absorption measurements show energy dependent pathways for the nitrophenyl-phenol-base adduct. At high energy excitation there are two pathways: 1) a photo-EPT transition where the molecule is excited to an elongated proton transfer state, and 2) a trapped proton state, where the molecule undergoes a singlet-triplet intersystem crossing and the proton is transferred from the triplet nitrophenyl-phenol molecule to the base. At low energy excitation only the photo-EPT state is observed.
Chapter 5 describes the ultrafast photo-EPT that gives rise to the increased emission of hydroxycoumarin in aqueous or basic solutions. Our spectroscopic data also show base concentration dependent tautomerization in the excited molecule. In the presence of excess base femtosecond transient absorption measurements and time-correlated single-photon counting experiments can chart the progress as the phenolic proton is shuttled across the molecule forming a neutral excited state tautomer.
To my family and friends.

Thanks for all your support.
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<tbody>
<tr>
<td>1-MeId</td>
<td>1-methylimidazole</td>
</tr>
<tr>
<td>A</td>
<td>initial configuration of the GFP protein</td>
</tr>
<tr>
<td>A*</td>
<td>initial neutral excited state</td>
</tr>
<tr>
<td>A/T</td>
<td>adenine/thymine base pair</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>AOM</td>
<td>acousto-optic modulator</td>
</tr>
<tr>
<td>APTS</td>
<td>8-Aminopyrene-1,3,6-trisulfonate</td>
</tr>
<tr>
<td>BBO</td>
<td>beta barium borate</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CPA</td>
<td>chirped pulse amplification</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-dichloroethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>d^mC</td>
<td>5-methyl-2’-deoxycytidine</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylforamide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>dnb^-</td>
<td>3,5-dinitrobenzoate anion</td>
</tr>
<tr>
<td>EPT</td>
<td>Concerted electron-proton transfer</td>
</tr>
<tr>
<td>ESDPT</td>
<td>excited state double proton transfer</td>
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<tr>
<td>ESPT</td>
<td>excited state proton transfer</td>
</tr>
<tr>
<td>ET</td>
<td>electron transfer</td>
</tr>
<tr>
<td>ETPT</td>
<td>electron transfer followed by proton transfer</td>
</tr>
<tr>
<td>FHG</td>
<td>fourth harmonic generation</td>
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FROG  Frequency Resolved Optical Gating
fsTA  femtosecond transient absorption
FUV  Far-Ultraviolet
FWHM  full width half max
G/C  guanine/cytosine base pair
gd  groove/density
GFP  Green Fluorescent Proteins
h  Planck’s constant
H$_2$Q  hydroquinone
Hdnb  3,5-dinitrobenzoate
HFC  hydroxycoumarin
HFC---B  hydroxycoumarin hydrogen bound to 1-methylimidazole base
His190  histidine
HOMO  highest occupied molecular orbital
HPTS  8-hydroxy-1,3,6-pyrenetrisulfonic acid
I*  neutral transition state
ICT  intramolecular charge transfer
ICT-EPT  intramolecular charge transfer electron-proton transfer
IR  instrument response
ISC  intersystem crossing
k  rate constant
K$_A$  acid dissociation constant
KIE  kinetic isotope effect
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>LBO</td>
<td>lithium triborate</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MLCT</td>
<td>metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>MS-EPT</td>
<td>multisite electron-proton transfer</td>
</tr>
<tr>
<td>NADP</td>
<td>nicotinamide adenine dinucleotide phosphate</td>
</tr>
<tr>
<td>NI</td>
<td>National Instruments</td>
</tr>
<tr>
<td>NOPA</td>
<td>Non-collinear Optical Parametric Amplifier</td>
</tr>
<tr>
<td>NPP</td>
<td>nitrophenyl-phenol</td>
</tr>
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<td>nitrophenyl-phenol hydrogen bound to a base molecule</td>
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</tr>
<tr>
<td>nsTA</td>
<td>nanosecond transient absorption</td>
</tr>
<tr>
<td>OEC</td>
<td>oxygen evolving complex</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical Parametric Amplifier</td>
</tr>
<tr>
<td>P680+</td>
<td>oxidized Photosystem II primary donor with absorption maximum at 680 nm</td>
</tr>
<tr>
<td>PCET</td>
<td>Proton Coupled Electron Transfer</td>
</tr>
<tr>
<td>pH</td>
<td>logarithm of the reciprocal of hydrogen ion concentration</td>
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<td>photoinduced electron-proton transfer</td>
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<tr>
<td>pK_A</td>
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<td>excited state pK_A</td>
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<td>Photomultiplier Tube</td>
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<td>-----------------------------------</td>
</tr>
<tr>
<td>PTET</td>
<td>proton transfer followed by electron transfer</td>
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<tr>
<td>PyOH</td>
<td>1-Pyrenol</td>
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<tr>
<td>S₀</td>
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<td>S₁</td>
<td>Singlet excited state</td>
</tr>
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<td>SFG</td>
<td>sum frequency generation</td>
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<td>second harmonic generation</td>
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<td>TA</td>
<td>Transient Absorption</td>
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<td>Time Correlated Single Photon Counting</td>
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<td>Time-Dependent Density Functional Theory</td>
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<td>tetrahydrofuran</td>
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<tr>
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<td>Ultraviolet</td>
</tr>
<tr>
<td>Yₐ</td>
<td>tyrosine amino acid</td>
</tr>
<tr>
<td>ΔpKₐ</td>
<td>delta or difference pKₐ</td>
</tr>
<tr>
<td>ΔA</td>
<td>delta absorbance</td>
</tr>
</tbody>
</table>
List of Symbols

$^1\text{n}\pi^*$ lone pair electron to singlet pi* electronic transition

$^1\text{n}\sigma^*$ lone pair electron to singlet sigma* electronic transition

$^3\text{n}\pi^*$ lone pair electron to triplet pi* electronic transition

$\text{ANPP}$ Absorption of nitrophenyl-phenol

$\text{AHFC}$ Absorption of hydroxycoumarin

$\nu$ frequency

$\ell$ pathlength

$\nu(\text{O-H})$ equilibrium coordinate of oxygen and hydrogen

$\epsilon$ molar absorptivity

$\lambda_{\text{max}}$ wavelength maximum

$\pi\pi^*$ pi to pi* electronic transition

$\tau$ lifetime
Chapter 1

Introduction: Ultrafast Investigation of Photoinduced Electron-Proton Transfer in Hydrogen bonded Organic Molecule Systems
1.1 Introduction

This dissertation reports photoinduced electron-proton transfer (EPT) between organic molecule-base adduct systems. These systems undergo intramolecular charge transfer (ICT) where the electron is transferred to an internal electron acceptor while the proton is transferred to an external base. Femtosecond transient absorption was used to excite the ICT band in these hydrogen bound molecular systems and monitor the excited state evolution of this system on a femtosecond and picosecond time scale. Changes in the spectral signature of the molecule allow detection of proton motion and electron relaxation. These experiments were done in an effort to understand the chemistry involved in proton coupled electron transfer (PCET).

PCET describes the concerted motion of both the proton and the electron, versus two step processes in which the proton is transferred followed by electron transfer (PTET) or the alternative variation of electron transfer followed by proton transfer (ETPT).\(^1\)\(^,\)\(^2\) EPT is a type of these reactions where the motion of a proton is coupled with the motion of the electron. In order to fully comprehend the complex dynamics of PCET, a knowledge of electron transfer (ET) and proton transfer (PT) separately is necessary. Electron transfer in molecular systems can be considered in terms of Marcus theory, where the rate of electron transfer can be calculated if the relative energies of the species involved are known.\(^3\)\(^,\)\(^4\) Proton transfer requires a more complex quantum mechanical depiction, and for these hydrogen bonded examples can be modeled using a dynamic proton transfer equilibrium between the acid and the base.\(^5\) The concerted motion of proton and electron transfer allows the avoidance of high energy intermediates as well as avoiding charge build up in photo-triggered and excited state reactions.\(^1\)\(^,\)\(^6\) Many biological systems use the charge shuttling capabilities inherent in PCET to avoid charge buildup.\(^7\)\(^,\)\(^8\)

Sunlight provides a renewable fuel source that could alleviate our dependence on fossil fuels. Despite the ease with which plants capture and use light, solar devices capable of mimicking nature and cost effectively harnessing energy have proven an elusive challenge. Concerted EPT reactions, in which electrons and protons are transferred simultaneously, play a central role in these energy
conversion reactions in both chemistry and biology. Plants have an efficient system for collecting energy from sunlight, by absorbing photons to create sugars for fuel. This ability to capture solar energy to create solar fuels would be a remarkable achievement for renewable energy. One of the ways plants do this is PCET. This process, PCET, is a mechanistic pathway through which nitrogen fixation, water oxidation, respiration, and other important biological processes take place. PCET occurs in all green photosynthetic plants specifically in photosystem II (PS II) with the oxygen evolving complex. In PS II at the oxygen evolving complex (OEC), energy from sunlight is used to oxidize water into O₂ and protons. This is an efficient system; the OEC reaction center of photosynthetic plants can oxidize 100 water molecules in a minute.

In this work we are exploring both the range and microscopic details of EPT reactivity including those in which simultaneous or near simultaneous transfer of both electrons and protons occurs photochemically. EPT reactions are also responsible for the rapid excited state relaxation and photostability of DNA and other biological molecules. Developing a better understanding of the basic physical and chemical processes involved in photosynthesis in general and PCET in particular, will further our fundamental knowledge of chemical systems and allow for the development of more efficient solar devices.

1.2 Summary of Research

Experiments to probe EPT and other excited state dynamics presented in this dissertation were done using ultrafast techniques. The primary technique used to investigate excited state absorptions was femtosecond Transient Absorption (fSTA). When necessary, additional spectroscopic techniques such as nanosecond Transient Absorption (nsTA), Time Correlated Single Photon Counting (TCSPC), and Coherent Raman were performed.

The experiments discussed in this dissertation were performed on two organic model systems. The first was 4-hydroxy-4'-nitrobiphenyl (nitrophenyl-phenol) with tert-butylamine base in either 1,2-dichloroethane (DCE) or acetonitrile (ACN) solvent. The second model system was
7-hydroxy-4-(trifluoromethyl)-1-coumarin (hydroxycoumarin) with 1-methylimidazole base in toluene solvent. Nitrophenyl-phenol is an organic molecule with a twisted conjugated ring system shown in Figure 1.1, while hydroxycoumarin, Figure 1.2 is a flat conjugated ring system. These organic compounds form hydrogen-bonding adducts with the base molecules in the ground state. In addition, both of these molecules contain an ICT absorption band. This is an important spectroscopic property. The photo-ICT causes a shift in electron density from one side of the molecule to the other, dramatically changing the proton affinity and pKₐ of the molecules following excitation. This change in electron density creates the driving force for the electron-proton transfer, and provides a photo trigger so that changes in the excited state can be monitored on ultrafast timescales with our experimental techniques.

![Nitrophenyl-phenol molecule](image1)

**Figure 1.1.** Nitrophenyl-phenol molecule.

![Hydroxycoumarin molecule](image2)

**Figure 1.2.** Hydroxycoumarin molecule.

The first model system, nitrophenyl-phenol shows singlet-triplet effects in the absence of a base molecule following excitation. In the presence of tert-butylamine, excitation of the hydrogen
bonded adduct results in some molecules undergoes EPT while some protons remain trapped on the nitrophenyl-phenol molecule and are not transferred until the molecule undergoes intersystem crossing to the triplet. Figure 1.3 depicts the ultrafast EPT event, highlighting the concerted intramolecular electron transfer and intermolecular proton transfer along the hydrogen bond axis. These excited state dynamics are found to be dependent on the excitation energy and solvent.

**Figure 1.3.** Photo-EPT in the nitrophenyl-phenol base adduct system.

The second system is hydroxycoumarin complexed with 1-methylimidazole. Hydroxycoumarin, in nonpolar solvent without base or hydrogen bonding molecules, is weakly emissive. Addition of a small amount of hydrogen bonding base, dramatically increases the emission intensity. This increase in intensity is due to photo-EPT as the base acts as a proton acceptor following excitation, shown in Figure 1.4. At excess base concentrations the proton is shuttled across the molecule, forming an excited state tautomer.

**Figure 1.4.** Photoinduced ultrafast proton transfer between hydroxycoumarin and 1-methylimidazole.
1.3 Important Chemical Features

There are many chemical features that play an important role in the excited states of chemical systems. The first, hydrogen bonding, helps to create the initial configuration that will influence excited state dynamics. Our simple model systems lack the protein scaffold found in PS II or the water molecules precise placement in the Mn₄ cluster present in OEC. Instead we rely on ground state hydrogen bonding to create an associated complex. The formation of a ground state hydrogen bond between the organic molecules and the base is also important to the spectroscopic measures. This ground state configuration of hydrogen bond association plays an important role in the excited state dynamics that occur following photon absorption, specifically photo-EPT. To further this research we looked for H-bonded organic molecules that would form adducts in the ground state, thus setting the stage for photoinduced EPT. Nitrophenyl-phenol and hydroxycoumarin both form hydrogen bond with their respective base molecules in solution. Hydrogen bonding is dependent on the relative pKₐ’s of the chromophore and base, as well as the solvent environment.

The pKₐ’s of the chromophores and bases studied in this dissertation were specifically chosen to be similar in the ground state so that they would form a strong hydrogen bond. Shifts in ground state absorbance show that they do. Evidence of H-bonding in the ground state is directly observed in the absorption spectra, where for both molecular systems the maximum of the ICT absorption band of red shifts with the addition of base as the hydrogen bond is formed. The hydrogen bound state is distinctive from the anion. Whereas hydrogen bonding induces a red-shift of 10-20 nm, the addition of strong base to create the anion is characterized by a red shift of 90-130 nm after the proton is removed. This initial hydrogen bonding is important to the ultrafast proton transfer seen in conjunction with photo-excitation.

The relative pKₐ or proton affinity of the main nitrophenyl-phenol molecule and the hydrogen bonding base affect the strength and length of the hydrogen bond created. For example nitrophenyl-phenol has a pKₐ of ~ 8.95 for the phenolic proton (-OH). The base, tert-butylamine has
a $pK_a$ of $\sim 10.7$. Hydrogen bond strength can be qualitatively predicted by the $\Delta pK_a$ or the difference in the base $pK_a$ and the acid $pK_a$, Equation 1.1. For nitrophenyl-phenol and tert-butylamine, the $\Delta pK_a$ is 1.75. This hydrogen-bonding can also be detected using UV-Vis absorption measurements as solvochromatic shifts to lower energy are spectral signs of hydrogen bond formation.

$$\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid}) \quad \text{Equation 1.1}$$

Another chemical feature, photoacidity, arises from photon induced electron transfer across the molecule or ICT, which causes a dramatic decrease in excited state $pK_a$ relative to the $pK_a$ in the ground state. Nitrophenyl-phenol and hydroxycoumarin are both super photoacids. In nitrophenyl-phenol, excitation transfers electron density from the phenolic ring to the nitro group dramatically changes the $pK_a$ and proton affinity. Before excitation nitrophenyl-phenol has a $pK_a$ of 8.95. Afterwards this $pK_a$ decreases to $pK_a^* \sim 0$, becoming much more acidic. A similar effect is seen in hydroxycoumarin as the ground state $pK_a$ of 7.26 is calculated to change to $pK_a^* \sim -6$, as photoexcitation drives electron density from the phenolic end of the hydroxycoumarin to the carbonyl end. In both cases this change in $pK_a$ provides the driving force for proton transfer in the excited state to the hydrogen bound base is in close proximity.

This provides a light switch mechanism for turning on acidity in the molecule. In the case where the nitrophenyl-phenol molecule is hydrogen bound to a tert-butylamine base, following excitation the base acts as a proton acceptor. The ground state $\Delta pK_a$ for nitrophenyl-phenol-tert-butylamine adduct is 1.75, following excitation it is $\Delta pK_a^* \sim 10.65$. The once stable short hydrogen bond in the ground state is no longer favorable. Ultrafast spectroscopy techniques are used to investigate the excited state changes in this molecular system.

The solvent used for these experiments will also affect the excited state dynamics. Since hydrogen bonding with the organic molecules was important, solvents that would not form hydrogen bonds were used. Solvent polarity also plays a role as nonpolar solvents would tend to stabilize neutral species over charged species, while polar solvents will stabilize charged species over neutral
species. Experiments for nitrophenyl-phenol with different solvents are presented in Chapter 4. Toluene was used for the investigation of hydroxycoumarin.

1.4 Overview of the Dissertation

The remainder of this dissertation is divided into 4 chapters. Chapter 2 is a literature review of recent work related to proton coupled electron transfer. This chapter discusses the phenomena of superacids and superbases. Chapter 2 also highlights work investigating EPT and excited state proton transfer (ESPT) in different chemical systems, organic molecules, metal complexes, and biological molecules.

The experimental methods are described in Chapter 3. The main technique used for the experiments in this dissertation, femtosecond transient absorption (fsTA), is described in detail including a description of the excitation laser source, experimental setup, and data collection methods. Supplemental experimental techniques, including nsTA, TCSPC, and Coherent Raman are described briefly. This chapter also contains a section on sample preparation and characterization methods.

Chapter 4 discusses the excited state photophysics of nitrophenyl-phenol. Ultrafast transient absorption techniques are used to monitor the excited state dynamics of the nitrophenyl-phenol molecule with and without tert-butylamine base, in different solvents, and with two different excitation wavelengths. Spectral evidence for the resulting fast proton transfer, triplet conversion, and relaxation dynamics are presented and discussed.

Chapter 5 discusses photo-EPT and tautomerization seen when hydroxycoumarin solutions with base molecules are excited. Femtosecond transient absorption measurements as well as the Time-Correlated Single-Photon Counting technique were used to monitor the initial fast proton motion as well as the base concentration dependent tautomerization.
1.5 References


Chapter 2

Literature Review
2.1 Overview

Excited state proton coupled electron transfer (PCET) reactions play an important role in chemical and biological processes.\textsuperscript{1-4} A better understanding of excited state PCET reactions, including kinetics, dynamics, and the role of driving forces are important for possible design of artificial photosynthetic devices for the production of solar fuels.\textsuperscript{5, 6}

Given the change in electronic structure between ground and excited states, differences in reactivity often appear for excited states with dynamics that are significantly different from the ground state. This is a common observation for molecules containing dissociable protons. Changes in electronic structure induced by light absorption in these cases can lead to significant changes in acid-base properties triggering PCET.\textsuperscript{7, 8} Photo-protection in many organic and biological molecules following UV absorption is often due to PCET reactions that quickly release excitation energy and prevent dissociation or damage to the molecular structure.\textsuperscript{9-11} Investigation of excited state PCET reactions has also given insight into how photosynthetic reactions are driven following light excitation.\textsuperscript{12}

At the microscopic level excited state PCET reactions are influenced by a number of microscopic factors including local changes in molecular structure, solvent structure, and the local hydrogen bonding environment. The roles that they play on excited state kinetics and thermodynamics are being explored both experimentally and theoretically.\textsuperscript{1, 3, 4, 6, 13-22} In one treatment, the quantum nature of proton nuclear motion and electrostatic coupling with surrounding polar solvent determines whether the proton motion is electronically adiabatic or nonadiabatic with regard to proton motion.\textsuperscript{4, 21, 22}

Electronic structural changes in the excited state can greatly affect proton affinity and pK\textsubscript{A} values in the excited state. This is especially true for intramolecular charge transfer
(ICT) excited states of weak organic acids such as phenols or the coumarin dyes. Application of Density Functional Theory (DFT) has allowed estimation of pKₐ’s for many organic acids and solvents. An estimate of excited state pKₐ’s is available by application of the Förster equation, Equation 2.1, in which hνₐ is the absorption energy of the protonated acid and hνₐ⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ of the corresponding base.

\[ pK^*_A = pK_A - \frac{(hν_{HA} - hν_{A^-})}{2.3RT} \]  

Equation 2.1

Experimental distinctions between excited state PCET where “reactions involving the transfer of an electron and a proton may be sequential, where either the electron or the proton transfers first, or concerted, where the electron and proton transfer simultaneously” are difficult to determine. Rate constants are predicted to increase with increasing driving force as excited vibronic product states become accessible.

2.2 Excited State Superacids

There is a class of molecules that undergo dramatic increases in pKₐ upon excitation. Enhanced acidity accompanying changes in electronic structure dramatically affect pKₐ’s and can significantly influence reaction dynamics for proton transfer events. Enhanced acidity is common for charge transfer excited states in molecules containing dissociable protons. The example of 2-naphthol is illustrated in Figure 2.1 in which the acidity for the phenolic proton increases from the ground state to the excited state following ICT.

As noted above, the decrease in excited state pKₐ’s can be considerable. For molecules with pre-formed H-bonds proton transfer is in competition with excited state decay. For applications of excited state super acids an ideal photoacid should have pKₐ = 8.
Figure 2.1. A model representation of charge redistribution in the ground state and excited state of protonated photoacids. Figure from Silverman, 2008.24

and pK\textsubscript{A}* $< 2$, and deprotonate in a few nanoseconds in aqueous solutions following electronic excitation and undergo slow reprotonation.8

Photoacids can be used as optical triggers to rapidly increase local acidity and to induce chemical reactions.7 Thus photoacids can be used as optically controlled proton donors, given initial hydrogen bonding conditions allow it. The importance of prior H-bonding has been demonstrated in excited state proton reactions of 8-hydroxy-1,3,6-pyrenetrisulfonic acid (HPTS), a common photoacid, and acetate base.7 HPTS and the acetate base associate in the ground state. This creates a hydrogen-bonding network that sets the stage for proton transfer with creation of the photoacid. Addition of bromide salts to the solution inhibits the hydrogen bonding network and proton transfer rate. The importance of H-bonding is due to vibronic coupling within the vibrational wave function overlap, this overlap decreases exponentially with the proton transfer distance. 22

HPTS and other pyrene photoacids with related structures have been extensively studied. 7, 24-27 Some studies have investigated changes in pK\textsubscript{A} as a result of molecular substitutions, shown in Figure 2.2 for HPTS, 1-Pyrenol (PyOH), and 8-Aminopyrene-1,3,6-trisulfonate (APTS).24 For HPTS charge redistribution is followed by proton dissociation due to enhanced acidity in the excited state.24 For APTS, deprotonation occurs first, followed by charge rearrangement, pointing to a decrease in basicity of the deprotonated state relative to the ground state.24
Multisite electron-proton transfer (MS-EPT) was observed in reductive fluorescence quenching by three isomeric free-base meso-(pyridyl)porphyrins by phenols. In these reactions, quenching occurs by electron transfer to the porphyrin excited-state and proton transfer to the hydrogen bound pyridine, Figure 2.3. The distance and driving force for electron transfer were tuned and rate enhancements greater than a factor of 10 were observe.¹⁴

2.3 Excited State Superbases

The converse of super acids, superbases, has also been observed, in excited states in which charge transfer excitation creates a basic site. Chen et al. found evidence for superbase intervention following excitation of an arginine amide containing peptide. In this case the amide becomes a superbase following electronic excitation, Figure 2.4.²⁸ The electronic excitation is delocalized over the amide group in the π* orbital, which leads to N-Cα bond cleavage forming C radical fragments.
**Figure 2.3.** Excited state reductive quenching by MS-EPT in free-base meso-(pyridyl)porphyrins. Figure from Prashanthi, 2009.\textsuperscript{14}

\[ k_q > 10 \text{ times} \]

A - electron acceptor
D - electron donor

**Figure 2.4.** The arginine superbase mechanism for C-N bond cleavage. Figure from Chen, 2006.\textsuperscript{28}
2.4 Organic Molecules

There is an extensive literature on PCET and excited state hydrogen bond dynamics in organic molecules. Aromatic molecules can have “highly polar charge-transfer states of \( \pi^* \), \( \pi^* \), or \( \pi^* \) character which drives proton transfer.”23 Computational studies designed to gain an understanding of the conical intersections which couple \( S_1 \) and \( S_0 \) surfaces and allow for ultrafast internal conversion to the ground state were conducted on indole H-bonded to pyridine, and ammonia.23 The results of calculations on these molecules highlight the importance of hydrogen bonding prior to excitation. Fast proton transfer triggered by electronic excitation is dependent on vibronic overlap between the proton donor and acceptor.

Pyridine-pyrrole hydrogen bonded assemblies, have been extensively studied as models for guanine/cytosine (G/C) and adenine-thymine (A/T) Watson-Crick base pairs. Recent calculations generated the intersecting energy-coordinate diagram in Figure 2.5. They found that two crossings, an avoided crossing and a conical intersection, are important in understanding excited state hydrogen bond dynamics involved in photoinduced electron-driven proton transfer in the pyridine-pyrrole system.9,13

Femtosecond pump-probe electron-ion coincidence spectroscopic measurements were performed on 2-aminopyridine dimers.11 They display two reaction channels for proton/hydrogen transfer, ultrafast (sub-50 fs) and slower (~75 ps) components.11 Similar to related molecules, this molecule undergoes internal conversion to the charge transfer state that corresponds to electron transfer from the proton donor to the proton acceptor and a net hydrogen transfer reaction.11
Figure 2.5. Potential energy surface diagrams ($S_2$, $S_1$, $S_0$) involved in radiationless deactivation of the lowest $^1\pi\pi^*$ excited state of the H-bonded pyrrole-pyridine. Illustrative classical paths (in yellow) indicate the Franck-Condon excitation (arrow), and relaxation on the $S_1$ and $S_0$ surfaces, restoring the initial ground-state configuration. Figure from Frutos, 2007.\textsuperscript{9}

There is considerable debate concerning whether excited state double proton transfer (ESDPT) in 7-azaindole dimers is a concerted or stepwise process, Figure 2.6. (7AI$_2$)\textsuperscript{29-31} Excitation-wavelength dependent fluorescent experiments done by Takeuchi and Tahara, show high energy transients with bi-exponential decay (0.2 ps and 1.1 ps) and lower energy transients with a single exponential decay (1.1 ps).\textsuperscript{31} The 0.2 ps decay at higher energy is attributed to a $^1L_b$ ($S_2$) $\rightarrow$ $^1L_a$ ($S_1$) transition, while the 1.1 ps decay is assigned to double
proton transfer from the $^1L_a (S_1)$ state. Thus a concerted process takes place and the biexponential time components can be explained by electronic relaxation.$^{31}$

![Diagram of concerted and stepwise mechanisms of proton transfer in 7-azaindole dimers.](image)

**Figure 2.6.** Illustration of concerted and stepwise Excited State Double Proton transfer in 7-azaindole dimers. Figure from Sekiya, 2008.$^{30}$

Oxidation of oligodeoxynucleotides residue, 5-methyl-2'-deoxycytidine (d$m$C), by photosensitized 2-methyl-1,4-naphthoquinone (NQ) is illustrated in Figure 2.7. The NQ molecule when excited at 355 nm forms a triplet $^3$(NQ)$^*$. This triplet reacts to create a d$m$C radical which based on solution conditions undergoes either reversible or irreversible deprotonation. The product distribution is pH dependent, at pH 5, 5-formyl-2'-deoxycytidine is formed and below pH = 4.5, the N3 position is protonated and one-electron oxidation hindered.$^{32}$
2.5 Metal Complexes

The emitting Metal-to-Ligand Charge Transfer (MLCT) excited state of the complex Ru(bpy)$_2$(bpz)$_2^{2+}$ (bpz is 2,2'-bipyrazine) undergoes electron proton transfer (EPT) reduction with added hydroquinone (H$_2$Q). The mechanism is shown in Figure 2.8. In the lowest excited state bpz is the acceptor ligand with an increase in pK$_A$ compared to the ground state. In the quenching mechanism, Figure 2.8, preassociation occurs between H$_2$Q and the bpz ligand followed by EPT which is favored over reductive electron transfer to give Ru(bpy)$_2$(bpz$^-$)$^+$ and H$_2$Q$^+$.\(^{33}\)

A related mechanism was proposed in the reductive quenching of the emitting MLCT excited state of [Ru(bpy)$_2$(pbim)]$^+$ which oxidizes ubiquinol or plastoquinol analogues in acetonitrile by PCET. The mechanism for this process is shown in Figure 2.9 for the [Ru(bpy)$_2$(pbim)]$^+$ ubiquinol example.\(^{34}\) Theoretical calculations were used to investigate
the associated EPT pathway. These calculations predict that the kinetic isotope effect (KIE) will increase for ubinquinol but that this same KIE will decrease for plastiquinol.

\[
\begin{align*}
(bpy)_2\text{Ru}^{\text{III}}(bpz)^{2+} & \quad + \quad H_2Q \quad \xrightarrow{K_A} \quad (bpy)_2\text{Ru}^{\text{III}}(bpz\cdots H_2Q)^{2+} \\
(bpy)_2\text{Ru}^{\text{II}}(bpz)^{2+} & \quad + \quad H_2Q \quad \xleftarrow{k_{\text{red}}^+} \quad (bpy)_2\text{Ru}^{\text{II}}(bpzH\cdots HQ)^{2+} \\
(K'_A = k_{1A}/k_{1D}) & \quad \xrightarrow{k_{D}} \quad k_D \\
(bpy)_2\text{Ru}^{\text{II}}(bpzH)^{2+} & \quad + \quad HQ
\end{align*}
\]

**Figure 2.8.** Mechanism for EPT reductive quenching of \([(bpy)_2\text{Ru}^{\text{III}}(bpz^-)]^{2+}\) by \(H_2Q\). Figure from Concepcion, 2007.\(^{33}\)

**Figure 2.9.** Illustration of reductive EPT quenching of the emitting MLCT excited state of \([\text{Ru}(bpy)_2(pbim)]^+\) by ubiquinol. Figure from Ludlow, 2009.\(^{34}\)

PCET involvement has also been invoked in the photodimerization of \([\text{Ru}^{\text{II}}(bpy)_2(L-L)]^{2+}\) (\(L-L = \text{trans-1,2-bis(4\text{-}(4\text{'-methyl})-2,2\text{'-bipyridyl}) ethane}\)) in solutions between pH 7 to pH 12. In the proposed mechanism, Figure 2.10, MLCT excitation is followed by intramolecular oxidative quenching by the remote bipyridinium to give the
byridinium radical. The radical induces cyclodimerization with a second complex followed by re-oxidation by the Ru(III) formed by excited state quenching.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.10.png}
\caption{Photodimerization of [Ru\textsuperscript{II}(bpy\textsubscript{2})(L-L)]\textsuperscript{2+} (L-L = trans-1,2-bis(4-(4'-methyl)-2,2'-bipyridyl) ethane) in aqueous solution. Figure from Zhang, 2008.\textsuperscript{35}}
\end{figure}

As a model for sensitized electron transfer in Photosystem I, PCET reactions were also investigated in polypyridyl Ru(II) and Re(I) complexes with tyrosine-like ligands, Figure 2.11. In these experiments, oxidation of intramolecularly bound tyrosine was investigated by laser flash photolysis following oxidative quenching of the Ru and Re-based MLCT excited states.\textsuperscript{20} These experiments explored the pH dependence of the PCET oxidation of the tyrosine-like ligands to address the literature debate surrounding its nature. Experiments show quenched emission lifetime rates for Re(P-Y), which support the PCET assignment.
In a related study, a series of tyrosine analogues were attached to a Ru complex and the rate and mechanism of PCET varied based upon the strength of hydrogen bonding of the dissociating proton, Figure 2.12. The three molecules studied represented proton release to the solvent (RuY), and the ligand acting as an internal base for proton transfer in the case of Ru-SA and Ru-PA. For Ru(Y) and Ru-SA, the rate changes in discreet steps as a function of pH. Each step in the rate ladder represents a different mechanism and the rates vary by 5 orders of magnitude over the pH range from 2-10 for the molecules studied.

In a related experiment Freys, et al, investigated concerted excited state EPT in a H-bonded molecular assembly between the iridium (III) \textit{bis}(2-(p-toyl)pyridine)- 2,2’-biimidazole complex IrbiimH$_2^+$ and a H-bonded to 3,5-dinitrobenzoate anion (dnb’), an aromatic acceptor as shown in Figure 2.13. This complex forms a hydrogen-bonded 1:1 adduct with benzoate ions, “proton delocalization can then be monitored directly by optical spectroscopy due to the close proximity of the acidic N-H protons to the metal.
Figure 2.12. Structures of Ru(bpy)$_3^{2+}$ (RuY), a salicylic acid derivate (Ru-SA), and a 2-hydroxyphenylacetic acid derivate (Ru-PA). Figure from Irebo, 2008.\textsuperscript{37}

Figure 2.13. Illustrating excited state EPT quenching mechanism in the H-bonded adduct between IrbiimH$_2^+$ and the benzoate anion, dnb$. Figure from Freys, 2008.\textsuperscript{15}

Following photoexcitation they were able to follow the spectroscopic handle of the IrbiimH$_2^+$ complex or formation of Hdnb to monitor proton release to the base.

Cu complex systems in which a Cu$^{II}$-$\text{C}$ bond forms a with tri-(pyridylthio)methyl (tptm), a tetradeutate tripodal ligand tridentate ligand, to create [CuF(tptm)] and [Cu(tptm)(OH)].\textsuperscript{16} These complexes form supramolecular layers, which can be intercalated with H$_2$O or H$_2$O and hydroquinone, Figure 2.14. The strong hydrogen bonds formed
between the Cu-ligand structures and the intercataled water molecules as well as the metals' ability to switch between divalent and trivalent states drive research into whether these complexes are able to mimic the PCET reaction taking place in Photosystem II (PS II).\textsuperscript{16}

![Figure 2.14. Illustrating the intercalated array of hydroquinone molecules between layers in [CuF(tptm)]. Figure from Kinoshita, 2008.\textsuperscript{16}](image)

Photochemically induced PCET has been studied in metal porphyrins including temperature and isotope dependence studies,\textsuperscript{19} ligand-field dependence studies,\textsuperscript{18} and the influence of spacers between amidinium-amidine acid-base electron transfer acceptor and the porphyrin.\textsuperscript{17} Concerted electron-proton transfer was observed following excitation of the porphyrin, by monitoring the transient absorption growth and decay of the porphyrin cation. Temperature studies on the zinc porphyrin dyads, Figure 2.15, illustrate the importance of vibrational overlap in concerted EPT reactions by highlighting the effects of bath-induced changes to the proton coordinate.\textsuperscript{19}
Experiments with porphyrin frameworks having spacer modifications that maintain \( \pi \)-conjugation but extend the distance between the hydrogen bonded amidinium-amidine base and the porphyrin, demonstrate that concerted EPT occurs between the porphyrin and the hydrogen bound ligand. The spacer between the amidine and porphyrin creates a stronger wavelength dependence between the amidinium/amidine protonation state due to the added rotational dimensions allowed between the proton acceptor and donor, thus making experiment observation of changes in electron and proton motion more spectroscopically accessible.\(^{17}\) By introducing a spacer, another degree of freedom is introduced into the rotational plane of the porphyrin molecule and the hydrogen bonding amidinium.

Photochemically initiated EPT has been shown to occur from adsorbed DMF to the oxide in WO\(_3\) and MoO\(_3\) thin films.\(^{38}\) Net photo-injection of hydrogen into the metal oxide films, Figure 2.16, is induced by an electronic transition which triggers net charge transfer from the transferring H atom toward a surface M=O causing C-H bond rupture.\(^{38}\)
2.6 Biological Molecules

Understanding how biological molecules balance excitation energy from multiple photons while maintaining high oxidation states can play an important role in photosynthesis mimicking solar devices. Excited state PCET plays a role in photosynthetic oxygen production by PS II and the oxygen evolving complex (OEC).\textsuperscript{39} In order to oxidize two water molecules to produce oxygen, four photons must be absorbed.\textsuperscript{39, 40}

In the photosynthetic apparatus excited state energy is converted into transiently stored redox equivalents that drive PCET reactions for water oxidation and NADP reduction. Photochemically driven PCET in DNA base pairs is utilized to avoid photo-damage.\textsuperscript{41} The mechanisms by which coupled proton transfer events assist in excited state energy dissipation and photostability in DNA molecule base pairs has been explored by ultrafast transient laser techniques.\textsuperscript{42, 41} Proton transfer events in photoexcited Watson-Crick DNA base pairs occur on extremely rapid time scales. Calculations on guanine-cytosine (GC) base pairs predict
conical intersections that connect the $\pi\pi^*$ excited state to the ground state.\textsuperscript{41} The net proton transfer event is illustrated in Figure 2.17.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Watson-Crick ground state guanine-cytosine base pair, shown following excitation and resultant excited state proton transfer. Figure from Markwick, 2007.\textsuperscript{41}}
\end{figure}

These charge transfer pathways connect excited states with ground states and avoid photodamage through rapid relaxation directly to the ground state through conical intersections.\textsuperscript{41, 43} Similar ultrafast deactivation through a conical intersection is also observed in Watson-Crick adenine-thymine (AT) base pairs.\textsuperscript{10}

Hydrogen bonding is an integral feature of most biological structures, and may play a general role in excited state dynamics and reactivity following charge transfer excitation of peptides.\textsuperscript{43} Green Fluorescent Proteins (GFP) offer an example where hydrogen bonding and proton transfer play important roles in excited state dynamics based on recent
experimental and theoretical studies.\textsuperscript{44-49} Prior hydrogen bonding ensures that proton transfer events triggered by photoexcitation can occur following light absorption. This conclusion is supported by computational studies.\textsuperscript{45, 49}

Ultrafast time-resolved fluorescence studies show that the neutral transition state (I\textsuperscript{*}) is formed very rapidly (< 1 ps) following excitation to the initial neutral excited state (A\textsuperscript{*}).\textsuperscript{48} The rapid (sub-picosecond) time scale means the A\textsuperscript{*} \rightarrow I\textsuperscript{*} transition occurs more rapidly “than excess energy can be dissipated, and the initial I\textsuperscript{*} state is formed vibrationally hot.”\textsuperscript{48} “Pre-existence of a low-barrier or barrierless H-bond between the phenol group of the chromophore and a side chain of aspartate” ensures facile proton transfer.\textsuperscript{48} Figure 2.18, shows the initial configuration of the GFP protein, A. Following excitation and the sequence, A \rightarrow A\textsuperscript{*} \rightarrow I\textsuperscript{*}, the intermediate state, I\textsuperscript{*}, either relaxes to the ground state and returns to A, or follows an alternate path to B\textsuperscript{*} which decays to a long lived B state.\textsuperscript{47-49} This structure helps create a series of hydrogen bonding protons throughout the molecule or a proton wire effect that facilitates proton shifts through this bonded system. An example of the proton wire effect is illustrated in Figure 2.19 which is observed following excitation in wild type GFP.\textsuperscript{46}
Figure 2.18. Illustration of interconversion between A and B forms of the green fluorescent protein (GFP) chromophore through I*. Figure from Stoner-Ma, 2008 (adapted from Brejc et al).48

Figure 2.19. Proton wire effect leading to excited state proton transfer (ESPT) following excitation in wild-type GFP. Excitation at 370-400 nm, leads to stepwise proton transfer through the structure to Glu222. Figure from Remington, 2006.46
2.7 References


Chapter 3

Experimental Methods
3.1 Introduction

Experiments to probe Electron-Proton Transfer (EPT) dynamics presented in this dissertation were done using ultrafast techniques. The primary technique used to investigate excited state absorptions was femtosecond Transient Absorption (fsTA). When necessary, additional spectroscopic techniques such as nanosecond Transient Absorption (nsTA), Time Correlated Single Photon Counting (TCSPC), and Coherent Raman were performed.

FsTA is an ultrafast pump-probe technique. Our experimental setup allows us to probe excited state absorption or in some cases stimulated emission from 250 fs to 900 ps, providing transient spectra at early times. In the case of nitrophenyl-phenol where additional excited state dynamics continue beyond the fsTA experimental capabilities, additional nsTA experiments were done to probe from 10 ns to microseconds. Alternatively in the case of hydroxycoumarin, TCSPC was used to supplement the fsTA data. TCSPC is a sensitive emission technique with an instrument response of 200 ps, capable of measuring emission out to 56 ns. Finally, Coherent Raman techniques were used to obtain spectra at 20 fs of the excited molecules.

The first section of this chapter discusses the fsTA pump-probe technique in detail. Including a description of the laser source, pump pulse generation, probe pulse generation, experimental setup, and data collection methods. The second section of this chapter briefly describes the ultrafast techniques used to take additional measurements: nsTA, TCSPC, and Coherent Raman. The final section describes sample preparation and characterization.
3.2 Femtosecond Transient Absorption Technique (FsTA)

Femtosecond transient absorption is an ultrafast pump-probe technique that offers insight into changes in ground versus excited state populations on the ultrafast timescale. This technique is a valuable tool in understanding charge and energy transfer in molecular systems. An overview of the experimental setup is shown in Figure 3.1. One of the main components is the femtosecond laser light source, which is converted into both the pump pulse and the white light probe pulse, to excite and monitor changes in the sample. The experiment also includes the sample setup and data collection optics and equipment.

![Figure 3.1.](image)

**Figure 3.1.** Femtosecond transient absorption experimental setup. The main components of the fsTA apparatus, shown in the diagram, include the laser light source, white light generation optics, pump beam generation equipment, sample setup, and data collection equipment.
3.2.1 Laser Source

The laser source used in our fsTA experiments was a Clark CPA 2001. CPA stands for chirped pulse amplification. The laser system has been described in detail previously.\textsuperscript{1, 2} This laser has a double level design, shown in Figure 3.2.

\textbf{Figure 3.2.} Femtosecond transient absorption laser (Clark CPA 2001). The Clark laser operates by creating an ultrafast weak seed pulse. This pulse is then chirped and overlapped with a Nd:YAG high power pulse inside of the main laser Z-cavity. Correct alignment and cavity timing allow these two beams to interact inside the Ti:Sapphire crystal to create the 775 nm laser output pulse. This pulse is then recompressed in time to create a high power, ultrafast pulse (~780 mW, 150 fs FWHM).

The “fast” time component or injection beam is created on the bottom level of the laser. The injection beam starts with a small diode coupled to a fiber-optic ring oscillator. This ring oscillator is made up of positive and negative dispersive materials, as well as four
wave plates and a birefringent filter. As the light makes multiple trips through the ring these elements amplify the pulse intensity while compressing it in time. This intensified pulse is then sent through prisms to further compress the beam, before being frequency doubled from 1550 nm to 775 nm in the PPLN crystal. The injection beam at this point while only ~ 2.5-3 mW, is compressed in time, therefore before it can be used as a laser seed pulse it must be stretched out in time or chirped to avoid damage to the laser cavity optics. The stretcher cavity relies on a grating as well as a series of mirrors to temporally disperse or chirp the laser pulse. The stretched injection beam is then sent into the Z-cavity of the main Ti:Sapphire laser using a polarization gated entry on the upper level of the laser system. This injection beam provides the short time component of our eventual laser pulse, but an additional seed beam is required to obtain the high output power. This power component comes from the ORC. The ORC consists of a lamp pumped Nd:YAG rod. The 1064 nm fundamental is frequency doubled with an LBO crystal to output 532 nm light. This ORC uses a Q-switch to create a pulsed beam. Power for this pulsed output is set by adjusting the lamp current so that a 7 W output is achieved. The ORC pulse is introduced into the main Z-cavity via a pump through mirror. The two beams, injection and ORC, are overlapped inside the Ti:Sapphire rod to generate a third laser pulse that is both fast and high power.

Timing of the introduction of the injection beam, resulting pulse buildup, and output of the laser pulse are controlled through a high voltage applied to the Pockel cell and polarization gated optics. Applying a high voltage to the Pockel cell turns on its ability to act as a wave plate. Thus, the overlap timing of the two pulses can be controlled by the high voltage Pockel cell and polarization gating optics in the cavity. The first high voltage signal is used to time the injection and start of the buildup in the laser cavity. A second high
voltage pulse again changes the wave plate properties of the Pockel cell, rotating the polarization of the output pulse so that it gets reflected or dumped from the laser cavity.

This output pulse is still temporally stretched and must be compressed to create ultrafast 150 fs pulses. Pulse compression is comparable to the pulse stretching done in the lower half of the laser cavity to the injection beam. A grating is used to separate the 8 nm of bandwidth that makes up the 775 nm pulse. This beam travels through the compressor cavity in a way that forces leading wavelengths along a longer path while allowing trailing wavelengths a shorter path and the chance to catch up, thus shortening the pulse in time. The output pulse is a 1 KHz rep rate pulse, ~ 800 mW, with a pulse width of approximately 150 fs.

Compression cavity alignment is important. The pulse width is extremely dependent on the angles and positions of the grating and mirrors inside the compression cavity. To measure the pulse width of the laser beam we used a lab built autocorrelator. The autocorrelator setup is shown in Figure 3.3. The front reflection of the autocorrelator measurement pulse is picked off before the white light is generated. This beam is sent through a wave plate to produce a vertically polarized beam. This beam is sent through two irises on the autocorrelator base plate to ensure reproducible alignment. The irises are used for initial alignment, but remain fully open when autocorrelation measurements are taken. From there, the beam passes through a 50/50 beam splitter to create a duplicate beam. Both of these beams are focused so that they physically overlap inside the BBO crystal. One of the beams, the front reflection from the beam splitter, uses mirrors mounted on a small motorized stage. As the two beams are temporally overlapped in the BBO crystal, they interact through sum frequency generation (SFG) to create a new third beam. The SFG
intensity is measured with a photodiode. By scanning the delay stage, or pulse overlap, as the SFG beam intensity is measured a temporal picture of the laser’s pulse width is created. The laser outputs a beam with an autocorrelation FWHM of 250 fs. The autocorrelated graph is 1.55 times the pulse width of the laser due to measurement factors. Based on the autocorrelation measurement the compressor mirrors within the laser can be tweaked to optimize compression.

Figure 3.3. Femtosecond autocorrelator used to measure pulse width. The incoming laser beam is split, and the resultant two beams are focused into a BBO crystal. The overlap interaction between the two beams and the BBO crystal creates a Sum Frequency Generated (SFG). By varying the overlap of the one beam relative to the other and measuring the intensity of the generated SFG signal, the pulse width of the laser beam can be measured.

The compressed laser output pulse is split using a 95/5 beam splitter. The 5% portion of the beam is used to generate the white light probe pulse, with a small part being used in
the autocorrelator to monitor pulse width over the course of our experiments. The 95% portion of the beam is used to generate the pump pulse.

3.2.2 Pump Pulse

For the fsTA experiments described in this dissertation several pump wavelengths were used: 355 nm, 335 nm, and 388 nm. To generate the 388 nm pulse the 775 nm laser pulse was focused into a BBO crystal to produce second harmonic generation (SHG). This frequency doubled 388 nm beam was then used as the pump excitation beam.

Generation of the 355 nm and 335 nm beams, however, is more complicated. To create these beams from our lasers 775 nm output pulse requires an OPA, and two BBO doubling crystals. The 775 nm beam is first sent to the OPA, which is a commercially made system from Clark-MXR Inc, Figure 3.4. The OPA uses a beam splitter to separate the 775 nm input beam into two pulses. The front reflection is used to create a white light continuum by focusing it through a sapphire window. The unused portion of the beam will pass through another beam splitter to become the seed and amplifier pulses. The white light and seed beam are focused and overlapped inside the upper half of the BBO crystal. The crystal angle is set to produce the desired output wavelength of 1420 nm (or 1340 nm). The spatial and temporal overlap of the seed and white light beams in the crystal are also very important. The mirrors leading to the white light generation optics are set on a manually adjustable stage so that temporal overlap is possible. Proper alignment through the BBO crystal then produces a weak beam of the desired wavelength. This beam is then reflected off an end mirror back through the bottom half of the crystal where it is overlapped with the
amplifier beam. This double pass setup allows the OPA to produce 1420 nm (1340 nm) wavelength beams with a power of ~130 mW.

**Figure 3.4.** Optical Parametric Amplifier (OPA). The OPA uses a white light seed and first pass weak pulse to select the desired wavelength within the BBO crystal. A second pass through with a higher powered pulse is then used to amplify the output pulse.

This 1420 nm (1340 nm) beam is then focused into another BBO crystal to produce a second harmonic generated (SFG) pulse at 710 nm (670 nm). The SFG signal is then focused through a second BBO doubling crystal to produce the fourth harmonic generation (FHG) pulse of 355 nm (335 nm) that will be used as the pump pulse to excite the sample.
3.2.3 Probe Pulse

To create the white light probe pulse, the 5% beam from the 95/5 beam splitter was used. The polarization of the beam was set at vertical to the laser table as that will allow us to set the pump angle relative to the vertical probe beam and for optimal reflection from the glass window used to create the two probe beams. The weak beam is then focused through a CaF$_2$ window to generate a white light continuum. The high peak power of the ultrafast pulse focused into the CaF$_2$ window induces self-focusing inside of the window, which causes spectral broadening. The CaF$_2$ window is mounted on a motorized stage which transverses the optic back and forth in the beam path to prevent burns and degradation to the window. This method generates a white light continuum from 380-700 nm. The white light is then collimated and bounced off right cornered mirrors mounted on a motorized stage. This stage contains a computer controlled encoder and can be moved in micron sized steps. Micron fine control of the pathlength traveled by the white light is extremely important for pump probe transient absorption measurements. By moving the stage mounted mirrors, we increase or decrease the distance the white light or probe beam travels relative to the pump beam. Once time zero is established it allows precise, reproducible transient measurements.

After the white light is created and aligned with the stage mirrors it is sent across the table to a thick glass window where a front and back reflections are created. The reflection off the front face will become the signal beam in the sample, and the reflection off of the back face will become the reference beam. The reference beam allows changes in white light intensity to be compensated for during the experiment. The vertical polarization becomes important, because the front and back reflections are used to create the signal and reference
probe beams. Vertically polarized light reflects optimally from the window mounted perpendicular to the table.

### 3.2.4 Sample Setup

Samples discussed in this thesis were liquid solutions in 2 mm pathlength cuvettes. The cuvette holder was placed on manual micrometer controlled platforms, so that fine positioning was possible. The signal and reference beams are focused using powerful lenses to create a ~ 280 micron spot size at the center of the sample. The reference white light beam is stepped down from the usual 4.25 inches above the laser table to 4 inches. This is done so that it passes through the sample cell parallel to but ~ 0.25 inches lower than the signal white light probe pulse.

The pump pulse passes through a wave plate and focusing lens. The wave plate allows us to control the polarization of the pump pulse relative to the vertical polarization of the white light. These experiments were all done with the pump pulse set at the magic angle of 54.7 degrees to avoid any anisotropy effects in the sample measurements. The pump beam was focused to ~ 1400 micron spot size with a pump power of 0.60-1.0 mW. Precise overlap between the pump and probe signal beams in the sample is important. The probe beam path is set perpendicular with the sample cuvette, while the pump beam enters at a slight angle to maximize overlap through the sample while avoiding the mirrors that direct the white light. Spatial overlap between the two beams is set using a 50 micron pinhole. This pinhole is mounted with a glass slide on the front to recreate the thickness and center point of the 2 mm cuvettes used in our experiments. By placing the pinhole in the center of the white light signal beam the pump beam can then be aligned for maximum overlap.
After exciting and passing through the sample, the pump pulse passes the white light collection optics and is reflected onto a white card placed in front of a photodiode. The pump scatter is measured during the experiments to monitor changes in intensity. After passing through the sample, the signal and reference white light beams are collected and recollimated using lenses located after the sample cell. The two beams are then focused onto the slit of the Spex 270 cm spectrophotometer. The beams are still spatially separated with the signal beam ~ 3-4 mm above the reference beam on the detector entrance slit. Before reaching the spectrophotometer the white light is filtered through neutral density, to control white light intensity.

### 3.2.5 Data Collection

In the fsTA experiments, the white light probe signal and reference beams are collected and used to calculate delta absorbance ($\Delta A$). In our experimental setup, we take full spectral images at individual time points. After all of the experimental data is taken at one time point the stage moves to the next time point and data collection is repeated. This is done using the computer controlled micron stage mentioned in the probe pulse section. The white light beam is directed to the sample in part by two right cornered mirrors mounted onto this stage. Since light travels at $3\times10^8$ m/s, if you increase the pathlength by moving the stage 1 micron the white light has to travel that distance twice, thus delaying it relative to the pump by ~6 fs. We can use the fine control of the motorized stage to vary the pathlength of the white light probe beam relative to the excitation pump beam, allowing us to control the time delay between the pump and probe beams in the sample. Thus we can monitor changes to the excited state absorption on the ultrafast time scale. Our delay stage is 8 inches or
200,000 microns long, limiting us to a total possible time delay of 1.2 ns. The pathlengths of the pump and the probe beams are set so that time-zero where the two beams overlap occurs about one quarter of the way into the stage. This allows us to take ground state measurements with the ‘negative delays,’ before the sample has been excited, leaving the remainder of the stage travel length, about 150,000 microns or ~900 ps, as ‘positive delays’ for excited state transient absorption measurements.

For one experiment, we build up spectral pictures at multiple time points. Since the delay stage is computer controlled it can be moved using a Labview program in tandem with the data collection program. Once the stage is parked at the selected time, data is collected using a Jobin Yvon Symphony LN (Liquid Nitrogen) cooled CCD camera. The CCD camera is mounted onto a Spex spectrophotometer mentioned previously. The CCD camera has a 1024 x 256 pixel chip onto which the white light signal and reference probe beams were imaged. The spectrometer and the CCD camera run with a computer controlled Labview program and their respective software interfaces. The signals are collected and processed using Labview software coupled to the NI data acquisition card. Full images of the chip are taken during experimental setup to ensure proper alignment. For the fsTA measurements the chip is split, the software bins linear strips on the top and bottom portions of the chip to create a spectral profile of both the signal and the reference beams. An entrance slit on the spectrophotometer controls the exposure time for the camera. Our measurements were taken for 800 ms, this optimizes light collection without saturating the sensitive CCD detector.

Our transient absorption measurements are calculated as $\Delta A$, in a simplified form $\Delta A = A_{\text{excited state}} - A_{\text{ground state}}$. Positive going peaks in our TA spectra represent excited state absorptions, while negative going peaks represent ground state bleaches. In some
circumstances, for example in the case of hydroxycoumarin with intense emission, we also see stimulated emission as a negative going feature in our transient absorption spectra. The full equation used to calculate $\Delta A$ is shown in Equation 3.1. In the equation the subscript represents whether the intensity represents the signal or reference beam, while the superscript represents the blocked or unblocked states of the pump/probe beams. A state of on/off signifies that the pump beam is reaching the sample, while the probe beam is being blocked by computer controlled mechanical shutters placed in the beam paths on the laser table. The $\Delta A$ equation shows the complexity of measuring one transient absorption spectrum. By factoring in the intensity of both the signal and the reference beams, we are able to correct for changes in the white light over the course of data collection. The off/off measurement enables us to subtract off background room light collected in the absence of both the pump and probe beams. The on/off measurement corrects for pump scatter at the detector, and the off/on spectrum measures the baseline white light spectrum without excitation. All of these measurements, as well as the on/on data are necessary to calculate an accurate $\Delta A$ spectrum.

$$\Delta A = \log \left\{ \frac{I_{\text{on/off}}}{I_{\text{off/off}}} \right\} \left\{ \frac{I_{\text{on/sig}}}{I_{\text{off/sig}}} \right\}$$

Equation 3.1.

Since time delay is such a critical aspect of the fsTA experiments it is important to have an accurate way to set and measure the time-zero overlap of the pump and the probe beam. Since the white light pulse used to probe the sample is created by inducing a spectral and temporal chirp across the beam, it is also necessary to correct for this in the fsTA spectra. Temporal chirp in the white light means that if the 450 nm portion of the probe beam overlaps with the pump beam at time-zero, the 500 nm portion of the white light will not overlap with the pump beam until several picoseconds later. So while the spectral measurements are taken at a certain time point due to the position of the delay stage, the
spectra need to be corrected for the white light chirp. To do this we use a polarization gating technique called frequency resolved optical gating (FROG). The FROG technique uses the electronic response of CCl₄ to measure the pump probe interaction and thus the white light chirp. In order to take FROG measurement the stage is set close to time-zero, and a cuvette of CCl₄ is placed in the sample holder. The reference white light beam is blocked completely and a polarizing cube is placed in the signal beam path between the sample and the detector. With the pump beam blocked, the polarizing cube is rotated so that it blocks the white light from reaching the detector. In the absence of pump excitation there should be no white light signal reaching the detector. When the pump interacts with the CCl₄ sample it excites an electronic response in the liquid. This electronic response is brief, but when it corresponds with a portion of the white light pulse it alters its polarization. Thus white light that passes through the sample at the same time as the pump pulse will be detected due to its rotated polarization that will no longer be blocked by the set polarizing cube. A series of measurements over the picoseconds before and after time zero give a spectral picture of the white light chirp, Figure 3.5. By fitting a quadratic equation to the time wavelength peaks across this FROG image, we are able to determine the time delay across the chirped white light pulse. The transient absorption spectra can then be shifted based on this equation to correct for the white light chirp.

The absence of FROG spectral data for longer wavelengths in Figure 3.5 is not an indication of low white light intensity in this region. Since the pump beam used in these polarization gated FROG measurements is 355 nm, this technique works best for white light wavelengths closer to the pump wavelength. At longer wavelengths, farther from the pump frequency, group velocity mismatch causes a loss in the signal intensity.
Figure 3.5. Spectra of a polarization gated frequency resolved optical gating (FROG) measurement overlaid with cubic fit equation. The solid line equation is used to correct for white light chirp.

The Spex spectrophotometer has two computer controlled gratings. One is a 1200 groove/density (gd) grating, and the other is a 300 gd grating. Due to the length of our spectrometer and the size of our CCD chip, they allow us to image a spectral window of either ~ 70 nm or ~300 nm respectively. Past experiments in the Papanikolas Group had been done primarily using the 1200 gd, measuring 70 nm sections of the white light and piecing together spectra when necessary. Many of the experiments presented in this dissertation were done using the 300 gd grating. This grating offers a larger white light
sampling range, which is important when comparing higher energy singlet dynamics with redder wavelength triplet features or when monitoring the growth of a new stimulated emission band. By taking larger spectral scans we were able to better compare the decay and growth between these excited state dynamics. In addition to these benefits of using the 300 gd grating there were also some drawbacks to using the larger grating. White light alignment had to be carefully set up and monitored to ensure stability over such a large wavelength window. Also, because white light intensity varied, signal to noise was an issue for sections of the TA spectrum. More time measurements were also necessary at early times, to ensure we could correct for the white light chirp with the FROG data. It was necessary to fit the FROG data to a cubed equation for the 300 nm window, representing the white light chirp, instead of a squared equation used for FROG data when dealing with the 70 nm window.

Data is collected in “sets” of delays. The sets each contain 18 time delays. The first and last delay are the same and repeated throughout all of the sets taken for a single sample on a single day. This allows data to be corrected for changes in white light signal and for different sets to be scaled in intensity relative to one another. The second delay in the set is a negative delay to obtain a transient absorption signal before excitation. The rest of the delays in the set are generated by multiplying maximum time value by a logarithmic range of points from 1 to 1000. This generates a series of delay time values that span the entire time window with a higher density of points at earlier times.

For experiments done with the 1200 g/d grating, 70 nm white light spectrum, 6 sets of delays were taken. Experiments with the 300 g/d grating required more data points at early times to correct for white light chirp across the entire 300 nm spectrum, and 9 sets of delays
were used. Each delay set is run 3 times and averaged with a Labview program. For a full set of samples, the 6 or 9 sets are pasted into an excel spreadsheet which normalizes the spectra and compiles it. This creates an averaged array of the non-time corrected data set. Depending on the signal to noise, one day’s data was used independently or if necessary multiple days of data with the same sample and delays sets were averaged together. This single or averaged days data is then pasted into the FROG correction excel spreadsheet. With the square (6 sets) or cubic (9 sets) line fit equation this spreadsheet calculates a correction factor for the white light chirp at each wavelength and applies it to all the data.

The Labview program mentioned previously collects the data for each of these sets. The selected time values are fed into an excel spreadsheet which generates a list of experimental commands to collect the data. The code contains commands that allow the Labview program to control most aspects of the fsTA data collection: white light stage delay, pump and probe beam block shutters, spectrometer shutter, and CCD camera data collection. Individual measurements are taken and saved with a specific file name so that the averaging program, used to combine similar sets can access the files.

Femtosecond experiments on hydroxycoumarin in toluene showed a strong nuclear response from the toluene solvent. Since the FROG only measures an electronic solvent response, additional experiments were needed to quantify the nuclear response. To do this fsTA data was taken on plain toluene solvent. This data showed changes in the white light due to pump interaction. The instrument response increased for toluene solvent to 800 fs. This was taken into account when analyzing data with toluene solvent.
3.3 Additional Ultrafast Techniques

Additional ultrafast and time resolved measurements were necessary to fully understand the complex dynamics of the investigated systems. FsTA, while a powerful technique is not able to monitor the molecules outside of the 250 fs-900 ps experimental window. The following techniques were used to obtain excited state information outside of the fsTA time window; nsTA, TCSPC, and Coherent Raman. These experiments were performed with the help of collaborators within our lab and the chemistry department. These supplementary techniques will be described here briefly for completeness.

3.3.1 Nanosecond Transient Absorption

Nanosecond transient absorption experiments were done with the help of Dr. Kyle Brenneman from the Meyer Lab, and were performed with instrumentation described previously.\(^4\) In brief, samples were prepared in a 2 mm pathlength quartz cuvette to maintain consistent concentrations with experiments performed using the femtosecond TA apparatus. All samples were argon degassed for at least 30 minutes just prior to performing experiments. The third harmonic of a Continuum Surelite II-10 Nd:YAG laser system (355 nm, 5-7 ns, 1 Hz, 0.4 mJ/pulse) served as an excitation source. White light probe pulses generated by a 150 W pulsed Xe lamp were passed through the sample at 90° relative to excitation and were collected by an Applied Photophysics laser kinetic spectrometer consisting of an f3.4 monochromator and Hamamatsu R928 PMT. Given the small pathlength of the cuvette, the cuvette was oriented at 45° relative to both pump and probe pulses. The output from the PMT is sent to a LeCroy WavePro 7100A oscilloscope interfaced to a PC. Electronic synchronization and control of the experiment are achieved by
electronics and software of local design. Kinetic traces, (average of 100) decaying to (at least) >5 lifetimes of the transient observed, were acquired and averaged at each wavelength. Quantitative analysis of the average decay curves was done using the algorithms of SigmaPlot (Systat Software, Inc.). Transient absorption probed anywhere between 300 nm and 800 nm was measured with a sensitivity of 1 mOD.

3.3.2 Time-Correlated Single-Photon Counting (TCSPC)

Time Correlated Single Photon Counting experiments were done with the help of Brian Mehl from the Papanikolas Lab. This experiment has been described in detail elsewhere,\textsuperscript{5-7} briefly the apparatus consists of a mode-locked Ti:Sapphire oscillator (Spectra Physics Tsunami) tuned to output a 720 nm pump pulse. This pulse is frequency doubled to 360 nm using a BBO crystal. The repetition rate of the pulse is adjusted by an acousto-optic modulator (AOM) used in a single pass configuration from 76 MHz down to 7.6MHz. The femtosecond pulses selected by the AOM excite the sample and the emitted light is collected at 90° relative to excitation, focused onto the slit of a 240 mm focal length single grating monochromator, and delivered to a cooled, multichannel plate-photomultiplier tube (MCP, Hamamatsu R3809U-51). The signal from the MCP is amplified, sent into a 200 MHz constant fraction discriminator (CFD, Tennelec 454) and then used as the start pulse for a time-to-amplitude converter (TAC, Tennelec 864). The stop pulse is obtained by focusing 10% of the excitation beam onto a Si:PIN photodiode, whose output is sent into a variable delay box, then to a CFD, and finally to the TAC. The TAC’s output is sent to a multichannel analyzer that is interfaced to a PC. The instrument response of the apparatus with a 360 nm excitation pulse is 200 ps at the full width half max (FWHM).
3.3.3 Coherent Raman

Coherent Raman experiments were done by Stephen Miller from the Moran Lab. The experiments were done on an interferometer described previously. The data shown in this thesis represent the solution signal minus the pure solvent spectra, or a difference spectra.

The light source for these experiments is a Ti:Sapphire laser which outputs 180 fs, 800 nm pulses. The Coherent Raman experiment was done with 2 narrowband “pump” pulses, and one broadband “probe” pulse. To obtain the narrowband pulses, the fundamental from the Ti:Sapphire is stretched spectrally using diffraction gratings. A slit is then placed between the diffraction gratings to select the wavelength and bandwidth of 1-2 nm. This 800 nm narrowband beam is frequency doubled using a BBO crystal to obtain the 400 nm, 500 fs time width pulse. The broadband pulse was created by a home-built Non-collinear Optical Parametric Amplifier (NOPA). The NOPA allows for broad bandwidth pulses. It was tuned to create 710 nm pulses with approximately 50 nm of bandwidth. This pulse is frequency doubled through a BBO crystal to produce the 355 nm broadband pulses, with a 45 fs time width. The pulse energies were approximately 50-100 nJ, and were focused to a spot size of ~ 120 micron FWHM in the sample. Polarization of the signal and broadband pulses were set orthogonal to the polarization of the narrow band pulse to repress the raman response from the toluene solvent.

Signals were detected by interferometry on a back illuminated CCD (Princeton Instruments PIXIS 100B) using a 0.3 m spectrograph. The signal was integrated for three seconds, and spectra represent 75 averages. To correct for scattered light, a mechanical shutter was placed in the broadband pulse beam, so that an “on” and “off” measurements
could be taken. The measurement interferograms were then processed using a Fourier transform algorithm to select out and process the signal spectra.

3.4 Sample Preparation and Characterization

3.4.1 Materials and Preparation for the Nitrophenyl-phenol experiments

4-hydroxy-4’-nitrobiphenyl (nitrophenyl-phenol) was purchased from TCI America and used as received. 1,2-dichloroethane (DCE) (> 99.8 %), toluene (> 99.9 %), butyronitrile (99 %), dichloromethane (99.6 %), tetrahydrofuran (> 99.9 %), tert-butylamine (≥ 99.8 %), 1-methylimidazole (99 %), diisopropylamine (99.95 %), triethylamine (99 %), 4-(dimethylamino)pyridine (99 %) were purchased from Aldrich and used as received. Acetonitrile (99.8 %) was purchased from Aldrich and dried over molecular sieves (4 Å, 8-12 mesh purchased from Acros) to reduce the amount of water present. Pyridine (99.9 %) was purchased from Fisher and used as received.

The biphenyl was weighed and added to a 10 mL sample of DCE. For the base, tert-butylamine was pipetted into DCE solvent, to make stock solutions. From these solutions, samples were made to the desired concentration. In this report specifically the fsTA experiments were done on 0.3 mM biphenyl in DCE and when appropriate with 90 mM tert-butylamine. The samples were then placed into a 2mm quartz FUV cuvette and degassed with Ar gas for 30 minutes prior to data collection. All solutions and samples were prepared fresh daily, to avoid sample degradation.

3.4.2 Materials and Preparation for the Hydroxycoumarin experiments

7-hydroxy-4-(trifluoromethyl)-1-coumarin (hydroxycoumarin) (98%), 1-methylimidazole (99%), and toluene (Chromasolv Plus for HPLC, >99.9%) were all
purchased from Sigma-Aldrich and used as received. Solutions were prepared by first creating stock solutions of the HFC and 1-meImid in toluene. The stock solutions were then used to make final solutions of the appropriate concentrations. For time resolved experiments, samples with concentrations of 0.34 mM coumarin with no base, 2 mM 1-methylimidazole (low) base, and 500 mM 1-methylimidazole (excess) base were prepared. Samples were placed in a 2 mm quartz cuvette. Prior to time resolved emission measurements the samples were deaerated by bubbling Argon gas through the sample for ~30 minutes. Solutions and samples were made fresh daily.

3.4.3 UV-Vis Characterization

The extent of hydrogen bond association in ground state molecules is measurable from changes in ground state absorption. UV-Vis absorption measurements were done using an Agilent Technologies Model 8453 diode-array spectrophotometer. Initial absorption measurements were done in a 1 cm cuvette and then repeated in a 2 mm cuvette to recreate the pathlength and concentration conditions used in the femtosecond transient absorption measurements.

3.4.4 Steady State Emission Characterization

The degree of tautomerization in hydroxycoumarin excited state systems as a function of 1-methylimidazole base concentration can be determined by steady state emission measurements. Steady state emission measurements were taken using PTI QuantaMaster Emission Spectrometer. Samples were excited with 355 nm light and the sample emission was scanned from 360 nm to 700 nm using background correction. Emission collected using
the 2 mm cuvette required it be placed at a 45 degree angle relative to the excitation and emission collection slits in the spectrometer. Slit widths of 0.35 mm were used.
3.5 References


Chapter 4

Ultrafast Investigation of Light-Driven Electron-Proton Transfer in a Nitrophenyl-phenol-Amine Adduct
4.1 Introduction

Despite the ease with which plants capture and use light, solar devices capable of mimicking nature and cost effectively harnessing energy have proven an elusive challenge. Nature has perfected the art of utilizing the sun’s energy, but behind the elegant simplicity lies a complicated process. This process, Proton coupled electron transfer (PCET), is a mechanistic pathway through which nitrogen fixation, water oxidation, respiration, and other important biological processes take place.\textsuperscript{1-4} PCET also occurs in all green photosynthetic plants specifically in photosystem II (PS II) with the oxygen evolving complex (OEC).\textsuperscript{1, 2} The concerted motion of proton and electron transfer allows the avoidance of high energy intermediates as well as avoiding charge build up in photo triggered and excited state reactions.\textsuperscript{5, 6} Many biological systems use the charge shuttling capabilities inherent in PCET to avoid charge buildup.\textsuperscript{7, 8}

PCET describes the concerted motion of both the proton and the electron, versus two step processes in which the proton is transferred followed by electron transfer (PTET) or the alternative variation of electron transfer followed by proton transfer (ETPT).\textsuperscript{5, 9} Electron-Proton Transfer is a type of these reactions where the motion of a proton is coupled with the motion of the electron. An understanding of the dynamics and timescale of these reactions will facilitate in the development of biomimetic solar cell devices as well as the design of light harvesting catalysts in the production of solar fuels.

A specific example is the proposed multisite electron-proton transfer (MS-EPT) pathway proposed in the oxidation of tyrosine $YZ$ by P680$^+$ in the PS II reaction center with histidine (His190) acting as the proton acceptor base, Figure 4.1.\textsuperscript{1, 10-12} With these experiments we are exploring both the range and microscopic details of EPT reactivity.
including analogs of Figure 4.1 in which simultaneous or near simultaneous transfer of both electrons and protons occurs photochemically. EPT reactions are also responsible for the rapid excited state relaxation and photostability of DNA and other biological molecules. These experiments were done in an effort to understand the chemistry involved in EPT, and to develop a broader understanding of the basic physical and chemical processes involved in photosynthesis in general and PCET in particular. This will further our fundamental knowledge of chemical systems.

Figure 4.1. Scheme of proton coupled electron transfer between P680⁺ and tyrosine in photosystem II.

In order to fully comprehend the complex dynamics of PCET, a knowledge of ET and PT transfer separately is necessary. Electron transfer in molecular systems can be considered in terms of Marcus theory, where the rate of electron transfer can be calculated if the relative energies of the species involved are known. Proton transfer and the many factors that affect it are also important. For our experimental systems proton transfer is facilitated if the species involved are hydrogen bound. Hydrogen bonding is dependent on the pKₐ’s of the involved systems as well as the solvent environment.

We report here initial results on a model reaction in which intramolecular charge transfer (ICT) to an internal electron acceptor is accompanied by proton transfer to an
external base, a reaction related to proton transfer to the solvent from excited state “super acids.” Femtosecond transient absorption is a powerful spectroscopic tool and with this technique we are able to excite a hydrogen bound molecular system and to monitor the excited state evolution on a femtosecond and picosecond time scale. Specifically we are able to follow the coupled motion of the proton and electron transfer between a nitrophenyl-phenol (Figure 4.2) and tert-butylamine hydrogen bonded adduct following ultrafast excitation. Changes in the spectral signature of the molecule allow detection of proton motion and electron relaxation. Proton transfer in our model system is affected by solvent and $\Delta pK_A$, which in turn influences the heavy atom distance. The ultrafast laser system allows us to trigger an initial charge transfer and watch the resulting excited state dynamics on the time scale that they are occurring.

The experiments discussed in this chapter were performed primarily on nitrophenyl-phenol with tert-butylamine base in either dichloroethane (DCE) solvent or acetonitrile (ACN) solvent. The two organic compounds form a hydrogen-bonding adduct in the ground state. Nitrophenyl-phenol is an organic molecule with a twisted conjugated ring system.

![Figure 4.2. Nitrophenyl-phenol molecule.](image)

This molecule is a super photoacid which means its ground state $pK_A$ is higher than its excited state $pK_A$ due to changes in excited state electronic structure. This change in $pK_A$ provides the driving force for proton transfer in the excited system, given a hydrogen bonded
base is in close proximity to act as a proton acceptor. The base, tert-butylamine forms a ground state hydrogen bond with nitrophenyl-phenol and acts as a proton acceptor in the excited state. Two solvents were used to probe solvent effects on energy levels, and photoinduced dynamics. The less polar of the two, DCE, has a dielectric constant of 10.4. The more polar solvent ACN has a dielectric constant of 36.2.

To investigate photo-EPT between nitrophenyl-phenol and the base, there are four chemical properties that play an important role (Figure 4.3): hydrogen bonding, ICT photoexcitation, photoacidity, and ring twisting in the excited molecule. The first, hydrogen bonding, helps to create the initial configuration that will influence excited state dynamics. Our simple model system lacks a protein scaffold found in PS II or the water molecules precise placement in the Mn4 oxygen evolving complex. Instead we rely on ground state hydrogen bonding to create an associated complex. This ground state configuration of hydrogen bond association plays an important role in the excited state dynamics that happen following photon absorption, specifically photo-EPT.

![Figure 4.3. Chemical properties of nitrophenyl-phenol that affect the ground state and excited state dynamics.](image)
The pKₐ of proton affinity of the main nitrophenyl-phenol molecule and the hydrogen bonding base affect the strength and length of the hydrogen bond created. Nitrophenyl-phenol has a pKₐ of ~ 8.95 for the phenolic proton (-OH). The base, tert-butylamine, which most of the experiments discussed in this chapter used has a pKₐ of ~ 10.7. Hydrogen bond strength can be qualitatively predicted by the ΔpKₐ or the difference in the base pKₐ and the acid pKₐ, Equation 4.1. For nitrophenyl-phenol and tert-butylamine, the ΔpKₐ is 1.75. Hydrogen-bonding can also be detected using UV-Vis absorption measurements. Solvochromatic shifts to lower energy are spectral signs of hydrogen bond formation.

\[ \Delta pK_A = pK_A(\text{base}) - pK_A(\text{acid}) \]  
\textit{Equation 4.1}

The second important chemical feature is the ICT absorption in nitrophenyl-phenol. ICT causes the electronic changes that produce the driving forces for photo-EPT, as it changes the proton affinity of NPP–OH---B. The ICT band also provides a photo trigger so that changes to the excited state can be monitored on ultrafast timescales. Application of DFT (vida infra) confirms an ICT origin for the low lying absorption band resulting in a nπ* excited state with considerable charge transfer character.

The third chemical feature, photoacidity, arises from photon induced electron transfer across the molecule. Excitation transfers electron density from the phenolic ring to the nitro group dramatically changes the pKₐ and proton affinity. Before excitation nitrophenyl-phenol has a pKₐ of 8.95. Afterwards this pKₐ decreases, becoming more acidic. Based on the absorption measurements and the Forster equation, Equation 4.2, we are able to approximate the new pKₐ* of this excited state molecule following absorption.\textsuperscript{26} Absorption measurements give hν₁ = 29,400 cm⁻¹ for nitrophenyl-phenol, and
$h\nu = 25,000 \, \text{cm}^{-1}$ for nitrophenyl-phenolate anion. These values suggest a decrease of
~ $9 \, \text{pK}_A$ units as a result of excitation, creating a very acidic molecule with $\text{pK}_A^* \sim 0.05$.

$$pK_a^* = pK_a - \frac{(h\nu_{HA} - h\nu_{A^-})}{2.3RT} \quad \text{Equation 4.2}$$

This provides a light switch mechanism for turning on acidity in the molecule. In the
case where the nitrophenyl-phenol molecule is hydrogen bound to a tert-butylamine base,
following excitation the base acts as a proton acceptor. The ground state $\Delta \text{pK}_A$ for
nitrophenyl-phenol-tert-butylamine adduct is 1.75, following excitation it is $\Delta \text{pK}_A^* \sim 10.65$.
The once stable short hydrogen bond in the ground state is no longer favorable. Ultrafast
spectroscopy techniques are used to investigate the excited state changes in this molecular
system.

The final chemical property that affects the excited state dynamics we see in the
nitrophenyl-phenol system is the ring angle. The two rings do not lie in the same plane,
instead one is twisted at an angle of 34.5 degrees relative to the other. This ring angle
hinders delocalization of the $\pi$ bonds across the entire molecule. Changes to the ring angle
and the electronic configuration as a result of proton position give rise to the spectral changes
we see, such as ground state stabilization and fast singlet-triplet intersystem crossing. The
dramatic changes to the molecules electron density following ICT excitation also affect the
ring angles. As the excited rings twist in an attempt to dissipate energy they are creating
angular momentum. This affects singlet-triplet dynamics in the nitrophenyl-phenol system.
4.2 Experimental Methods

4.2.1 Materials and Sample Preparation

Materials. 4-hydroxy-4'-nitronitropheny1-phenol (nitrophenyl-phenol) was purchased from TCI America and used as received. Toluene (> 99.9 %), butyronitrile (99 %), dichloromethane (99.6 %), tetrahydrofuran (> 99.9 %), tert-butylamine (≥ 99.8 %), 1-methylimidazole (99 %), diisopropylamine (99.95 %), triethylamine (99 %), 4-(dimethylamino)pyridine (99 %) were purchased from Aldrich and used as received. Acetonitrile (99.8 %) was purchased from Aldrich and dried over molecular sieves (4 Å, 8-12 mesh purchased from Acros) to reduce the amount of water present. Pyridine (99.9 %) was purchased from Fisher and used as received. 1, 2-dichloroethane (DCE) (> 99.8 %) was purchased from Aldrich, dried over molecular sieves to remove excess water, and then filtered through a 20 µm filter to remove dust and any residual molecular sieve particles.

Preparation: Nitrophenyl-phenol was weighed and added to a 10 mL sample of DCE to create a stock solution. For the base, tert-butylamine was similarly added to DCE solvent, and from these solutions, samples were made of the appropriate concentration. In this report specifically the fsTA experiments were done on 0.3 mM nitrophenyl-phenol in DCE and when appropriate with 90 mM tert-butylamine. Samples in acetonitrile solvent were prepared in a similar manner, but with concentrations of 0.3 mM nitrophenyl-phenol with 1 mM tert-butylamine base. The samples were then placed into a 2mm quartz FUV cuvette and degassed with Ar. Samples and stock solutions were prepared fresh daily.
4.2.2 Absorption

UV-Vis measurements were taken with a Shimadzu UV 3600 UV-Vis NIR spectrophotometer and an Agilent Technologies Model 8453 diode-array spectrophotometer. These UV-Vis measurements were useful in characterizing the molecule as well as providing an indication of hydrogen bonding. Initial absorption measurements were done in a 1 cm cuvette and then repeated in a 2 mm cuvette to recreate the pathlength and concentration conditions used in the femtosecond transient absorption measurements. UV-Vis spectra of the sample also proved to be extremely important, as they provided a way to detect degradation resulting from the transient absorption experiments.

4.2.3 Femtosecond Transient Absorption

Femtosecond transient absorption measurements were done using a pump probe technique that has been described in Chapter 3 in detail. Briefly, the excitation source was a Clark 2001 chirped pulse amplification (CPA) laser system that outputs a 800 mW, 775 nm, pulse at a 1 kHz repetition rate, with an autocorrelation full width half max of 250 fs. The probe pulse was generated by focusing a small portion of the beam into a CaF2 window to generate a white light continuum from 380 - 700 nm. The spot size at the sample was ~ 280 micron. The 388 nm pump pulse was created by second harmonic generation of the 775 nm beam by using a beta barium borate (BBO) crystal. The 355 nm pump pulse was created with a tunable Clark Optical Parametric Amplifier (OPA) (1420 nm) and subsequent second (710 nm) and fourth (355 nm) harmonic generation. The data was collected at magic angle polarization (54.7 degrees) with pump beam focused to ~1400 micron spot size and power of 0.60 mW. Samples with concentrations of 0.3 mM nitrophenyl-phenol with or without
90 mM tert-butylamine base were prepared with DCE solvent. Samples in acetonitrile solvent were prepared with concentrations of 0.3 mM nitrophenyl-phenol with 1 mM tert butylamine base. Samples were placed in a 2 mm quartz cuvette and degassed with Ar gas for 30 minutes prior to data collection.

4.2.4 Nanosecond Transient Absorption

Transient absorption experiments on the nanosecond time scales were performed with instrumentation described previously and in Chapter 3. In brief, samples were prepared in a 2 mm pathlength quartz cuvette to maintain consistent concentrations with experiments performed using the fsTA apparatus. All samples were argon degassed for at least 30 minutes just prior to performing experiments. The third harmonic of a Continuum Surelite II-10 Nd:YAG laser system (355 nm, 5-7 ns, 1 Hz, 0.4 mJ/pulse) served as an excitation source. White light probe pulses generated by a 150 W pulsed Xe lamp were passed through the sample at 90° relative to excitation and were collected by an Applied Photophysics laser kinetic spectrometer consisting of an f3.4 monochromator and Hamamatsu R928 PMT. Given the small pathlength of the cuvette, the cuvette was oriented at 45° relative to both pump and probe pulses. The output from the PMT is sent to a LeCroy WavePro 7100A oscilloscope interfaced to a PC. Electronic synchronization and control of the experiment are achieved by electronics and software of local design. Kinetic traces, (average of 100) decaying to (at least) >5 lifetimes of the transient observed, were acquired and averaged at each wavelength. Quantitative analysis of the average decay curves was done using the algorithms of SigmaPlot (Systat Software, Inc.). Transient absorption probed anywhere between 300 nm and 800 nm was measured with a sensitivity of 1 mOD.
4.2.5 Coherent Raman

Coherent Raman experiments were done on an interferometer described previously and in Chapter 3. The data shown in this thesis represent the solution signal minus the pure solvent spectra, or difference spectra. The light source for these experiments is a Ti:Sapphire laser which outputs 180 fs, 800 nm pulses. The Coherent Raman experiment was done with two narrowband “pump” pulses, and one broadband “probe” pulse. To obtain the narrowband pulses, the fundamental from the Ti:Sapphire is stretched spectrally using diffraction gratings. A slit is then placed between the diffraction gratings to select the wavelength and bandwidth of 1-2 nm. This 800 nm narrowband beam is frequency doubled using a BBO crystal to obtain the 400 nm, 500 fs time width pulse. The broadband pulse was created by a home-built Non-collinear Optical Parametric Amplifier (NOPA). The NOPA allows for broad bandwidth pulses. It was tuned to create 710 nm pulses with approximately 50 nm of bandwidth. This pulse is frequency doubled through a BBO crystal to produce the 355 nm broadband pulses, with a 45 fs time width. The pulse energies were approximately 50-100 nJ, and were focused to a spot size of ~ 120 micron full width half max (FWHM) in the sample. Polarization of the signal and broadband pulses were set orthogonal to the polarization of the narrowband pulse to repress the raman response from the toluene solvent.

Signals were detected by interferometry on a back illuminated CCD (Princeton Instruments PIXIS 100B) using a 0.3 m spectrograph. The signal was integrated for three seconds, and spectra represent 75 averages. To correct for scattered light, a mechanical shutter was placed in the broadband pulse beam, so that an “on” and “off” measurements could be taken. The measurement interferograms were then processed using a Fourier transform algorithm to select out and process the signal spectra.
4.2.6 DFT Modeling

Theoretical calculations were carried out by using Density Functional Theory (DFT) as implemented in Gaussian03, revision D.02. Becke’s three-parameter hybrid functional with the LYP correlation functional (B3LYP) was used with the 6-31g split-valence basis set. Franck-Condon vertical excitation energies and oscillator strengths were obtained with non-equilibrium Time-Dependent Density Functional Theory (TD-DFT) as implemented in Gaussian03. The solvent (1,2-dichloroethane) was modeled by means of the Integral Equation Formalism Polarizable Continuum Model (IEF-PCM), as implemented in Gaussian03. The geometries of O2N-OH, O2N-O-H---NH2(CH3)3, and O2N-O- were fully optimized (B3LYP, 6-31g, gas phase). Similarly, the geometry of O2N-O----H-NH2(CH3)3 was optimized but keeping the O-H distance fixed at 1.621 Å. This distance was selected from a full optimization using water as the solvent (IEF-PCM). The intense lowest energy transition in each case corresponds to the ICT band and therefore determines the energy of the ICT excited state above the ground state for each particular species.

4.3 Results and Discussion

The excited state behaviors of both nitrophenyl-phenol alone and with the base adduct tert-butylamine were investigated by ultrafast femtosecond and nanosecond transient absorption measurements. Nitrophenyl-phenol base complex was also investigated using a Coherent Raman technique, and additional calculations of excited states using DFT. Femtosecond transient absorption measurements were performed in two different solvents, primary experiments were done in DCE at two different excitation wavelengths and repeated in acetonitrile with one excitation wavelength to investigate solvent effects on the ultrafast dynamics.
4.3.1 Nitrophenyl-phenol

Nitrophenyl-phenol has an intermolecular charge transfer (ICT) absorption band in the ultraviolet region. This band is due to an electron transfer from one side of the nitrophenyl-phenol molecule to the nitro group on the opposite end. The energy of this ICT band is dependent on solvent and proton position on the phenolic oxygen. The presence of the proton affects the overall electronic structure of the nitrophenyl-phenol ring molecule, and thus changes in absorption energy allowing us to monitor the protons' position.

Ground state UV-Vis measurements were used as an indication of the extent of hydrogen bonding between nitrophenyl-phenol with different base molecules and in different solvents. The primary solvent used for these measurements was DCE. Nitrophenyl-phenol has an ICT absorption at $\lambda_{\text{max}} = 335$ nm in DCE. When organic bases from tert-butylamine ($\text{pK}_A = 10.7$ in water at $25^\circ\text{C}$) to pyridine ($\text{pK}_A = 5.25$) are added to solutions of nitrophenyl-phenol in DCE, the lowest energy absorption band at $\lambda_{\text{max}} = 335$ nm shifts incrementally to lower energy as the strength of the base increases to a limiting value of 354 nm for tert-butylamine. This ground state shift is due to hydrogen bonding between the phenolic OH group on nitrophenyl-phenol and base molecules, Figure 4.4.

Figure 4.4. Scheme of hydrogen bonding between nitrophenyl-phenol and tert-butylamine.
The tert-butylamine base (pK\textsubscript{A} = 10.7) is not strong enough to deprotonate the nitrophenyl-phenol (pK\textsubscript{A} = 8.95), and instead forms a short hydrogen bond as a result of this small ΔpK\textsubscript{A} (1.75). Thus tert-butylamine forms a strong hydrogen bond in solution with nitrophenyl-phenol and provided an excited state system with a large driving force towards proton transfer. UV-Visible absorption spectra of nitrophenyl-phenol, nitrophenyl-phenol with base, and nitrophenyl-phenol anion in DCE are shown in Figure 4.5. Nitrophenyl-phenol in DCE has a 335 nm ground state absorbance band. Upon addition of tert-butylamine, the absorption maximum shifts to lower energy (λ\textsubscript{max} = 354 nm) as a result of H-bonding between nitrophenyl-phenol and base, Figure 4.5. Complete deprotonation to give the anion, p-O\textsubscript{2}NC\textsubscript{6}H\textsubscript{4}C\textsubscript{6}H\textsubscript{4}O\textsuperscript{−} occurs with addition of tetra-n-butylammonium hydroxide. The nitrophenyl phenol anion absorption is shifted even further to lower energy

![Graph](image)

**Figure 4.5.** UV-Visible absorption spectra for nitrophenyl-phenol, nitrophenyl-phenol hydrogen bound to tert-butylamine, and the nitrophenyl-phenolate anion in DCE. Absorption maxima and absorbing species are indicated above the spectra.
\( \lambda_{\text{max}} = 466 \text{ nm} \), consistent with a higher energy ground state due to proton loss on the nitrophenyl phenol. For tert-butylamine in DCE, \( K_A = 104 \pm 10 \text{ M}^{-1} \) at 23±2 °C with adduct formation > 90% complete with 0.3 mM nitrophenyl-phenol and 90 mM base. Association constants for other bases are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Base</th>
<th>pKₐ Base</th>
<th>( K_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>5.25</td>
<td>25 ± 2</td>
</tr>
<tr>
<td>1-methylimidazole</td>
<td>6.95</td>
<td>250 ± 20</td>
</tr>
<tr>
<td>DMAP</td>
<td>9.6</td>
<td>310 ± 40</td>
</tr>
<tr>
<td>tert-butylamine</td>
<td>10.68</td>
<td>104 ± 10</td>
</tr>
<tr>
<td>triethylamine</td>
<td>10.7</td>
<td>580 ± 60</td>
</tr>
<tr>
<td>diisopropylamine</td>
<td>11.05</td>
<td>31 ± 4</td>
</tr>
</tbody>
</table>

Table 4.1. Association constants for nitrophenyl-phenol in DCE for a variety of bases.

The association constants in Table 4.1 were calculated from ground state absorption spectral shifts using the Benesi-Hildebrand equation.\(^{13} \) For these calculations, absorbance measurements were taken at a variety of base concentrations from 0-300 mM, with nitrophenyl-phenol (NPP, NPP--B) concentrations of 0.3 mM. Starting from the association equation:

\[
\text{NPP} + \text{B} \rightleftharpoons K_A \text{NPP} \cdots \text{B}
\]

\[ K_A = \frac{[\text{NPP} \cdots \text{B}]}{([\text{NPP}][\text{B}]-[\text{NPP} \cdots \text{B}])} \]

\[ \text{Equation 4.3} \]

\[ \text{Equation 4.4} \]
Since \([B] \gg [NPP]\), we approximate \([B] \sim ([B]-[NPP \cdots B])\), thus simplifying the equation to:

\[
K_A = \frac{[NPP \cdots B]}{B \cdot ([NPP]_o - [NPP \cdots B])} \quad \text{Equation 4.5}
\]

For a sample with no base \(A_{NPP} = \epsilon_{NPP} \cdot [NPP]_o\), as the solvent does not absorb. Rearrangement gives Equation 4.6, where pathlength, a constant for all samples, is removed for simplicity.

\[
[NPP]_o = \frac{A_{NPP}}{\epsilon_{NPP}} \quad \text{Equation 4.6}
\]

As base is added, the absorption equation becomes more complicated.

\[
A_{NPP \cdots B} = \epsilon_{NPP} \cdot ([NPP]_o - [NPP \cdots B]) + \epsilon_{NPP \cdots B} \cdot [NPP \cdots B] \quad \text{Equation 4.7}
\]

Rearrangement of Equation 4.7 gives an equation that can be substituted into Equation 4.5 for \([NPP \cdots B]\).

\[
A_{NPP \cdots B} = \epsilon_{NPP} \cdot [NPP]_o + \epsilon_{NPP} \cdot [NPP \cdots B] + \epsilon_{NPP \cdots B} \cdot [NPP \cdots B] \quad \text{Equation 4.8}
\]

\[
[NPP \cdots B] \cdot (\epsilon_{NPP \cdots B} - \epsilon_{NPP}) = (A_{NPP \cdots B} - A_{NPP}) \quad \text{Equation 4.9}
\]

\[
[NPP \cdots B] = \frac{(A_{NPP \cdots B} - A_{NPP})}{(\epsilon_{NPP \cdots B} - \epsilon_{NPP})} \quad \text{Equation 4.10}
\]

Substituting Equation 4.10 and Equation 4.6 into Equation 4.5 gives:

\[
K_A = \frac{(A_{NPP \cdots B} - A_{NPP})}{B \cdot (\epsilon_{NPP} / (A_{NPP \cdots B} - A_{NPP}) / (\epsilon_{NPP} \cdot (A_{NPP \cdots B} - A_{NPP}) / (\epsilon_{NPP} \cdot (A_{NPP \cdots B} - A_{NPP})))} \quad \text{Equation 4.11}
\]

Rearrangement gives the equation:

\[
\frac{1}{[B]} = K_A \cdot A_{NPP} \cdot (\epsilon_{NPP \cdots B} - \epsilon_{NPP}) \cdot \left(\frac{1}{A_{NPP \cdots B} - A_{NPP}}\right) - K_A \quad \text{Equation 4.12}
\]

While the dependent and independent variables are switched, a linear fit to \(\frac{1}{(A_{NPP \cdots B} - A_{NPP})}\) versus \(\frac{1}{[B]}\) gives the \(K_A\) value as the y-intercept. The graph for nitrophenyl-phenol and tert-butylamine in DCE is shown in Figure 4.6.
Figure 4.6. Linear fit of nitrophenyl-phenol absorption as a function of tert-butylamine base concentration to obtain the $K_A \sim 104 \pm 10 \text{ M}^{-1}$ of hydrogen bond association between these molecules in DCE.

The equation can be rearranged to a more traditional form that also allows a linear fit and gives the $K_A$ value, Equation 4.13.

$$\frac{1}{(A_{\text{NPP-B}} - A_{\text{NPP}})} = \frac{\epsilon_{\text{NPP}}}{K_A \epsilon_{\text{NPP}} (\epsilon_{\text{NPP-B}} - \epsilon_{\text{NPP}})} \left( \frac{1}{[B]} \right) + \frac{\epsilon_{\text{NPP}}}{\epsilon_{\text{NPP}} (\epsilon_{\text{NPP-B}} - \epsilon_{\text{NPP}})}$$  \hspace{1cm} \text{Equation 4.13}

Table 4.1 shows the $K_A$ values calculated for a variety of bases with nitrophenyl-phenol in DCE.

Further studies of the solvent effects on the excited state dynamics between nitrophenyl-phenol and tert-butylamine were done. Similar hydrogen bonding spectral shifts occurred in a variety of solvents, Table 4.2. From these measurements, acetonitrile was used for additional excited state measurements, despite its lower association constant as it provides an opportunity to investigate the ultrafast dynamics in a more polar solvent environment.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>dielectric constant</th>
<th>$K_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>130 ± 4</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>7.32</td>
<td>2 ± 0.7</td>
</tr>
<tr>
<td>1,2-dichloroethane (DCE)</td>
<td>10.4</td>
<td>104 ± 10</td>
</tr>
<tr>
<td>Butyronitrile</td>
<td>20.7</td>
<td>11.7 ± 0.9</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>36.2</td>
<td>12 ± 1</td>
</tr>
</tbody>
</table>

Table 4.2. Association constants for nitrophenyl-phenol with tert-butylamine in a variety of solvents with a range of dielectric constants.

4.3.2 Nitrophenyl-phenol in DCE

Transient absorption measurements were first performed on nitrophenyl-phenol in DCE without added base. Femtosecond and nanosecond transient absorption measurements were used to measure the excited state absorbance of the nitrophenyl-phenol molecule following 355 nm excitation.

4.3.2.1 355 nm Excitation: FsTA and NsTA

Delta absorbance spectra covering a 400 - 700 nm spectral window following photoexcitation near the maximum of the absorption band at 355 nm are shown as a function of pump-probe delay in Figure 4.7. At our earliest observation time (250 fs), we observe two absorptions – a prominent band centered at 440 nm and the beginnings of a broad absorption at 650 nm. During the first 10 ps, the 440 nm feature decays completely as the red band reaches a maximum in amplitude. The evolution of this band is followed on longer time scales using nsTA spectroscopy; the TA spectrum observed at 10 ns is shown superimposed on fsTA data in the figure. The 650 nm band is observed to decay without a change in shape.
Figure 4.7. Transient absorption spectra for nitrophenyl-phenol in 1,2-dichlorehane obtained at 1 ps (a), 3 ps (b), 20 ps (c) and 10 ns (d). Kinetic data (not shown) indicates that the 450 nm band observed at early times converts into the 650 nm band with a time constant of 3 ps, which then decays with a 2.4 µs lifetime. The magnitude of the high energy band is typically in the range of 10-15 mOD for both fsTA and nsTA at early observation times.

on a 2.4 µs timescale. This long lifetime and isosbestic behavior between the two absorptions suggests that (1) the 650 nm band corresponds to absorption from a triplet excited state and (2) the 440 nm band initially observed arises from the optically prepared singlet excited state. The decay at 440 nm and concurrent growth at 650 nm reflect a rapid (10 ps) intersystem crossing (ISC) in nitrophenyl phenol in DCE. Thus, excitation of the nitrophenyl-phenol at 355 nm in DCE gives \( ^1n\pi^* \), with \( \lambda_{\text{max}} = 450 \text{ nm} \), followed by rapid intersystem crossing to the ICT triplet, \( ^1(\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
The presence of a long-lived triplet is confirmed by time-resolved EPR experiments performed by Malcolm Forbes group. These experiments probed the triplet character of the nitrophenyl-phenol transient by transient EPR measurements at 77 K in a toluene glass. Following laser flash excitation, a strongly spin polarized spectrum was obtained typical of a randomly oriented triplet state with a large D value (~950 Gauss; 0.089 cm⁻¹). The triplet undergoes nonradiative decay to the ground state with $\tau = 2.4 \mu$s.

The triplet formation in this case can be explained due to the non-planarity of the nitrophenyl-phenol rings. Based upon Gaussian calculations carried out by Javier Concepcion in the Meyer lab, the nitrophenyl-phenol system is not a flat delocalized $\pi$ system, but instead in the ground state the rings are offset by a 34.5 degree angle. The ground state anion has a ring angle of 12.6 degrees consistent with a ring flattening and delocalization of the $\pi$ state to stabilize the charged anion state. Given this ring twisting in response to the change in electron density caused by the loss of the proton, it is reasonable to assume that some ring twisting occurs to compensate for the dramatic change in electron density induced by the charge transfer. This ring twisting is suspected to provide the angular momentum necessary to allow the spin flip for ISC. The process is summarized in Figure 4.8. It can be seen that despite the dramatic changes to the electron density and proton affinity, the phenolic proton is trapped on the nitrophenyl-phenol molecule.
4.3.3 Nitrophenyl-phenol with tert-butylamine in DCE

Transient absorption measurements were also performed on nitrophenyl-phenol in DCE with the added base, tert-butylamine. In addition to femtosecond and nanosecond transient absorption techniques, Coherent Raman experiments and DFT calculations were performed on the nitrophenyl-phenol and tert-butylamine molecule system to measure the effects of ground state hydrogen bond interaction on the nitrophenyl-phenol molecule.

4.3.3.1 355 nm Excitation: FsTA and NsTA

A related but more complex pattern of events occurs following excitation of the nitrophenyl-phenol/tert-butylamine adduct following excitation at 355 nm. FsTA experiments were performed on the nitrophenyl-phenol with base system, resulting in the spectra seen in Figure 4.9. At the earliest observation times (250 fs), a band appears at $\lambda_{\text{max}} = 410$ nm and by 1 ps a less intense feature appears at 600 nm. The loss of absorbance
on the low energy side of the 410 nm band, between 430 nm and 450 nm, matches further growth at 600 nm.

**Figure 4.9.** Transient absorption difference spectra at early times for the nitrophenyl-phenol/tert-butylamine adduct in DCE following 355 nm excitation obtained at: 1 ps (a), 3 ps (b), and 50 ps (c). The magnitude of the high energy band is typically in the range of 10-15 mOD for both fsTA and nsTA at early observation times.

At first glance the dynamics in the hydrogen bound system seem analogous to the two band singlet-triplet case of nitrophenyl-phenol alone. However in the hydrogen bound system the decay of the initially present 410 nm band (τ ~ 4.5 ps) does not correlate to the growth of the 600 nm band (τ ~ 1.5 ps). Closer inspection of the decay kinetics within the 410 nm band reveal that transients from different wavelength slices decay with different lifetimes. Monitoring the wavelength of the ‘410 nm band’ at both 410 nm and 440 nm shows that what appears to be one band, is in reality two. Figure 4.10 shows the TA signal
Figure 4.10. Transients of 0.3 mM nitrophenyl-phenol with 90 mM tert-butylamine base in DCE. Pump 355 nm. Blue points represent the decay in the transient absorption signal at 410 nm, on the high energy side of the blue absorption band; green points show the decay of the low energy side at 440 nm. Non-linear least squares analysis reveals time constants of 4.5 ps and 1.5 ps for the 410 nm and 440 nm decays, respectively. The red points show the kinetic growth of the 600 nm absorption band, which appears with a 1.5 ps time constant. The similarity between the time scales for the decay of the low-energy side and the growth of the red absorption band indicate that they correspond to the same dynamical process, namely singlet-triplet inter-conversion. The magnitude of the high energy band is typically in the range of 10-15 mOD for the fsTA measurements at early delays.

observed at 410 nm, 440 nm, and 600 nm. The decay kinetics suggest that the initially formed 410 nm band is composed of two overlapping features that decay at different rates, one centered at 390 nm (τ ~ 4.5 ps) corresponding to the 410 nm transient and the other at 420 nm (τ ~ 1.5 ps) corresponding with the 440 nm transient. Furthermore, the decay at 420 nm is concurrent with the growth at 600 nm (τ ~ 1.5 ps), indicating that the growth of the red
absorption band is correlated with the decay of the low-energy side of the blue absorption band. The kinetic data suggests that three absorptions are contributing to the TA spectrum; a red absorption initially at 600 nm, and two overlapping absorptions at approximately 390 nm and 420 nm with a $\lambda_{\text{max}}$ at 410 nm whose unresolved superposition gives rise to the blue absorption band. Due to the match in decay of the 420 nm band, with the growth in the 600 nm band, these features are assigned to the singlet and triplet states, respectively.

The triplet band that initially appears with a low broad peak at 600 nm, Figure 4.11, closely resembles the triplet band observed in the nitrophenyl-phenol only spectra, Figure 4.7. The nitrophenyl-phenol base complex triplet band then grows in and begins to blue shift over the next 3-5 ps, illustrating the simultaneous growth of the triplet state and the spectral effects of proton interaction with the phenolic oxygen. The 600 nm feature has been assigned to the triplet state with the proton transferred to the base yet still hydrogen bound to the triplet nitrophenyl-phenol. Within 100’s of ps this 600 nm band evolves to 550 nm. We interpret this shift as dissociation of the proton base complex and formation of the triplet anion.

Figure 4.11 depicts, along with fsTA data, results from nsTA experiments on nitrophenyl-phenol-amine adduct in DCE. The nsTA technique is then used to monitor the triplet relaxation and the eventual recombination to form the initial ground state complex. At the earliest observation time for nsTA (10 ns), two features are present – the triplet absorption centered at 550 nm along with a less intense absorption centered at 450 nm. The feature at 550 nm decays while the intensity at 450 nm grows with matching kinetics ($\tau \sim 15$ ns) and a clear isosbestic point. The 550 nm intermediate disappears with $k = 6.7 \times 10^7 \text{ s}^{-1}$, ($\tau \sim 15$ ns), to give ground state anion $O_2N-O^-$ with $\lambda_{\text{max}} = 450$ nm. It returns
to the nitrophenyl-phenol by diffusional proton transfer from HB\(^+\) which occurs on the µs timescale, O\(_2\)N-O\(^-\) + \(^1\)H-B → O\(_2\)N-O-H---B.

**Figure 4.11.** Transient absorption difference spectra at long times for the nitrophenyl-phenol/tert-butylamine adduct in DCE following 355 nm excitation obtained at: 3 ps (a), 50 ps (b), 300 ps (c), 10 ns (d), 20 ns (e), and 40 ns (f). The magnitude of the high energy band is typically in the range of 10-15 mOD for both fsTA and nsTA at early observation times.

Our assignment of the transient absorption results suggests the presence of two intermediates following 355 nm excitation. One, with \(\lambda_{\text{max}} \sim 420\) nm, is consistent with the lowest nπ* singlet ICT state of the nitrophenyl-phenol but with \(\lambda_{\text{max}}\) shifted \(\sim 20\) nm to lower energy due to H-bonding to the base, Figure 4.12 (4a). It subsequently undergoes: i) spin interconversion to the corresponding triplet, \(\lambda_{\text{max}} \sim 600\) nm, on the tens of picosecond timescale, Figure 4.12 (4b), ii) proton transfer to the base, Figure 4.12 (4c), iii) separation of \(^1\)H-B on the hundreds of picosecond time scale, Figure 4.12 (4d), iv) decay of triplet anion to
the ground state with \( k = 6.7 \times 10^7 \text{ s}^{-1} \), Figure 4.12 (4e). The final step, on the \( \mu \text{s} \) time scale, is diffusional back proton transfer from \( ^{\ddagger} \text{H-B} \) to \( \text{O}_2\text{N}---\text{O}^- \).

\[
\begin{align*}
\text{O}_2\text{N}---\text{O}---\text{H} \cdots \text{B} & \xrightarrow{\text{hv}} \; \text{O}_2\text{N}---\text{O}^{\ddagger} \cdots \text{H} \cdots \text{B}^{\ddagger} \; (4a) \\
\text{O}_2\text{N}^{\ddagger}---\text{O}^{\ddagger} \cdots \text{H} \cdots \text{B} & \xrightarrow{} \; \text{O}_2\text{N}---\text{O}^{\ddagger} \cdots \text{H} \cdots \text{B}^{\ddagger} \\n\text{O}_2\text{N}^{\ddagger}---\text{O}^{\ddagger} \cdots \text{H} \cdots \text{B} & \xrightarrow{} \; \text{O}_2\text{N}---\text{O}^{\ddagger} \cdots \text{H} \cdots \text{B} \\
\text{O}_2\text{N}---\text{O}^{\ddagger} & \xrightarrow{} \; \text{O}_2\text{N}---\text{O}^{\ddagger} \\
\text{O}_2\text{N}---\text{O}^{-} & \xrightarrow{} \; \text{O}_2\text{N}---\text{O}^{-} \\
\end{align*}
\]

**Figure 4.12.** Scheme of excitation dynamics following 355 nm excitation of nitrophenyl-phenol with *tert*-butylamine in DCE.

### 4.3.3.2 388 nm Excitation: FsTA

Additional insight is gained by exciting the low energy side of the ICT absorption band with a pump excitation wavelength of 388 nm. Figure 4.13 shows femtosecond TA spectra obtained following 388 nm excitation of the hydrogen bonded adduct. Immediately within our instrumental response, two spectral features are present; a narrow high energy band and a broad low energy band. The high energy feature (395 nm) appears instantaneously and, in contrast to the 355 nm TA spectra, is not composed of multiple bands. This band decays with a lifetime (\( \tau \sim 4 \text{ ps} \)) similar to the 390 nm blue side of the 410 nm high-energy band observed following 355 nm excitation. The 420 nm portion of the 410 nm high energy band that is observed following 355 nm excitation is not present when the nitrophenyl phenol is excited at 388 nm.
Figure 4.13. Transient absorption difference spectra for the nitrophenyl-phenol/tert-butyamine adduct following 388 nm excitation obtained at: 1 ps (a), 3 ps (b), 20 ps (c), 50 ps (d) and 300 ps (e). The individual points are the 300 ps spectrum from the 355 nm data set presented for comparison. The magnitude of the high energy band is typically in the range of 10-15 mOD for the fsTA measurements at early delays.

The lower energy spectral feature is centered roughly at 550 nm at early times and does not decay or shift appreciably within the time scale of our fsTA experiment. This spectrum is similar in shape to the TA spectrum observed at 300 ps in the 355 nm data, Figure 4.11, and based on this we assign it to the triplet nitrophenyl phenol anion stabilized by the protonated base, $^3(^{-}O_2N{-}O \cdots ^{+}H{-}B)$. However, unlike the 355 nm data, it is present at early pump-probe delay times, suggesting that the $^3(^{-}O_2N{-}O \cdots ^{+}H{-}B)$ species is formed rapidly following 388 nm excitation but more slowly following 355 nm excitation. This could reflect that the formation of the $^3(^{-}O_2N{-}O \cdots ^{+}H{-}B)$ species following 355 nm excitation is preceded by an excited state interconversion process.
These observations are consistent with Figure 4.14 (5a-5c). In this scheme excitation at 388 nm results in appearance of ground and excited state proton loss products at the earliest observation times. Based on these observations, ultrafast, 388 nm excitation of O$_2$N-O-H····B gives a mixture of ground and triplet excited state anions H-bonded to $^+$H-B. On this time scale, light absorption is an optical analog of Figure 4.1 in which intramolecular electron transfer occurs in concert with proton transfer to the acceptor base.

$$\text{O}_2\text{N}--\text{O}--\text{H}\cdots\text{B} \xrightarrow{\text{hv}} ^1(\text{O}_2\text{N}--\text{O}--\text{H}\cdots\text{B})^* \quad (5a)$$

$$^1(\text{O}_2\text{N}--\text{O}^+\cdots\text{H}--\text{B})^* \xrightarrow{} \text{O}_2\text{N}--\text{O}^+\cdots\text{H}--\text{B} \quad (5b)$$

$$\text{O}_2\text{N}--\text{O}^+\cdots\text{H}--\text{B} \xrightarrow{} \text{O}_2\text{N}--\text{O}--\text{H}\cdots\text{B} \quad (5c)$$

*Figure 4.14.* Scheme of excitation dynamics following 388 nm excitation of nitrophenyl-phenol with tert-butylamine in DCE.

### 4.3.3.3 Coherent Raman

The fsTA data was limited by the 250 fs IR window of the experiment. A Coherent Raman technique was used to obtain data at an earlier time, Figure 4.15. This technique has an IR of ~20 fs. The Coherent Raman spectrum shows the difference between the ground state and excited state vibrational resonances. The positive going feature at ~2850 cm$^{-1}$ is the ground state band while the negative feature at 2970 cm$^{-1}$ is assigned to the excited state signal. The presence of this excited state signal feature within 20 fs suggests ultrafast proton transfer. Where the molecule is photoexcited to an elongated proton-transferred excited state.
The Raman result points to ultrafast proton transfer and yet, from the Franck-Condon principle, a truly concerted event, with electron and proton transfer occurring simultaneously between equilibrium coordinate positions, is not possible. Excitation is a vertical process along the coupled nuclear coordinates including the proton transfer coordinate. In the initial H-bonded ICT excited state, $O_2N-O-H \rightarrow^{h\nu} (O_2N-O^{-}H-B)^*$, the proton is initially frozen in the equilibrium coordinate of $\nu$(O-H) in the ground state. It is highly elongated from the equilibrium coordinate of the $\nu$(N-H) mode in the equilibrated photoproduct. Proton transfer occurs as a redistribution along the proton transfer coordinate to the equilibrium coordinate for $\nu$(N-H) in $(O_2N-O^{--}H-B)^*$. Proton transfer is followed
by relaxation in the other coupled vibrational and solvent modes to give the final thermally equilibrated, deprotonated ICT excited state completing the proton transfer event.

This Coherent Raman spectrum supports an excited state assignment of the 410 nm band. Our results point to a photochemical electron-proton transfer or photo-EPT process in which proton transfer occurs before solvent and vibrational relaxation occur. Photo-EPT is analogous to rapid intramolecular proton transfer in certain types of excited states and is distinguished from excited state proton transfer by time scale with proton transfer preceding relaxation of other coupled intramolecular and solvent modes. If exploited, it could be of significance in photocatalysis with high energy e⁻/H⁺ intermediates created in a single excitation act rather than stepwise as in photosynthesis, for example.

4.3.3.4 DFT Modeling

In addition to the ultrafast experiments, DFT calculations were done on nitrophenyl-phenol. The geometries of O₂N-OH, O₂N-O-H --- NH₂(CH₃)₃, and O₂N O⁻ were fully optimized (B3LYP, 6-31g, gas phase). Similarly, the geometry of O₂N-O⁻ --- H-NH₂(CH₃)₃ was optimized but keeping the O-H distance fixed at 1.621 Å. This distance was selected from a full optimization using water as the solvent (IEF-PCM). The intense lowest energy transition in each case corresponds to the ICT band and therefore determines the energy of the ICT excited state above the ground state for each particular species. Figure 4.16 shows isodensity surfaces for the two orbitals involved in the lowest energy transition for O₂N-O-H (HOMO and LUMO). These isodensity surfaces illustrate the dramatic change in electron density following ICT excitation.
Figure 4.16. Molecular orbital calculations for the lowest energy transition for nitrophenyl-phenol.

Measurements were also done to calculate the ground state absorption band for nitrophenyl-phenol without added base, with base, and for the deprotonated anion. Figure 4.17 shows the calculated absorption spectra for O$_2$N-O-H, O$_2$N-O-H --- NH$_2$(CH$_3$)$_3$ and O$_2$N-O$^-$ --- $^+$H-NH$_2$(CH$_3$)$_3$. The spectra have been corrected by adding 7389 cm$^{-1}$ to match the absorption maximum for the lowest energy absorption for O$_2$N-O-H in 1,2-dichloroethane (335 nm). As can be observed, the calculated spectra for O$_2$N-O-H --- NH$_2$(CH$_3$)$_3$ and O$_2$N-O$^-$ --- $^+$H-NH$_2$(CH$_3$)$_3$ ($\lambda_{\text{max}} = 356$ nm and $\lambda_{\text{max}} = 412$ nm) are a close match with the experimental spectra ($\lambda_{\text{max}} = 354$ nm and $\lambda_{\text{max}} = 390$ nm), providing additional support for the assignments. These calculations match the ground state
absorption measured for the H-bonded molecule and support the assignment of the 410 nm ground state proton transfer band.

**Figure 4.17.** DFT calculated absorption spectra for O$_2$N-OH, O$_2$N-O-H---N(CH$_3$)$_3$ and O$_2$N-O---H-N (CH$_3$)$_3$ in DCE. The peak half-width at half-height was chosen as 2685.83 cm$^{-1}$ in all cases.

DFT calculations also reveal that the inter-ring torsional angle decreases from 34.5 degrees in O$_2$N-O-H to 26.6 degrees in O$_2$N-O---H-N (CH$_3$)$_3$ to 12.6 degrees in the anion O$_2$N-O$^-$ consistent with enhanced electronic delocalization between the aromatic rings, further supporting an excited state twisting mechanism that facilitates ISC.$^4$ These calculations provide information and support for the excited state ring-twisting that gives rise to fast ISC between the singlet and triplet.
4.3.3.5 Assignment

One interpretation, supported by DFT calculations, comes from an examination of the absorption spectra for the various ground-state nitrophenyl-phenol species. The 390 nm absorption band is situated between the absorption bands for the ground state H-bound adduct (354 nm) and the completely deprotonated anion (466 nm), suggesting that the 390 nm absorption corresponds to the ground state absorption of a nitrophenyl phenol anion hydrogen bound to a protonated base, namely $\text{O}_2\text{N-O}^- \cdot \cdot \cdot \cdot \cdot +\text{HB}$. Observation of this species following excitation of the H-bound adduct implies both proton transfer and back electron transfer have occurred within our instrument response (250 fs). The decay of the 390 nm feature with a 4.5 ps lifetime corresponds to back proton transfer.

Further evidence for the spectral assignments and the potential energy surface (PES) depiction is provided by directly comparing fsTA spectra collected using different pump wavelengths. TA spectra at 1 ps are shown in Figure 4.18 for nitrophenyl-phenol with and without base following 355 nm excitation and the spectrum of nitrophenyl-phenol/tert-butylamine adduct using the 388 nm pump. Considering the TA spectra collected using 355 nm excitation, the overlap between the 450 nm in the nitrophenyl-phenol molecule (Figure 4.18), can be seen to clearly coincide with the 430-450 nm portion of the 410 nm band, also assigned as an S1 state. Comparison of the TA spectra of the adduct excited at either 355 nm Figure 4.18 (a) or 388 nm Figure 4.18 (c) reveals a distinct difference depending upon pump wavelength. While there appears to be two overlapping high energy absorption bands following 355 nm excitation pump pulse, only one band centered at 395 nm, appears from 388 nm excitation. This excitation dependent behavior is consistent with the potential energy surfaces depicted in Figure 4.19.
Figure 4.18. Compilation of transient absorption difference spectra at 1 ps for: nitrophenyl-phenol/tert-butylamine adduct following 355 nm excitation (a), nitrophenyl-phenol without base following 355 nm excitation (b), and nitrophenyl-phenol/tert-butylamine adduct following 388 nm excitation (c). The magnitude of the high energy band is typically in the range of 10-15 mOD for the fsTA measurements at early delays.
The second intermediate provides evidence for photochemical EPT with proton transfer to H-bonded tert-butylamine at our earliest observation time, < 250 fs. This intermediate has a $\lambda_{\text{max}} = 390$ nm and decays with $\tau \sim 4.5$ ps. Its properties are consistent with the nitrophenyl-phenolate anion, $\text{O}_2\text{N-O}^- (\lambda_{\text{max}} \sim 466$ nm) with $\lambda_{\text{max}}$ blue shifted due to H bond stabilization of the ground state, $\text{O}_2\text{N-O}^- \cdots \text{^tHB}$. This assignment is corroborated
by DFT calculations (Supplemental Information). In addition, $\lambda_{\text{max}}$ for the anion is shifted to 426 nm in 1:1 V:V CH$_3$CN:H$_2$O due to the H bond interaction with H$_2$O.

A second interpretation based on the Coherent Raman experiments is that the 390 nm band is the absorption of the excited state nitrophenyl-phenol anion hydrogen-bound molecule. This assignment would imply direct excitation to the elongated proton transfer excited state and that the 4.5 ps decay lifetime represents relaxation and back proton transfer. Evidence for this second assignment comes from excited state absorption shifts as a function of proton transfer as well as Coherent Raman spectra. This assignment would fit with blue shifted excited state absorption measurements for 440 nm for the excited state molecule, to 420 nm for the hydrogen bound excited state singlet, with the 390 nm band representing the excited state anion still hydrogen bound to the protonated base.

4.3.4 Nitrophenyl-phenol with tert-butylamine in acetonitrile

4.3.4.1 355 nm Excitation: FsTA

To probe solvent effects on the excited state dynamics, FsTA experiments were done in ACN solvent. The more polar ACN solvent should more favorably stabilize charged states compared to DCE. The FsTA spectra nitrophenyl-phenol without base in ACN, excited at 355 nm, is shown in Figure 4.20. Similar to the DCE experiments, within our IR of 250 fs, a single high energy band appears. Over the next tens of picoseconds the 425 nm decays while a broad lower energy band grows in at 650 nm, within 15 ps. This lower energy 650 nm band persists longer than the FsTA experimental time scale. These bands represent the singlet-triplet transition, as seen in the DCE solvent samples. The difference between the two solvents can be seen in the higher energy singlet transient absorption band in ACN. In
ACN this band has a $\lambda_{\text{max}} = 425$ nm, while in DCE the nitrophenyl-phenol singlet without base absorbs with a $\lambda_{\text{max}} = 440$ nm. This energy shift is due to ACN solvent destabilization of the neutral species, due to increased solvent polarity.

FsTA experiments were also performed with base, excited at 355 nm. Since the $K_a$ for nitrophenyl-phenol and tert-butylamine is $12 \pm 1$ M$^{-1}$ in ACN samples of 0.3 mM nitrophenyl-phenol and 1000 mM tert-butylamine were made. This concentration was used to obtain approximately the same 90% hydrogen bond association as the DCE samples. Figure 4.21 shows the fsTA spectra of nitrophenyl-phenol with tert-butylamine in ACN. Like the DCE base spectra, there are two main features: a high energy band that is present within our IR of 250 fs which decays over the next 4-5 ps with a lifetime of $\tau \sim 1.5$ ps, as well as a lower energy broad band that grows in and shifts to higher energy.

The high energy band has an absorption maximum at 400 nm, blue shifted in energy from the no base spectra at 410 nm. This corresponds to other measurements that have shown while the hydrogen bonding base association is stabilizing for ground state transitions, it represents a shift in higher energy in both the singlet and triplet excited states. The high energy band decays with a lifetime of $\tau \sim 1.5$ ps, unlike the DCE spectra we were unable to determine whether, based on decay lifetimes, this band contains multiple transient decay components. We were limited by low white on the edges due to the large spectral range we measured and our CCD detector’s sensitivity to pump scatter, so we were unable to probe farther into the UV with the 300 gd grating and 355 nm excitation pulse.
**Figure 4.20.** Transient absorption spectra for nitrophenyl-phenol in acetonitrile obtained at 1 ps (a), 10 ps (b), and 300 ps (c).

**Figure 4.21.** Transient absorption spectra for nitrophenyl-phenol with tert-butylamine in acetonitrile obtained at 1 ps (a), 2 ps (b), 100 ps (c), and 300 ps (d).
The lower energy band for ACN, like the DCE lower energy band, grows in at \( \sim 600 \) nm, Figure 4.21. The 600 nm band then shifts to higher energy. At 2 ps the triplet band, has shifted to 550 nm. By 100 ps it appears at 510 nm, and over 300 ps within the fsTA experimental window it has reached 480 nm. The ACN spectral shifts definitively depict the bands shift to higher energy as the proton is transferring from the triplet nitrophenyl-phenol to the base and dissociating. Figure 4.21 captures the dynamics of the evolving spectra as the proton is transferred from the nitrophenyl-phenol to the base. ACN facilitates this triplet proton transfer faster than the less polar DCE solvent.

4.4 Conclusions

4.4.1 Band Assignments

Femtosecond transient absorption has been used to probe the ultrafast dynamics involved in the photo-EPT reaction occurring between \textit{tert}-butylamine and photoexcited nitrophenyl-phenol. These experiments were done at two different excitation energies, 355 nm and 388 nm. Measurements were performed in two different solvents, DCE and ACN. Changing the solvent to a more polar or non-polar solvent will allow investigation of how the solvent stabilizes the energy levels of the different states relative to each other.

For the most part the spectral assignments for the nitrophenyl-phenol molecule in DCE and ACN are relatively straight forward. The singlet and triplet dynamics are easy to label. Figure 4.22 attempts to illustrate the spectra in terms of absorption and proton position for nitrophenyl-phenol in DCE. The one remaining question for DCE spectral assignments is: What gives rise to the 390 nm DCE band seen overlapped in the 355 nm excitation spectra
and alone at 388 nm excitation? This band decays with a lifetime of $\tau \sim 4.5$ ps and does not correspond to the growth of any triplet bands unlike the other high energy bands.

**Figure 4.22.** Summary of ground state and excited state absorptions of nitrophenyl-phenol in DCE solvent.

Based on our experiments and calculation for nitrophenyl-phenol in DCE we believe the band could represent one of two things. The first option, depicted as A in Figure 4.22 assigns the 410 nm to the ground state absorption of the nitrophenyl-phenol anion hydrogen
bound to the protonated base. This band assignment signifies direct excitation to an EPT excited state potential energy surface that is directly coupled to ground state relaxation. Evidence for this assignment arises from ground state absorption spectral shifts and DFT ground state absorption calculations.

Hydrogen bonding and the deprotonation red shift of the ground state absorption wavelength are depicted in Figure 4.22. These spectral changes arise due to the chemical nature of the nitrophenyl-phenol molecule. Nitrophenyl-phenol contains two π bonded ring systems, which are not flat but are twisted at a 34.5 degree angle from one another. As the proton is pulled off or removed from the phenolic oxygen these rings react by flattening in an attempt to increase delocalization across the two rings. A ground state absorption of 410 nm fits between the 355 nm hydrogen bound absorption and the 466 nm ground state anion absorption. DFT calculations for this ground state configuration match this assignment, Figure 4.17. In this case the 4.5 ps decay lifetime of this band would represent back electron transfer in the ground state to produce the initial molecule.

The second option for the 410 nm DCE band assignment is labeled as B in Figure 4.22, and is the excited state absorption band for the nitrophenyl-phenol anion hydrogen-bound molecule. This assignment would imply direct excitation to the elongated proton transfer excited state and that the 4.5 ps decay lifetime represents excited state decay and back proton transfer. Evidence for this second assignment comes from excited state absorption shifts as a function of proton transfer as well as Coherent Raman spectra. Shown in Figure 4.22, the excited state absorption spectra shifts to higher energy as the proton is removed. This is opposite from the red shift seen in the ground state. Without any hydrogen bonding base present, the singlet excited state absorption is seen at 450 nm in DCE. This
absorption shifts to \( \sim 430 \) nm when base is added. Similar effects are seen for the excited state triplet absorption which shifts from 650 nm with no base present, to 600 nm when nitrophenyl-phenol is hydrogen bound to tert-butylamine, and all the way to 550 nm when deprotonated. Based on this trend a 410 nm assignment for the molecule in configuration B would fit. Other evidence for the assignment of the 410 nm and arises from the Coherent Raman data. The Coherent Raman spectra in Figure 4.15, shows that within 20 fs of excitation, an excited state proton transfer event has occurred on very fast timescales.

Because of the potentially overlapping spectral shifts between the excited state and the ground state, we are unable to distinguish between a 410 nm assignment of either A or B. Regardless of the assignment, both represent an ultrafast photon induced proton transfer corresponding to photo-EPT, where the molecule has been excited to an elongate, proton-transfer excited state.

### 4.4.2 Solvent Effects

Figure 4.23 shows a similar simplified illustration of the spectral measurements for nitrophenyl-phenol in ACN. These spectra show many of the same trends we saw in the DCE samples: red shifts in the ground state and blue shifts in the excited state as the proton was pulled or removed. Differences between the two solvents include higher energy bands and faster proton transfer dynamics. These differences arise from ACN’s more polar properties. Due to signal to noise, we are unable to discern whether the high energy ACN band contains two bands equivalent to the photo-EPT band seen at 390 nm and the singlet excited state seen at 420 nm in the DCE measurements. If it is fact missing there could be many reasons, it could lie to the blue of our detection window with this grating and pump
wavelength configuration. Another explanation could be that the photo-EPT excited state
energy surface is not accessible with a 355 nm excitation pulse, and instead exists at a higher
or lower energy.

Figure 4.23. Summary of ground state and excited state absorptions of
nitrophenyl-phenol in acetonitrile solvent.

4.4.3 Energy Dependence

Experiments in DCE show that the excited species created is energy dependent. At
lower energy excitation, 388 nm, only the photo-EPT and triplet bands, where the proton has
transferred within 1 picosecond are evident. At the higher excitation energy, 355 nm, we see
the photo-EPT band as well as the singlet hydrogen bound excited state. The proton on this
singlet state is trapped and does not transfer to the base molecule until after the
nitrophenyl-phenol molecule has converted into the triplet. A possible potential energy
surface is depicted in Figure 4.19. Higher energy excitation gives both $^1\text{n}\sigma^*$ ICT-EPT and $^1\text{n}\pi^*$ ICT excited states, the latter H-bonded to \textit{tert}-butylamine. It subsequently undergoes spin interconversion to the H-bonded triplet followed by relatively slow proton transfer. The excitation wavelength dependence suggests possible overlapping absorptions and multiple excited states but attempts to resolve the absorption band at 354 nm into separate components in 2-methyl tetrahydrofuran at 77 K were unsuccessful.

### 4.4.4 Photo-EPT Model System

An explanation for the excitation wavelength dependence is given in Figure 4.19. It invokes a lowest energy ICT-EPT $^1\text{n}\sigma^*$ excited state in which proton transfer to \textit{tert}-butylamine occurs in concert with intramolecular charge transfer. With this interpretation the vertical Franck-Condon transition gives ICT-EPT $^1\text{n}\sigma^*$ state with the transferred proton considerably elongated along the O-H --- B axis. Subsequent relaxation dynamics are accompanied by a partial spin state change to give a mixture of proton loss ground state and triplet excited state anions. Partitioning between the two pathways is likely dictated by the initial location on the excited state potential surface, and dependent on both the proton coordinate and ring torsional angle.

Our results are significant in revealing a concerted, light-driven electron-proton transfer process on the <250 fs time scale. This appears to be one of an extended class of Light-Driven reactions in which both electrons and protons are transferred simultaneously or near simultaneously. Another example has been reported for reductive quenching of a metal complex excited state by hydroquinone and initial experiments provide evidence for related
phenomena in base adducts with coumarin. Light-driven EPT may be important in creating reactive intermediates with H-atom and EPT reactivities important in energy conversion.

Understanding the basic science behind electron and proton transfer events following light absorption helps us to better understand biological processes like photosynthesis and the photostability in systems like Guanine-Cytosine Watson-Crick base pairs. (REF) A knowledge of how photon energy is used and stored inside simple chemical systems also contributes to the base of knowledge required to create solar energy devices to capture the sun's energy and turn it into solar fuel or energy. Related ultrafast proton transfer has been observed in phenols and in a guanine-cytosine base pair tautomer and attributed to low lying excited states which are antibonding toward proton loss.
4.5 References


Chapter 5

Ultrafast Proton Transfer and Photoinduced Tautomerization of 7-Hydroxy-4-(Trifluoromethyl)-coumarin. Photochemical Electron-Proton Transfer.
5.1 Introduction

Based on previous work with nitrophenyl-phenol and tert-butylamine in dichloroethane solvent, we looked for evidence of photoinduced electron proton transfer (EPT) in the 7-hydroxy-4-(trifluoromethyl)-coumarin (hydroxycoumarin) and 1-methylimidazole hydrogen bound systems. Discussed in this chapter is the experimental evidence for ground state hydrogen bonding, photo-EPT, as well as emission data for the hydroxycoumarin molecule undergoing tautomerization at excess base conditions.

The combined motion of protons and electrons are also observed in excited states,\(^1\) where intramolecular excitations result in a shift in electron density that enhances the acidity of a dissociable proton.\(^2\) This is the basis behind many examples of excited state proton transfer (ESPT). In ESPT, proton transfer occurs in an equilibrated excited state following excitation and vibrational and solvent relaxation. Concerted photochemical electron-proton transfer (photo-EPT), in which both electron and proton transfers occur simultaneously\(^3\) would appear to be ruled out on fundamental grounds, since electronic excitation occurs rapidly on the timescale for nuclear motions, including proton movement.

We report here a novel coupled electron-proton transfer process that occurs following excitation of, hydroxycoumarin when it is H-bonded to the base, 1-methylimidazole, Figure 5.1. Coumarins are highly emissive laser dyes, which have been investigated for their ESPT properties.\(^4,5\) Coumarin and many of its derivatives received much attention in the 1970’s and 1980’s\(^5-11\) as tunable dye lasers were being extensively investigated. Hydroxycoumarin in particular and coumarin dyes in general emit weakly in the absence of a hydrogen bonding molecule.\(^4,7\) By adding small amounts of alcohol, water, or other bases capable of hydrogen-
bonding to the solution these coumarin molecules become highly robust emitters, thus their use as commercially marketed laser dyes.

\[
\begin{align*}
\text{Figure 5.1.} & \quad \text{Scheme of photoinduced ultrafast proton transfer between hydroxycoumarin and 1-methylimidazole.} \\
\end{align*}
\]

Hydroxycoumarin and the base molecule form a hydrogen bond in solution. Due to the ground state pK\textsubscript{A} of the phenolic proton on the hydroxycoumarin of 7.26 and the ground state pK\textsubscript{A} of 7.4 for the 1-methylimidazole they are predicted to form a strong hydrogen bond. Shifts in ground state absorbance show that they do. This initial hydrogen bonding is important to the ultrafast proton transfer seen in conjunction with photo-excitation. Hydrogen bond formation is important to electron-proton transfer systems\textsuperscript{12, 13} The initially close distance between the heavy atoms across the H-bond, O=HFC-O-H---B plays an important role in the photo-EPT dynamics.

The solvent used for these experiments was toluene, chosen for its inability to form hydrogen bonds with hydroxycoumarin. Toluene is a nonpolar solvent, with a dielectric constant of 2.4, and tends to stabilize neutral species over charged species. Toluene has a strong nuclear response to the femtosecond transient absorption pump pulse, affecting the instrument response for the experiments that will be discussed in more detail in the experimental section.
One important spectroscopic property of hydroxycoumarin is its ground state absorbance due to photoinduced intramolecular charge transfer (ICT). In the case of hydroxycoumarin the photo-ICT causes a shift in electron density for one side of the molecule to the other. It is estimated using the Förster equation (Equation 5.1) that ICT excitation results in an increased acidity of \( \sim 14 \) pK\(_A\) units.

\[
pK_A^* = pK_A - \frac{(h\nu_{HA} - h\nu_{A^-})}{2.3RT}
\]

Evidence of H-bonding in the ground state is directly observed in the hydroxycoumarin absorption spectra, where the maximum of the ICT absorption band of hydroxycoumarin in toluene red shifts from \( \lambda_{\text{max}} = 330 \text{ nm} \) to 342 nm in the presence of 1-methylimidazole. For the H-bonded adduct the association constant is \( K_{A1} = 2100 \text{ M}^{-1} \) by spectrophotometric titration. The hydroxycoumarin anion was prepared by deprotonation in an aqueous NaOH-acetonitrile mixture and precipitated by addition of bis(triphenylphosphoranylidene)-ammonium chloride ([PPN]Cl) to give the salt. The PPN\(^+\) anionic salt of hydroxycoumarin is soluble in toluene, and has an absorption that is even further red-shifted to \( \lambda_{\text{max}} = 421 \text{ nm} \).

For coumarin dyes with a carbonyl ring, additional emission properties were observed. Varying the pH or increasing the water concentration in a solution appears to broaden or shift the emission spectra.\(^8,11,14\) These change are due to the formation of new emissive species in solution. The anion and tautomer emit red shifted relative to the neutral molecule. A mixture of two or three of these species produces a broad emission spectra and makes hydroxycoumarin useful as a laser dye. We present here ultrafast experiments of hydroxycoumarin with excess 1-methylimidazole base in toluene, where tautomer formation is evident.
Photoexcitation leads to a dramatic change to the pKₐ’s or proton affinities of the phenolic proton and the carbonyl oxygen groups on the hydroxycoumarin molecule. Molecules that undergo increasingly acidic changes in pKₐ’s from the ground to excited states are termed photoacids, or in the case of dramatic changes, “super” photoacids.²,¹⁵ These molecules are of particular interest because of photo-switchable acidic properties. Due to its dual groups hydroxycoumarin is also a photobase, as following excitation of the ICT band the carbonyl groups pKₐ becomes increasingly basic in the excited state. We find that this spectroscopic data displays complicated excited state dynamics. An understanding of the kinetic timescales and underlying chemical dynamics that affect PCET systems following photon absorption is the goal of this research.

5.2 Experimental Methods

5.2.1 Materials and Preparation

7-hydroxy-4-(trifluoromethyl)-1-coumarin (hydroxycoumarin) (98%), 1-methylimidazole (99%), and toluene (Chromasolv Plus for HPLC, > 99.9%) were all purchased from Sigma-Aldrich and used as received. Solutions were prepared by first creating stock solutions of the hydroxycoumarin and 1-methylimidazole in toluene. The stock solutions were then used to make final solutions of the appropriate concentrations. Prior to time-resolved emission measurements the samples were deaerated by bubbling Argon gas through the sample for ~30 minutes.
5.2.2 UV-Vis Absorption

UV-Vis absorption measurements were done using an Agilent Technologies Model 8453 diode-array spectrophotometer. Initial absorption measurements were done in a 1 cm cuvette and then repeated in a 2 mm cuvette to recreate the path length and concentration conditions used in the femtosecond transient absorption measurements.

5.2.3 Steady State Emission

Steady state emission measurements were taken using PTI QuantaMaster Emission Spectrometer. Samples were excited with 355 nm light and the sample emission was scanned from 360 nm to 700 nm using background correction. Emission collected using the 2 mm cuvette required it be placed at a 45 degree angle relative to the excitation and emission collection slits in the spectrometer. Slit widths of 0.35 mm were used.

5.2.4 Femtosecond Transient Absorption

Femtosecond transient absorption measurements were done using a pump probe technique which has been described in detail in Chapter 3 and previously. Briefly, the excitation source is a chirped pulse Ti:Sapphire regenerative amplification laser system (Clark CPA 2001) which outputs a 800 mW, 775 nm pulse at a 1 kHz repetition rate, with an autocorrelation full width half max of 250 fs. The probe pulse was generated by focusing a small portion of the beam into a CaF₂ window to generate a white light continuum from 380-700 nm. The spot size at the sample was ~280 µm. The 355 nm pump pulse was created with a tunable Clark Optical Parametric Amplifier (OPA) (1420 nm) followed by second harmonic generation (710 nm) and fourth (355 nm) harmonic generation by focusing
the respective beams through beta barium borate (BBO) crystals. The data was collected at magic angle polarization (54.7 degrees) with pump beam focused to ~1400 µm spot size and power of 0.60 mW. Samples with concentrations of 0.34 mM hydroxycoumarin with 2 mM 1-methylimidazole low base and 500 mM 1-methylimidazole high base were prepared. Samples were placed in a 2 mm quartz cuvette and degassed with Ar gas for 30 minutes prior to data collection. The chirp in the white light was accounted for using an optical gating technique.16 Femtosecond experiments showed a strong nuclear response in the toluene solvent. Additional experiments were done to determine the increased instrument response at early times increased to 800 fs.

5.2.5 Time-Correlated Single-Photon Counting (TCSPC)

This experiment has been described in detail elsewhere17, 18 briefly the apparatus consists of a mode-locked Ti:Sapphire oscillator (Spectra Physics Tsunami) tuned to output a 720 nm pump pulse. This pulse is frequency doubled to 360 nm using a BBO crystal. The repetition rate of the pulse is adjusted by an acousto-optic modulator (AOM) used in a single pass configuration. The femtosecond pulses selected by the AOM excite the sample and the emitted light is collected at 90° relative to excitation, focused onto the slit of a 240 mm focal length single grating monochromator, and delivered to a cooled, multichannel plate-photomultiplier tube (MCP, Hamamatsu R3809U-51). The signal from the MCP is amplified, sent into a 200 MHz constant fraction discriminator (CFD, Tennelec 454) and then used as the start pulse for a time-to-amplitude converter (TAC, Tennelec 864). The stop pulse is obtained by focusing 10% of the excitation beam onto a Si:PIN photodiode, whose output is sent into a variable delay box, then to a CFD, and finally to the TAC. The TAC’s
output is sent to a multi-channel analyzer that is interfaced to a PC. The instrument response of the apparatus is 80 ps at the FWHM.

5.2.6 Coherent Raman

Coherent Raman experiments were done by Stephen Miller from the Moran Lab. The experiments were done on an interferometer described previously. The data shown in this thesis represent the solution signal minus the pure solvent spectra, or difference spectra. The light source for these experiments is a Ti:Sapphire laser which outputs 180 fs, 800 nm pulses. The Coherent Raman was done with 2 narrowband “pump” pulses, and one broadband “probe” pulse. To obtain the narrowband pulses, the fundamental from the Ti:Sapphire is stretched spectrally using diffraction gratings. A slit is then used between the diffraction gratings to select the wavelength and bandwidth of 1-2 nm. This 800 nm narrowband beam is then frequency doubled using a BBO crystal to obtain the 400 nm, 500 fs time width pulse. The broadband pulse was created by a home-built Non-collinear Optical Parametric Amplifier (NOPA). The NOPA allows for broad bandwidth pulses. It was tuned to create 710 nm pulses with approximately 50 nm of bandwidth. This pulse is then frequency doubled through a BBO crystal to produce the 355 nm broadband pulses, with a 45 fs time width. The pulse energies were approximately 50-100 nJ, and were focused to a spot size of ~ 120 micron full width half max (FWHM) in the sample. Polarization of the signal and broadband pulses were set orthogonal to the polarization of the narrowband pulse to repress the raman response from the toluene solvent.

The signals were detected by interferometry on a back illuminated CCD (Princeton Instruments PIXIS 100B) using a 0.3 m spectrograph. The signal was integrated for
3 seconds, and spectra represent 75 averages. To correct for scattered light, a mechanical shutter was placed in the broadband pulse beam, so that “on” and “off” measurements could be taken. The measurement interferograms were then processed using a Fourier transform algorithm to select out and process the signal spectra.

5.3 Results and Discussion

5.3.1 Ground State Absorption

Ground state absorption spectra are shown in Figure 5.4. As shown, the ICT band for hydroxycoumarin in toluene in the absence of base absorbs at 330 nm. This absorption is due to an ICT band that correlates to a shift in electron density from the phenolic portion of the molecule to the carbonyl, see Figure 5.2. With the addition of 1-methylimidazole base the absorption maximum red shifts to $\lambda_{\text{max}}=342$ nm. This red shift is evidence of hydrogen bonding in the ground state between hydroxycoumarin and 1-methylimidazole. Red shifts in hydrogen bonded molecules have been studied previously. In this instance the added base forms because of similar pK$_A$'s on the phenolic proton of the hydroxycoumarin and on the nitrogen on the 1-methylimidazole. The difference between the acid and the base pK$_A$, Equation 5.2, are excellent predictors of hydrogen bond strength. As reported earlier, the ground state pK$_A$ for hydroxycoumarin (-OH) is 7.26 and for 1-methylimidazole (N) is 7.4, giving a $\Delta$pK$_A$ of 0.14. Such a $\Delta$pK$_A$ is indicative of a short tight H-bond between molecule and base in the ground state. While the ground state energy level is lowered as a result of H-bond formation the excited state energy level is also lowered, resulting in an overall 1000 cm$^{-1}$ red shift in the ICT absorption band from 330 nm to 342 nm. From absorption spectral shifts over the range of 0.01 mM to 200 mM 1-methylimidazole in toluene, the
hydrogen bonding association constant was calculated to be $K_{A1} = 2100 \text{ M}^{-1}$ for the equilibrium in Figure 5.3.

$$\Delta pK_A = pK_A(\text{base}) - pK_A(\text{acid}) \quad \text{Equation 5.2}$$

![Diagram](image)

**Figure 5.2.** Photoacid/Photobase effects on hydroxycoumarin following intramolecular charge transfer.

![Diagram](image)

**Figure 5.3.** Scheme of hydrogen bonding adduct formation between hydroxycoumarin and 1-methylimidazole.

To ensure the hydrogen bound assignment of the 342 nm band, further ground state absorption measurements were done. In the presence of strong base, the anion is formed causing the ground state absorption to further red shift to 421 nm. The coumarin anion,
O=HFC-O⁻, was prepared by deprotonation in an aqueous NaOH-acetonitrile mixture with the anion precipitated by addition of bis(triphenylphosphoranylidene)ammonium chloride ([PPN]Cl) to give the corresponding [PPN⁺](O=HFC-O⁻) salt. The salt is soluble in toluene.

**Figure 5.4.** UV-Vis absorption measurements for 0.34 mM hydroxycoumarin with 0 mM (blue line), 0.01 mM (green line), and 0.1 mM (red line) 1-methylimidazole in toluene.

To determine the association constant for hydrogen bonding between hydroxycoumarin and 1-methylimidazole we use absorption measurements taken at a variety of base concentration from 0.01 to 2000 mM and the Benesi-Hildebrand equation described in Chapter 4. These calculations give Equation 5.3.

\[
\frac{1}{[B]} = \frac{K_{A1} A_{HFC} (\epsilon_{HFC-B} - \epsilon_{HFC})}{\epsilon_{HFC}} \times \left( \frac{1}{A_{HFC-B} - A_{HFC}} \right) - K_{A1}
\]

*Equation 5.3*
When \( \left( \frac{1}{[B]} \right) \) is graphed as a function of \( \frac{1}{(A_{HFC-B} - A_{HFC})} \), a linear fit can be found. This fit has a slope of \( \frac{K_{A1}A_{HFC}(\epsilon_{HFC-B} - \epsilon_{HFC})}{\epsilon_{HFC}} \) and a y-intercept of \( K_{A1} \) so that a linear fit of the data gives the \( K_{A1} \) association constant, shown in Figure 5.5.

**Figure 5.5.** Linear fit of absorption of hydroxycoumarin at 350 nm as a function of 1-methylimidazole base concentrations to obtain the \( K_{A1} \sim 2100 \text{ M}^{-1} \) of hydrogen-bond association between the molecules in toluene.

Evidence of H-bonding between the hydroxycoumarin and 1-methylimidazole in the ground state in toluene is observed by shifts in the hydroxycoumarin absorption spectrum as 1-methylimidazole is added the \( \lambda_{\text{max}} \) in toluene shifts from 330 nm to 342 nm. Based on absorption spectral shifts over the range 0.01 to 200 mM in 1-methylimidazole, we calculate an association constant of \( K_{A1} = 2100 \text{ M}^{-1} \).
5.3.2 Steady State Emission

We have used the emissive properties of hydroxycoumarin to probe coupled electron-proton transfer following photoexcitation. Steady state emission measurements show a weak excitation dependent emission band for a 0.34 mM hydroxycoumarin solution when no 1-methylimidazole is present in the toluene solution. When excited at 330 nm with no base, hydroxycoumarin emits weakly at 403 nm. While excitation of the same sample at 355 nm causes weak emission at 440 nm.

Addition of small amounts of base to the hydroxycoumarin toluene solution dramatically increases the emission intensity of the solution, Figure 5.6. The initial no base hydroxycoumarin solution excited at 355 nm emitted weakly at 440 nm. Upon addition of even 0.01 mM of 1-methylimidazole base this emission intensity dramatically increased to a strong band at $\lambda_{\text{max}}=460$ nm. At this concentration approximately 15% of the hydroxycoumarin are hydrogen bonded with base molecules. Continued addition of base up to 2 mM of ~73% hydroxycoumarin hydrogen bonding to the base results in incremental increases in the emission intensity at 460 nm, but with a small shoulder growth out to the red. With a strong base present to completely remove the proton, the hydroxycoumarin anion is strongly emissive at $\lambda_{\text{max}}=506$ nm. The blue-shifted emission in the adduct can be attributed to H-bond stabilization of the ground state compared to the anion, $(\text{O-HFC-O}---^+\text{H-B})^* \rightarrow \text{O}=\text{HFC-O}---^+\text{H-B}$.\textsuperscript{11} In accordance with other studies, we have assigned the 459 nm band to emission arising from a configuration in which the proton is transferred to the base, but still hydrogen bound to the hydroxycoumarin anion, i.e. $(\text{O-HFC-O}^+.\cdot\cdot\cdot\text{H}--\cdot\cdot\cdot\text{B})^*$.\textsuperscript{11} This could be viewed as emission arising from the anion that is blue shifted due to a stabilization of the anion ground state by H-bond interaction with the protonated base.
The dramatic increase in emission, even at low base concentrations, highlights the importance of the hydrogen bond between the base and hydroxycoumarin and its effect on the molecule’s fluorescence properties. These results are similar to the laser dye studies by Moriya, where solutions of water or alcohol enabled hydrogen bonding.\textsuperscript{22-24}

![Figure 5.6](image)

**Figure 5.6.** Room temperature steady state emission data for 0.34 mM hydroxycoumarin with 0.01 mM and 1 mM 1-methylimidazole in toluene. Samples were excited at 355 nm.

Steady state emission spectra at higher base concentrations (10 mM \(\rightarrow\) 200 mM) further show interesting dynamics, Figure 5.7. For solutions with continually higher base concentrations the steady state emission band decays at 460 nm, while a new band grows in at 520 nm with a shoulder at 570 nm. From the literature this 520 nm band is assigned to the hydroxycoumarin tautomer where the proton is now hydrogen bonded to the carbonyl portion of the hydroxycoumarin molecule.\textsuperscript{8, 22-24} Studies by Moriya described a water bridge in a similar 7-hydroxycoumarin system that allowed the proton to move from the newly created
“photoacidic” proton of the molecule to the “photobasic” carbonyl end of the molecule, Figure 5.8. In the case of the hydroxycoumarin with 1-methylimidazole in toluene there are no extra protons to be transferred. Therefore phototautomerization as shown in the emission date, Figure 5.7 must be base concentration dependent.

Figure 5.7. Room temperature steady state emission data for 0.34 mM hydroxycoumarin with 1 mM, 40 mM, 100 mM, and 200 mM 1-methylimidazole in toluene. Samples were excited at 355 nm.
Low temperature emission studies were carried out at 77K, in toluene glass, with the goal of further elucidating the protonation states of hydroxycoumarin. At these low temperatures, in the absence of hydrogen bonding base, hydroxycoumarin emission was observed with $\lambda_{\text{max}} = 398$ nm. Upon the addition of small amounts of 1-methylimidazole an emission band was observed at $\lambda_{\text{max}} = 439$ nm, however, no second emission band resulting from the tautomer at lower energy evolved, Figure 5.9. We have assigned the band to the deprotonated, but still hydrogen bound state of the hydroxycoumarin molecule due to the fact that the PPN$^+$ anionic salt of hydroxycoumarin was emissive at $\lambda_{\text{max}} = 446$ nm. This blue shift in the frozen media when compared to the room temperature solution is due to a lack of solvent reorganization as a result of the excited state. The absence of any emission from the tautomeric species can be attributed to the lack of a mechanism for delivering the proton to the carbonyl oxygen in a frozen state.
Figure 5.9. Room temperature steady state emission data for 0.34 mM hydroxycoumarin with 1 mM 1-methylimidazole (low base concentration) and 200 mM 1-methylimidazole (high base concentration). The spectra are overlaid with low temperature (77K) steady state emission data at high base concentrations (200 mM). Samples were excited at 355 nm.

From the concentration dependent emission studies the second association constant can be calculated for tautomer formation as a function of base concentration, Equation 5.14.

\[
\frac{1}{\Delta I} = \frac{1}{(I_o-I_f)K_{A2}} + \frac{1}{(I_o-I_f)}
\]

Equation 5.14

To determine the second association for tautomerization the formula was derived from emission intensity and the Benesi-Hildebrand approximation, similar to the method used to determine $K_{A1}$ from absorption measurements. Graphing \(\frac{1}{[B]}\) vs \(\frac{1}{\Delta I}\) from the steady state emission measurements creates a linear graph that is represented by Equation 5.14. A linear fit to the line produces the slope \(\frac{1}{(I_o-I_f)K_{A2}}\) and the y-intercept \(\frac{1}{(I_o-I_f)}\). Dividing the y-intercept by the slope gives the $K_{A2}$ value for tautomerization.
From this data and studies in the literature we assign the blue 460 nm emission band to the hydroxycoumarin anion still hydrogen bonded to the protonated base, and the 520 nm emission band to the hydroxycoumarin tautomer hydrogen bonded to the protonated base, Figure 5.10. Emission spectra show the effects of base concentration on the proton shuttling from one side of the molecule to the other.

![Diagram of tautomerization](image)

**Figure 5.10.** Scheme of excited state tautomerization of hydroxycoumarin in the presence of large quantities of 1-methylimidazole base.

### 5.3.3 Ultrafast Measurements

Ground state absorption and steady state emission measurements showed dramatic dependence of base concentration on hydroxycoumarin excited state dynamics. To investigate these systems, ultrafast measurements were done at three specific concentrations. The first was 0.34 mM hydroxycoumarin with no base to study dynamics from only hydroxycoumarin. The second solution was made with concentrations of 0.34 mM hydroxycoumarin with 2 mM 1-methylimidazole low base to form a solution where ~73 % of the hydroxycoumarin molecules were hydrogen bound, but where the base concentrations were too low for tautomerization to be seen. The final concentration was 0.34 mM hydroxycoumarin and 500 mM 1-methylimidazole (high) base to form a solution where, based on steady state emission measurements, ~95% of the hydroxycoumarin tautomer would form.
5.3.3.1 Femtosecond Transient Absorption

FsTA measurements were done on the three solutions. For the low and high base samples, fsTA spectra were obtained, while for the no base solution we were unable to detect a signal. With these hydroxycoumarin solutions we were not probing excited state absorption or ground state bleaches but stimulated emission from the excited hydroxycoumarin molecule. The fsTA experiment, while not optimized for emission collected the transient stimulated emission spectra for the low and high base samples simply because the emission intensity is so high.

5.3.3.1.1 Low Base Concentrations

Figure 5.11 shows the femtosecond stimulated emission spectra for the low base solution with 0.34 mM hydroxycoumarin and 2 mM 1-methylimidazole where ~73% of the molecules are hydrogen bonded. FsTA experiments were done with a 355 nm pump pulse. Immediately within our earliest instrument capabilities (~ 1 ps), a bleach appears at 460 nm. This prominent negative going peak at 460 nm is the stimulated emission spectra and corresponds to stimulated emission of the anion with the blue shift due to a ground state stabilization from the H-bond interaction with the base. As the emission lifetime is longer than the fsTA’s instruments collection window of 900 picoseconds, the stimulated emission spectra does not change except to decrease slightly in intensity over longer times. This band provides evidence of a hydrogen-bound emissive state.

The more interesting component for the low base sample can be seen in the 459 nm transient signal shown in Figure 5.12. In this figure the transient at 460 nm is overlaid with
Figure 5.11. Femtosecond transient absorption difference spectra for hydroxycoumarin with low base concentration (4 mM) or the 1:1 adduct, following 355 nm excitation obtained at 10 ps (blue line) and 600 ps (green line).

Figure 5.12. Femtosecond transient stimulated emission data for the hydroxycoumarin 1:1 adduct with 1-methylimidazole (2 mM) in toluene following 355 nm excitation and detected in a transient differential transmission mode. The red points represent the laser excitation pulse reacting with the solvent nuclear response in toluene. Blue points represent the experimental data at 465 nm, only data points outside of the instrument response are shown.
the signal of the toluene solvent nuclear response to the excitation laser pulse. The red points in the Figure 5.12 represent the instrument response (IR) of the experiment. The IR shown is 800 fs, which is larger than the usual IR of the experiment of 250 fs. This increase in IR is due to an interaction with the pump beam. The pump excitation beam induces a nuclear response in the toluene, represented in the graph.

The blue points in Figure 5.12 represent the transient signal at 459 nm. Early time data between 0.8-3 ps show an initial ultrafast growth in emission. This fast growth, the dramatic increase in emission intensity with the addition of an H-bonding base, and based on work described in the previous chapter we assign this to fast proton transfer as a result of photoinduced ICT. Where the hydroxycoumarin proton involved in H-bonding with the base shifts from the hydroxycoumarin molecule to the base molecule in response to the photoinduced ICT and changes in acidity that result, Figure 5.1. This assigns the 459 nm emission band to the hydroxycoumarin anion hydrogen bound to the protonated base. As the hydroxycoumarin anion alone emits at 506 nm.

5.3.3.1.2 Early Time

Emission from the adduct is rapid as shown by prompt appearance of stimulated emission in a femtosecond transient absorption experiment Figure 5.12. Based on this result, ~75% of the emission appears on a time scale short relative to the instrument response time (<1 ps) consistent with rapid proton transfer. The next question was whether this was a concerted process, Electron-Proton Transfer or a sequential process, Excited State Proton Transfer. The fsTA data was limited by the 800 fs IR window due to the toluene nuclear response. A Coherent Raman technique was used to obtain data at an earlier time, Figure 5.13. This technique has an IR of ~20 fs. Figure 5.13 shows the difference spectra
between the ground state and excited state vibrational resonances. In this spectrum, Figure 5.13, prompt loss of the ν(O-H) ground state band at 2900 cm\(^{-1}\) is observed with simultaneous appearance of a new excited state vibrational band at 3050 cm\(^{-1}\). Based on the shift to higher energy, the new band can be assigned to ν(N-H) in the ICT adduct (O-HFC-O\(^{+}\)H-B)* (B = 1-methylimidazole). Together the transient stimulated emission and Raman results point to a photochemical process or processes in which proton transfer from O=HFC-O-H to H-bonded 1-methylimidazole occurs on the timescale for the ν(O-H) vibrational period.

![Coherent Raman spectra](image)

**Figure 5.13.** Coherent Raman spectra that displays the difference between the ground state and excited state vibrational resonances.

The Raman result points to ultrafast proton transfer and yet, from the Franck-Condon principle, a truly concerted event, with electron and proton transfer occurring simultaneously between equilibrium coordinate positions, is not possible. Excitation is a vertical process
along the coupled nuclear coordinates including the proton transfer coordinate. In the initial H-bonded ICT excited state, O=HFC-O-H---B $\xrightarrow{hv}$ (O-HFC-O-'H---B)*, the proton is initially frozen in the equilibrium coordinate of $\nu$(O-H) in the ground state. It is highly elongated from the equilibrium coordinate of the $\nu$(N-H) mode in the equilibrated photoprodut. Proton transfer occurs as a redistribution along the proton transfer coordinate to the equilibrium coordinate for $\nu$(N-H) in (O-HFC-O-'H-B)*. Proton transfer is followed by relaxation in the other coupled vibrational and solvent modes to give the final thermally equilibrated, deprotonated ICT excited state completing the proton transfer event.

Our results point to a photochemical electron-proton transfer or photo-EPT process in which proton transfer occurs before solvent and vibrational relaxation occur. Photo-EPT is analogous to rapid intramolecular proton transfer in certain types of excited states and is distinguished from excited state proton transfer by time scale with proton transfer preceding relaxation of other coupled intramolecular and solvent modes. If exploited, it could be of significance in photocatalysis with high energy e$^-$/H$^+$ intermediates created in a single excitation act rather than stepwise as in photosynthesis, for example.

5.3.3.1.3 High Base Concentrations

Following the low (2 mM) base experiments additional experiments were done on the high (500 mM) base solutions. At the 500 mM base concentration the steady state emission data suggests the ~95% of the molecules should form the tautomer and indeed the cuvette glowed a fluorescent green matching the 520 nm band seen from steady state emission. FsTA data at 10 ps, 300 ps, and 800 ps are shown in Figure 5.14. The fsTA spectrum at early time appears identical to the low base data. At longer times, over the next hundreds of
picoseconds the blue 459 nm band decays as the green 520 nm band grows in. Thus with fsTA stimulated emission spectra we are able to image the tautomerization of hydroxycoumarin, Figure 5.10.

Increasing the 1-methylimidazole concentration alters both the steady-state and time resolved emission spectra. The steady state emission spectra show that as the base concentration increases the 450 nm band decays in intensity and a new emission band appears at $\lambda_{\text{max}} = 520$ nm with a shoulder at 559 nm. This second emission band is consistent with a tautomeric state of hydroxycoumarin, which has been discussed in the literature.$^5, 25$

![Image](image-url)

**Figure 5.14.** Femtosecond transient absorption difference spectra for hydroxycoumarin with high base concentration (500 mM), following 355 nm excitation obtained at 10 ps (blue line), 300 ps (green line), and 800 ps (red line). This spectra shows the changes to stimulated emission as the molecule undergoes tautomerization.
5.3.3.2 Time-Correlated Single-Photon Counting

Additional measurements were done using TCSPC technique. The instrument response for the TCSPC setup is 200 ps, so it is unable to detect the early time photo-EPT processes. While we are unable to resolve the growth of the emission band, we are able to observe its decay. This technique can measure out to ms, well beyond the fluorescent lifetime of both the hydrogen bonded anion (459 nm) and the tautomer (520 nm).

5.3.3.2.1 Low Base Concentrations

TCSPC time resolved emission spectra for the low base solution, 0.34 mM hydroxycoumarin with 2 mM 1-methylimidazole in toluene, are shown in Figure 5.15. The spectra at early times, 200 ps, show a band at 459 nm, which then uniformly decays over the next 13 ns. This hydroxycoumarin anion hydrogen bound to the base has an emission decay lifetime of 3 ns. Another image of this molecules spectral decay can be seen in Figure 5.16. This figure shows wavelength across the x-axis and time along the y-axis as intensity is represented by color contrast in the z-axis. This graph shows a time evolution picture of the hydroxycoumarin anion hydrogen bonded to the base decay.
Figure 5.15. TCSPC emission spectra for hydroxycoumarin with low base concentration (2 mM), following 360 nm excitation obtained at 200 ps, 800 ps, 1600 ps, 4000 ps, and 6000 ps.

Figure 5.16. TCSPC emission spectra for hydroxycoumarin with low base concentration (2 mM), following 360 nm excitation.
5.3.3.2.2 High Base Concentrations

A more complicated spectral picture is also seen in the TCSPC data for the high base (500 mM base concentration) hydroxycoumarin solutions. TCSPC spectral data of the high base solution are shown in Figure 5.17. At early times the spectra appears as a band at 459 nm, and over the next hundred’s of ps the spectra shifts to a band at 520 nm. This provides another view of the emission shift seen for the high base solution using fsTA techniques. The shift in emission from 459 nm to 520 nm represents changes to the hydroxycoumarin molecules emission as the H-bonding is shuttled from the photoacidic side of the molecule to the photobasic side, Figure 5.2. Figure 5.18 shows a spectral slice image of the emission intensities change with time. This spectral evolution indicates that the tautomerization or proton transfer from one side of the molecule to the other occurs in the excited state proton as depicted by Figure 5.10.

The hydroxycoumarin, 1-methylimidazole molecular system provides a simplistic model system with which to study EPT, rather than the more complicated examples of EPT in nature.26-28 Their similar ground state pK_A’s create an interesting ground state H-bound organic molecule with which to study photo-EPT in a controlled system. Evidence for H-bonding between the hydroxycoumarin -anion and the protonated base arise from the blue shift in emission from 506 nm for the anion to 459 nm for the H-bound hydroxycoumarin anion. This blue shift in emission intensity results from ground state stabilization for the H-bound species.
Figure 5.17. TCSPC emission spectra for hydroxycoumarin with excess base concentration (500 mM), following 360 nm excitation obtained at 100 ps, 200 ps, 400 ps, and 1400 ps.

Figure 5.18. TCSPC emission spectra for hydroxycoumarin with excess base concentration (500 mM), following 360 nm excitation.
5.4 Conclusions

The initial H-bonding sets up the system so that the initial bond distances at the time of photoexcitation are small enough to facilitate excitation to the photo-EPT state of HFC-O---H----B, where the molecule is excited to a state representative of an elongated bond between the H-B hydrogen bound to the hydroxycoumarin anion. This proton-transfer also accounts for the dramatic increase in emission intensity for the excited state anion, hydrogen bound or alone versus the hydroxycoumarin molecule. In the absence of any molecules that can act as a proton acceptor the hydroxycoumarin molecule and other coumarin derivatives are weak emitters.\textsuperscript{4,7}

Intramolecular charge transfer excitation of the O=HFC-O-H moiety leads to an electronic configuration in which proton transfer is highly favored, (\textsuperscript{–}O-HFC-O–\textsuperscript{–}H...:B)*. In the optically prepared state, the proton is located at the equilibrium coordinate of the ν(O-H) ground state mode and can transfer to the :N—R base as an ESPT process. Conversely, this same optically prepared configuration could also be viewed as the EPT photoproduct, but with a highly elongated ν(H-N) mode, i.e. (\textsuperscript{–}O-HFC-O–\textsuperscript{–}H—:B)*. Proton transfer then corresponds to vibrational relaxation of the ν(B-H) mode. Photo-initiated EPT is closely related to proton transfer from equilibrated excited states (ESPT) with the distinction between them a matter of timescale. In photo-initiated EPT, the proton transfers on a time scale that is short compared to relaxation of coupled intramolecular vibrational and solvent dipole modes. Such a process could be distinguished from ESPT on the basis of time scale for proton transfer, which would be commensurate with vibrational motion. These experiments also showed evidence for the mechanism behind tautomerization in hydroxycoumarin and related coumarin derivatives.
While the hydroxycoumarin molecule itself undergoes the ICT changes that cause it to form a photoacid and photobase, the base or proton accepting molecule and its ability to shuttle the proton from one end of the molecule to the other is what allows tautomerization to take place. The proton dependent emission characteristics of hydroxycoumarin are what cause its broad tunable lasing bands. By manipulating the pH or proton accepting molecules in the solution the hydroxycoumarin molecule can be forced to emit from a variety of forms.

In the fluid state, the base has the potential to shuttle protons to the carbonyl oxygen in the excited state. In aqueous solutions it has been suggested that this occurs via a hydrogen bonding bridge formed by a chain of water molecules.\textsuperscript{22, 23} A similar chain-like formation would not be present here in our system, however, as the only proton transfer agent in our studies is the 1-methylimidazole base. Nevertheless, the notion that the proton is shuttled from one end of the hydroxycoumarin to the other is supported by low temperature emission studies carried out in toluene glass at 77 K. An emission band appears at 439 nm, however, no second emission band is seen, consistent with the inability of the base to diffuse through the rigid medium.
5.5 References


