SPECTROSCOPIC CHARACTERIZATION OF THE STRUCTURAL DYNAMICS OF PHOTOEXCITED METALLOPORPHYRINS

by

Baxter Abraham

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

Summer 2018

© 2018 Baxter Abraham All Rights Reserved

SPECTROSCOPIC CHARACTERIZATION OF THE STRUCTURAL DYNAMICS OF PHOTOEXCITED METALLOPORPHYRINS

by

Baxter Abraham

Approved: _____

Brian J. Bahnson, Ph.D. Chair of the Department of Chemistry & Biochemistry

Approved: _

George H. Watson, Ph.D. Dean of the College of Arts & Sciences

Approved: _____

Ann L. Ardis, Ph.D. Senior Vice Provost for Graduate & Professional Education I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Lars Gundlach, Ph.D. Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Andrew V. Teplyakov, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Karl S. Booksh, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Matthew F. DeCamp, Ph.D. Member of dissertation committee

ACKNOWLEDGEMENTS

I would like to acknowledge and thank all those who have contributed to this work in one way or another. Foremost is Professor Lars Gundlach, for his mentorship and guidance. He introduced me to many of the topics in this thesis, and was a constant source of wisdom and motivation. I also thank the members of my dissertation committee, Dr. Andrew Teplyakov, Dr. Karl Booksh, and Dr. Matthew DeCamp, for their collective supervision of this work. I am thankful to Dr. Cecil Dybowski for extended conversations on teaching and research. Thank you to the past members of the Gundlach group, most notably Dr. Jesus Nieto-Pescador and Dr. Jolie Blake for making lab experiments easier and more fun. Thank you to current members as well, especially Zhengxin Li for keeping the lab running smoothly. Thank you to Susan Cheadle for help navigating any conceivable administrative task in the department.

I would also like to express considerable gratitude to Professor Lin X. Chen. Her support and mentorship helped to me to develop new scientific and professional directions. Similarly, I am thankful to Dr. Ryan Hadt, Dr. Dugan Hayes, and the other members of the solar energy conversion group for their hospitality and assistance during my time at Argonne lab. Additional thanks go to Chen group members at Northwestern: Dr. Denis Leschev, Dolev Rimmerman, Darren Hsu, and Jiyun Hong. Their acceptance and guidance over multiple beamtime experiments was both highly educational and enjoyable.

I am appreciative of too many members of the chemistry department to name, from whom I received varying forms of assistance. Thanks to those in the LDL basement for continuous unpredictable conversations and entertainment, particularly Chris Goodwin, Zachary Voras, Marcie Wiggins, and frequent special guest Mackenzie Williams. The establishment of the SAF café was very much appreciated. Thank you to Mingzhang Wang and Dr. Yichen Duan for numerous fun discussions, travels, and activities over the years. Thank you to Dr. Scott Shuler for help with organic chemistry and many fun evenings.

Finally, I am eternally grateful to my parents. Their continuous love and support made this work possible.

TABLE OF CONTENTS

LI LI A]	LIST OF TABLES							
Cl	napte	er						
1	INT	RODUCTION	1					
	$1.1 \\ 1.2 \\ 1.3 \\ 1.4$	Overview	$ \begin{array}{c} 1 \\ 3 \\ 5 \\ 8 \end{array} $					
2	EXI	PERIMENTAL METHODS	10					
	2.1 2.2 2.3	Abstract	10 10 13					
		2.3.1Noncollinear Optical Parametric Amplification2.3.2Cross-Correlation	$\frac{14}{17}$					
	2.4 2.5 2.6 2.7	Transient Absorption Spectroscopy	18 23 31 35					
		2.7.1Metalloporphyrins \ldots \ldots \ldots 2.7.2TiO2 \ldots \ldots \ldots	$\frac{35}{37}$					
3	ZIN SOI	C PORPHYRIN VIBRATIONAL DYNAMICS IN LUTION	40					
	3.1	Abstract	40					

	3.2	Background and Motivation	40
	3.3	Steady State Results	42
	3.4	Transient Absorption Results	46
	3.5	Pump-DFWM Results	55
	3.6	Discussion	63
	3.7	Conclusion	64
4	VIE	BRATIONAL DYNAMICS IN A HETEROGENEOUS	
	ELI	ECTRON TRANSFER SYSTEM	66
	41	Abstract	66
	4.2	Background and Motivation	66
	4.2 13	Transient Absorption Results	71
	4.0 4.4	DFWM Results	74
	4.5	Pump-DFWM Results	76
	4.6	Discussion	80
	4.7	Conclusion	80
	1.1		00
5	NIC	CKEL PORPHYRIN EXCITED-STATE LIGATION	82
	5.1	Abstract	82
	5.2	Background and Motivation	82
	5.3	Optical Results	86
	5.4	X-Ray Transient Absorption Results	91
	5.5	Discussion	99
	5.6	Conclusions	100
0	CII	AD A CORDUZATION OF AN INHERDENCE TO A MOLENIC	
0		ARACTERIZATION OF AN INHERENT TRANSIENT SORPTION ARTIFACT	102
	110,		102
	6.1	Abstract	102
	6.2	Background and Motivation	102
	6.3	Experimental Design	105
	6.4	Time-Domain Results	106
	6.5	Frequency-Domain Results	109
	6.6	Discussion	112
	6.7	Conclusions	114
7	SUI	MMARY	115
BI	BLI	OGRAPHY	118

Appendix

\mathbf{A}	COPYRIGHT PERMISSION	3.									•		13'	7

LIST OF TABLES

4.1	Table of Vibrational Mode Assignments for Raman-Active Frequencies (cm^{-1}) Observed in Zn-PE- $(COOH)_2$ and	
	$Zn-PE-(COOH)_2^+$ Bound to TiO_2	78
6.1	FWHM of Cross-Correlations and Transient Absorption	
	Rise Times at Different Concentrations.	112

LIST OF FIGURES

1.1	The general relaxation processes possible after photoexcitation are summarized with their typical corresponding timescales. Adapted with permission from [1]. Copyright 2005 Springer	4
1.2	Nonadiabtic (left) and adiabatic (right) heterogeneous electron transfer is shown through energy diagrams along the reaction coordinate. The coupling strength between the donor and acceptor states dictates the degree of adiabaticity. Franck-Condon factors can modulate vibrational coherence in the nonadiabatic case, but not for adiabatic reactions. Vibrationally hot products may be produced in either case. This process is investigated in Chapter 4	6
2.1	Raman Stokes, anti-Stokes, and Rayleigh scattering are the result of vibrational energy level transitions.	11
2.2	The NOPA contains a beamsplitter (BS), concave spherical mirrors (SM), and a lens pair that acts as a telescope. A variable delay stage allows for matching the timing of the pump and supercontinuum pulses in the amplification BBO. The amplification of the green portion of the white light is depicted.	15
2.3	At the correct alignment conditions, the NOPA outputs a very broadband amplified spectrum. The measured auto-correlation produces a pulse duration below 10 fs.	16
2.4	Transient absorption spectroscopy is performed using a chopped pump beam on a variable delay path, and a supercontinuum probe beam on an all-reflective path. The probe pulse is compressed with a dispersion compensation mirror (DCM) before its focus on the sample by an off-axis parabolic mirror (OAPM)	20
2.5	The detected spectrum of the supercontinuum probe pulse is spread across the visible region from 450 nm to 750 nm.	21

2.6	The time ordering of the pump-DFWM sequence consists of an initial actinic pulse to promote the system, to an electronically excited state, followed by a set of pulses that generate a DFWM signal on the excited state. Evolution of the excited state is tracked by varying 'T', and wavepacket dynamics are followed by scanning 't'. The DFWM pump and Stokes pulses are kept coincident in time	24
2.7	A vibrational wavepacket is prepared by impulsive excitation in an arbitrary excited state (ES_{α}) . DFWM pulses serve to probe the time-dependent evolution of the packet through resonant absorption to a higher-lying excited state (ES_{β}) .	25
2.8	In the initial setup, two beamsplitters (BS) separated an input pulse into three spots for the DFWM sequence. The beams were arranged into the corners of a square (BOXCAR geometry) and focused onto the sample solution by a shared off-axis parabolic mirror (OAPM). The actinic pump pulse was independently delayed, and focused by the same mirror.	27
2.9	The second pump-DFWM instrument utilized three beamsplitters (BS) to create the three pulse DFWM sequence. A fourth pulse is also created, but was blocked and not used. The shared reflective surfaces provide a passively phase stable setup. The actinic pump is focused along with the DFWM beams by a spherical mirror, redirected towards the sample. A vacuum chamber was used for solid-state samples, and a pinhole spatially selected the signal beam.	28
2.10	The raw oscillatory data of the DFWM pulse intensity is collected in the time domain over a time window scanned up to 2 ps (a). The first 100 fs are removed to avoid coherent artifact contributions. The signal is fit with a single exponential decay (b). The fit is subtracted from the signal in order to remove the non-oscillatory component (c). The data is then zero-padded and put through a discrete Fourier transform using a Hanning window to produce a frequency spectrum (d).	30
2.11	The laser pump generates an excited state probed by X-ray pulses. Pulse timing is described in the text. Adapted with permission from [2]. Copyright 2013 American Chemical Society	33

2.12	The sample chamber utilized a recirculating flowing jet. Two detectors on the sides of the sample chamber collect emitted X-ray fluorescence. A normalization detector collects X-ray emission from air before the sample. Reprinted with permission from [3]. Copyright 2013 American Chemical Society.	34
2.13	The structure of Zn-tetraphenylporphyrin consists of a porphyrin ring with phenyl groups at the <i>meso</i> positions	36
2.14	A scanning electron microscope image of the colloidal TiO_2 shows the size of the individual nanoparticles.	38
3.1	The normalized Soret absorption profile of Zn-TPP in THF is unaltered over a broad range of concentrations. There is no signature of J-aggregation at concentrations up to 100 μ M	43
3.2	The normalized fluorescence excitation-emission spectra of low concentration Zn-TPP solutions in THF do not show signs of broadening in either the Soret or Q bands over a 50 fold concentration change.	44
3.3	The LIFDI-MS spectrum of the sample shows that the isotopic pattern obtained over the course of the measurement (a) was identical to the calculated pattern for the Zn-TPP (b). Monitoring the field desorption spectrum (c) for demetallated Zn-TPP as current was increased did not produce any ion peaks (d)	45
3.4	The overlap of normalized spectra of the pump pulses used in this chapter with the absorption of Zn-TPP in THF illustrates the difference in excitation towards the high or low energy side of the Soret band.	46
3.5	The transient absorption map collected after 420 nm excitation shows dynamic features throughout the visible spectrum within the first picosecond.	47
3.6	The relaxation path for Zn-TPP following excitation of the Soret band involves multiple steps and electronic states. The initial component is thought to be either IVR or conversion through a nearly degenerate dark state. Internal conversion to S_1 follows, wherein further IVR occurs in two steps, before crossover to the long lived triplet state	48

3.7	Selected kinetic traces from transient absorption at 420 nm are fit with contributions from a minimum of six states. Each component contributes to the signal across the spectrum to a varying degree, including a fast 70 fs relaxation from an unclear state	49
3.8	Species-associated decay shows the spectral distribution of the 70 fs τ_1 contribution to the overall transient absorption dynamics that follow excitation at 420 nm.	50
3.9	The transient absorption map of the first picosecond of relaxation after excitation at 430 nm contains positive and negative features across the spectrum	51
3.10	Normalized kinetic traces from the transient absorption maps and their fits at selected wavelengths highlight the difference in early dynamics from excitation at 430 nm (black) versus 420 nm (blue). A slower rise is exhibited from higher energy excitation, while traces produced using a lower photon energy pump rise within the instrument response time. The data from 430 nm excitation can thus be fit with one fewer components	53
3.11	The map produced by normalizing and subtracting the data in Figure 3.5 from the data in Figure 3.9 shows major differences within the earliest dynamics. Dashed white lines highlight the region where positive crosses over to negative and shifting between vibrational or electronic states could be observed.	54
3.12	Subtraction of a stationary peak from a peak that is blue-shifting towards the same position produces a diagonal zero line. This simple simulation is representative of the expected result for Figure 3.11 in the event of vibrational relaxation, particularly at the area of its dashed lines.	55
3.13	The spectrum of the pulse centered at 510 nm used for the DFWM probing pulse sequence overlaps with the positive absorption in the Zn-TPP excited state. This region is also far from the ground-state absorption transition, allowing the excited state to be singled out for resonant enhancement.	56

3.14	Excited-state resonant pump-DFWM spectra at T=500 fs (a) and ground state resonant DFWM spectrum (b) show multiple peaks. Dominant features are a 385 cm ⁻¹ metal-pyrrrole stretch, 1352 cm ⁻¹ inner ring stretch, and a 910 cm cm ⁻¹ solvent mode denoted by an asterisk, which are preserved after photoexcitation to S_2	57
3.15	The major vibrational modes appearing in the pump-DFWM spectra are stretching of the Zn-N bond (a), which appears at 385 cm ⁻¹ , and stretching within the porphyrin interior across the <i>meso</i> carbon and pyrrrole nitrogen atoms (b) that appears at 1352 cm ⁻¹	57
3.16	The pump-DFWM map produced after excitation at 420 nm shows three major peaks and their behavior over the first several hundred femtoseconds following S ₂ activation. The peaks in the 1350 cm ⁻¹ and 380 cm ⁻¹ regions share the same phase, while the peak at 910 cm ⁻¹ was found to have π phase difference	59
3.17	The magnitude of the two molecular vibrational modes detected after 420 nm excitation shows an increase of the higher frequency peak, and an indiscernible change at the lower frequency over the first 600 fs of dynamics.	60
3.18	The peak in the 1350 cm^{-1} region of the pump-DFWM map in Figure 3.16 increases in frequency by 13 cm^{-1} and magnitude over time. A rate of 85 fs is fit to the frequency shift by tracking the position of the maximum of the peak, which is displayed by the dashed line.	60
3.19	The pump-DFWM map acquired after excitation at 430 nm shows nearly identical features to Figure 3.16. Peaks at 1352, 910, and 385 cm^{-1} are prominent, and features remain static over the time range measured.	61
3.20	Magnification of the 1350 cm^{-1} region of Figure 3.19 shows an absence of peak shifting. In contrast to Figure 3.18, this high frequency vibration does not change over time when a 430 nm pump pulse is employed.	62
4.1	The Zn-PE-(COOH) ₂ molecular structure contains of an alkyl bridge terminating in two carboxylic acid linkers that facilitate binding to the TiO2 surface. The porphyrin <i>meso</i> , α , and β carbons are labeled, as well as the three phenyl bridging groups.	68

4.2	The S ₂ electronic state of Zn-PE-(COOH) ₂ is impulsively populated by an actinic pulse, preparing a vibrational wavepacket on the energy surface. The fate of the wavepacket is probed after electron transfer by employing a DFWM pulse sequence at an appropriate delay. \ldots	69
4.3	The experimental scheme involves Zn-TPP chromophore molecules modified with bridge groups attached to a film of TiO_2 nanoparticles. Electron transfer is induced from the chromophore by an actinic pump pulse and occurs through the bridge group into the colloid. Vibrational dynamics of the molecule are then probed by a DFWM sequence.	70
4.4	The transient absorption map of Zn-PE-(COOH) ₂ bound to a colloidal TiO_2 film produced after 420 nm excitation to S ₂ exhibits both rapid and slow dynamics throughout the probed spectral region.	71
4.5	The transient absorption spectrum of Zn-PE-(COOH) ₂ chemisorbed to TiO ₂ at a delay of 5 ps after excitation of the Soret band shows characteristic broad porphyrin features across the visible region	72
4.6	Kinetic traces of Zn-PE-(COOH) ₂ bound to TiO_2 following S ₂ excitation are displayed. The traces are extracted from the data in Figure 4.4 at representative wavelengths of 480 nm (a) and 690 nm (b). The 85 fs injection time is evident as a rapid decay, followed by a slower decay of the post-injection species.	73
4.7	The DFWM spectrum of a thin film of an atase TiO_2 nanoparticles (a) reproduces the features found in its steady-state Raman spectrum (b).	74
4.8	The DFWM spectra of a colloidal TiO_2 thin film features peaks attributable to Zn-PE-(COOH) ₂ sensitization with the dye (a). The peak at 148 cm ⁻¹ is from TiO ₂ . The DFWM spectrum of Zn-TPP in THF solution (b) displays similar peaks. The peak at 910 cm ⁻¹ is from the solvent.	75
4.9	Pump-DFWM spectra of Zn-PE-(COOH) ₂ chemisorbed to TiO_2 shows several consistent peaks, highlighted by dashed red lines. At delays of 5, 8, and 12 ps following excitation of S ₂ the cation is the primary species	77

4.10	DFT calculated Raman spectra of the neutral and oxidized form of Zn-PE-(COOH)_2 predict differences in the accessible vibrational modes. The cation exhibits more modes of more even intensity below 1200 cm ⁻¹	79
4.11	Evolution of the amplitude of the four major vibrational peaks observed in the cation at 765 cm ⁻¹ , 885 cm ⁻¹ , 953 cm ⁻¹ , and 1380 cm ⁻¹ shows a slight decay of two modes associated with the bridge groups	79
5.1	Ni-TPPF-Ac consists of a Ni-tetraphenyl porphyrin substituted with fluorine atoms across the phenyl moieties. A carboxylic acid group is present to allow chemisorption to ${\rm TiO}_2$ for HET experiments	83
5.2	The DFT calculated major molecular orbitals involved in transition to the excited state of Ni-TPPF-Ac show inclusion of the central nickel atom. Compared to the HOMO of the ground state, electron density increases at the metal in the LUMO and LUMO+1 states that are populated after photoexcitation	85
5.3	The ground-state absorption spectrum of Ni-TPPF-Ac shows an intense Soret peak and a split Q band at lower energy (inset). Pump-probe measurements are performed with a pump pulse centered at 400 nm to achieve S_2 excitation.	87
5.4	The optical transient absorption map produced after 400 nm excitation exhibits centralized features in the 500 nm region. Ground-state bleach overlaps with excited-state absorption that persists for several nanoseconds.	88
5.5	Alternating positive and negative peaks are observed in the optical transient absorption spectrum of Ni-TPPF-Ac. Excited-state absorption overlaps with bleach from the Q band. A slight red-shift of the peaks occurs over the course of excited-state relaxation	89
5.6	Kinetic traces at 530 nm and 560 nm show differing dynamics. Three time constants fit both signals. The initial rise at 530 nm is matched by the fast decay at 560 nm	89
5.7	The rise of the Ni-TPPF-Ac optical transient absorption signal at 530 nm is affected by solvent. An additional time constant is observed in toluene relative to ethanol based experiments	90

5.8	X-ray absorption spectra of Ni-TPPF-Ac were collected for the ground state and at two time points after laser excitation. Slight differences are noticeable in the EXAFS, XANES, and pre-edge regions.	91
5.9	A peak in the pre-edge absorption region decreases in magnitude and blue-shifts after photoexcitation.	92
5.10	Subtraction of the ground state spectrum from the excited-state spectra is performed after rescaling to the pre-edge peak absorption in order to isolate absorption features induced by optical excitation. The pre-edge absorption peak is due to a $1s \rightarrow 4p$ transition	93
5.11	The Fourier transform of the data in Figure 5.10 shows slight differences in X-ray scattering paths of the atoms at different following photoexcitation. The large deviation at 120 ps returns towards the ground state structure by 1 ns.	94
5.12	EXAFS difference spectra at pump delays of 120 ps and 1 ns display a change in the Ni absorption after photoexcitation. The magnitude of the XTA signal decreases as the ground state recovers	95
5.13	The XANES region of Ni-TPPF-Ac is altered after photoexcitation. There is a significant change in the structure of the pre-edge peak and broad XANES absorption. Blue dashed lines indicate energy positions where kinetic scans are performed.	96
5.14	The raw XTA kinetics recorded at the pre-edge and XANES peak regions show similar biexponential relaxation dynamics and opposite signs.	97
5.15	Normalization of the XTA kinetics highlights the similar dynamics at both energies monitored	97
5.16	Identical X-ray absorption signals recorded before and after hours of irradiation verify the integrity of the sample throughout data collection.	98
5.17	After photoexcitation, the axial $4p_z$ orbital of Ni(II) is occupied by coordinating solvent molecule ligands.	100

6.1	A near-transform-limited femtosecond laser pulse is stretched in time after losing spectral components due to nonuniform absorption in the sample. Zn-TPP solution absorbs the middle portion of the pulse spectrum, causing a decrease in the spectral components of the pulse in the sample. The initial transform limit is no longer achieved, resulting in an inconspicuous loss of experimental time resolution.	104
6.2	Kinetic traces of Zn-TPP transient absorption signals at 520 nm show apparent concentration-dependent dynamics when normalized and overlayed. The excitation pulse travels through solutions of increasing concentration before interacting with probe pulse	106
6.3	The lines of best fit generated by a global fitting routine, from which the rise times reported in Table 6.1 were extracted, are displayed. Transient absorption at 520 nm is delayed as the concentration of Zn-TPP in the path of the pump beam increases from 0 to 25 μ M. The observed slope of the blue fit lines decreases as the optical density increases.	108
6.4	The SHG cross-correlation of the pump and probe pulses shows a distortion and increase in temporal width as the pump passes through Zn-TPP solutions of increasing concentration.	109
6.5	The spectrum of the pump pulse is altered in shape after passing through a cuvette of Zn-TPP solution. Distortions are more pronounced at higher concentration. The bandwidth of the excitation pulse slightly exceeds the Soret absorption peak width of the porphyrin, indicated by the red dashed curve.	110
6.6	A measured cross-correlation from Figure 6.4, in blue, can be qualitatively reproduced based on the spectrum of the pump pulse contributing to it. Converting the spectral measurement to the frequency domain and then performing a convolution with a 20 fs assumed Gaussian pulse representing the probe contribution produces the red curve	111
6.7	Transient absorption kinetic traces on high concentration samples, when recorded after deliberate optical alignment, exhibit minimal distortion of the initial dynamics by spectral filtering	113
A.1	Copyright permission for Figure 1.1	138
A.2	Copyright permission for Figure 2.11	139

A.3	Copyright permission for Figure 2.12	140
A.4	Copyright permission for material in Chapter 3 $\ldots \ldots \ldots$	141
A.5	Copyright permission for material in Chapter 4 $\ldots \ldots \ldots$	142
A.6	Copyright permission for material in Chapter 6 $\ldots \ldots \ldots \ldots$	143

ABSTRACT

Understanding the behavior of molecular excited states is critical to inform the design of photochemical reactions. Applications ranging from solar energy conversion to medicinal photochemistry rely on chemical reactions that are initiated by photoexcited molecules. Complete characterization of excited-state dynamics includes the description of electronic and structural contributions. In this work, the structural dynamics of several metalloporphyrin systems are investigated after photoexcitation. Metalloporphyrins are widely used in photochemical schemes due to their desirable optical properties, and their excited-state behavior is relevant for many applications. Transient absorption, pump-degenerate four-wave mixing, and X-ray transient absorption spectroscopies were the primary methods used to study the ultrafast processes accompanying excitation. Information was provided on electronic-vibrational coupling, vibrational coherence, structural reorganization, and solvent-chromophore interactions taking place in the excited-states of metalloporphyrins. Highlights include the identification of excited-state metal ligation and the probing of adiabaticity in heterogeneous electron transfer. An inconspicuous measurement artifact is also identified and characterized. Descriptions are included of experimental methods and instrumental systems that were developed to facilitate the measurement of ultrafast vibrational dynamics on increasingly complex systems.

Chapter 1 INTRODUCTION

1.1 Overview

Photo-activated chemical systems are an important component of many developing technologies. Scientific topics ranging from artificial photosynthesis, dye-sensitized solar cells, photocatalysis, photodynamic therapy, vision biology, photolithography, photodegradation and more all depend on the physical response of molecules to optical stimulation. [4, 5, 6, 7, 8, 9, 10, 11] These photochemical processes are all driven by the reactivity of the molecular components in their excited state. Complete characterization of the behavior of the excited states is therefore necessary for fundamental understanding of the photochemistry. Investigation of the excited-state dynamics of molecules is crucial for understanding the underlying reaction mechanisms.

Because of the short-lived nature of transient excited states, experimental challenges exist. Pump-probe laser spectroscopies are by far the most accessible and popular methods available to access the femtosecond timescales involved. This methodology has limitations on the amount of information that can be gained. Ultrashort laser pulses typically probe electronic transitions and are inherently capable of measuring electronic dynamics. However, chemical reaction pathways are often facilitated by nuclear dynamics along the reaction coordinate. Probing vibrational dynamics and structural reorganization is thus important for full characterization of the photochemistry of molecules. Advances have been made in spectroscopic methods in recent years to facilitate the investigation of structural dynamics on ultrafast timescales. Pump-Degenerate Four-Wave Mixing is utilized in this work and further developed to study vibrational dynamics in increasingly complex systems. X-ray transient absorption is also employed to unambiguously identify local structural dynamics. Metalloporphyrins studied in this work are an extensively used class of molecules, both in laboratory studies and real world applications. As such, their dynamics are representative and relevant to a wide range of photochemical systems.

The remainder of Chapter 1 provides a brief explanation of excited-state relaxation processes. A description of the role of electronic and nuclear contributions to relaxation dynamics is provided to serve as a framework for the results and motivations of this work.

Chapter 2 explains the experimental methods used throughout this work. A description of the operating principles and utility of each technique is provided. Detailed specifications are included for the experimental parameters used. The optical components of each home-built instrument are detailed, and data analysis procedures are explained. The chemical systems used are motivated and described as well. Sample preparation conditions and procedures are also discussed.

Chapter 3 presents experimental results from a relatively simple metalloporphyrin system: Zn-TPP in solution. The excited-state dynamics of molecular Zn-TPP are fully characterized. Coupled electronic and vibrational relaxation processes are observed and described. Vibrational relaxation is identified in the second singlet excited state and established as the mechanism for longstanding poorly understood dynamics. The coupling of specific vibrational modes to the excited state is observed, and the evolution of the vibrational energy is tracked over the initial picosecond of excited-state relaxation.

Chapter 4 describes experimental results from metalloporphyrin bound to a surface. Zn-TPP was modified to bind to TiO_2 . The resulting Zn-TPP/TiO₂ system is used to explore the role of vibrational effects in heterogeneous electron transfer. Ultrafast electron transfer is characterized for the system, and vibrational energy redistribution is observed. Vibrational modes identified in the solution phase from Chapter 3 are compared with those observed on the surface before and immediately after electron transfer. The evolution of vibrational coherence through interfacial electron transfer from the molecule is explored.

Chapter 5 presents an experimental study of metalloporphyrin in solution using a pulsed X-ray probe. The metal center is switched from Zn to Ni to better satisfy experimental conditions for the X-ray transient absorption. Structural dynamics that occur after photoexcitation are characterized. X-ray absorption provides direct structural information at the atomic scale, complementing vibrational results in the previous chapters. Interaction of the metal atom with the surrounding solvent environment is investigated to complement results from Chapter 3. The transient structure of the metalloporphyrin interior is directly probed through analysis of the extended X-ray absorption fine structure.

Chapter 6 describes experimental results that expose an artifact in transient absorption measurements on molecular systems like porphyrins that feature narrow linewidth absorption bands on the order of the excitation linewidth. The contribution from the artifact to measured signals could be misconstrued as dynamics from interactions between molecular structures. The artifact is characterized and clarified as a natural consequence of pulse distortions, which is revealed by concentration-dependent studies. Guidelines to minimize effects from this easily misattributed signal contribution are provided.

Chapter 7 concludes this work by summarizing the main results. Important points are recapitulated and highlighted.

1.2 Molecular Excited States and Dynamics

When a molecule interacts with light, a photon can be absorbed and promote a valence electron to a higher energy unoccupied orbital from the ground state. This electronic excitation is favored when the incident photon is resonant to the absorption transition, which is typically in the range of the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The transition dipole moment between the HOMO and LUMO then dictates the strength of the transition. After absorption, the molecule is in an electronic excited state. Based on the different electron distribution in the excited state, the bonds of the molecule can shift and the structure may differ from that of the ground state. The Franck-Condon principle and Born-Oppenheimer approximation can be taken together to find that immediately after excitation, the structure is in a vibrationally excited state and has not yet deviated towards its favored electronic excited-state configuration. [12, 13]



Figure 1.1: The general relaxation processes possible after photoexcitation are summarized with their typical corresponding timescales. Adapted with permission from [1]. Copyright 2005 Springer.

Relaxation towards the energetic minimum of the potential energy surface of the electronic excited state is known as vibrational relaxation. Vibrational relaxation typically occurs on the timescale of tens to hundred of femtoseconds in solution phase. Vibrational cooling can also occur if vibrational energy is distributed to surrounding solvent molecules. If lower lying electronic excited states are available, crossing can occur towards the lower energy states. Transitions between states with the same spin multiplicity is known as internal conversion. This process generally occurs on a picosecond timescale. Transitions between states of different spin multiplicity is known as intersystem crossing. Because spin flip must occur, this is a selection-rule forbidden transition. Spin-orbit coupling eases the transition. The timescale is accordingly slower, typically taking nanoseconds. A transition to the ground state can be mediated by the release of a photon. A radiative transition between states is referred to as fluorescence when the states have the same spin multiplicity, and phosphorescence when a spin flip occurs in the transition. The timescale of both emissive properties is based on the lifetime of the contributing excited state, indicated above. All of these relaxation processes can play a role in the relaxation of molecular excited states. Figure 1.1 summarizes the possible relaxation steps and timescales. The lifetimes and relaxation paths can dictate the reactivity of a photoexcited molecule. Short lifetimes can limit reactions kinetically, the energetic position of an excited state can thermodynamically favor a reaction, and the spin state can facilitate interactions with others of the same spin. For metalloporphyrins, all of the processes discussed contribute to the relaxation path and must be considered when interpreting the measured dynamics.

1.3 Nuclear Effects in Dynamics

As mentioned in section 1.2, nuclear motion has an effect on excited-state dynamics. Relaxation away from an initially prepared Franck-Condon state introduces structural motion and vibrational dynamics. Intramolecular vibrational energy redistribution and structural reorganization affect the behavior of the excited state. Intermolecular vibrational energy transfer to solvent molecules in the bath environment can also have an effect.

Ahmed Zewail famously experimentally demonstrated the importance of ultrafast nuclear dynamics in chemical reactivity, and was consequently awarded the 1999 Nobel prize in chemistry "for his studies of the transition states of chemical reactions using femtosecond spectroscopy". [14, 15] Since then, much progress has been made, and the coherence of vibrational states has been identified to play an important role in many excited-state reaction paths. [16, 17, 18, 19, 20, 21, 22, 23] Vibrational coherence is manifest as a superposition of vibrational states that evolve synchronously, producing a wavepacket. The dynamics of the wavepacket are apparent through quantum beats. A description of vibronic wavepacket dynamics can be found in reference [24]. The preparation of coherent vibrational states is discussed in section 2.5 and illustrated in Figure 2.7.



Figure 1.2: Nonadiabtic (left) and adiabatic (right) heterogeneous electron transfer is shown through energy diagrams along the reaction coordinate. The coupling strength between the donor and acceptor states dictates the degree of adiabaticity. Franck-Condon factors can modulate vibrational coherence in the nonadiabatic case, but not for adiabatic reactions. Vibrationally hot products may be produced in either case. This process is investigated in Chapter 4.

The behavior of vibrational coherence in a photochemical system can provide information on the reaction path. In particular, adiabatic and nonadiabatic reactions can be distinguished. The energy diagrams for nonadiabatic and adiabatic heterogeneous electron transfer (HET) are depicted in Figure 1.2 for reference. For general adiabatic reaction pathways, where crossing of the potential energy surfaces for reactant and product states is avoided, coherence would be expected to be preserved through the reaction. The oscillating wavepacket would be modulated by the reaction barrier, and create a product population with retained coherence. Adiabatic reactions facilitated by an avoided surface crossing can be very efficient by allowing a direct path to product state. The preservation of a coherent vibrational wavepacket can be an indicator of the conical intersection involved. Vibrational coherence in nonadiabatic reactions is a less common case. Quantum beats from the wavepacket in the reactant state must induce a coherence in the product state through the crossed energy surfaces. This is a more rare event, and requires specific overlap of the surfaces. The vibrational energy levels must align properly to allow modulation through the crossing. Franck-Condon factors thus control the coherence and the reaction path. In the case of HET reactions, the Franck-Condon overlap is much greater than in intermolecular reactions and the degree of adiabaticity is less clear, as discussed and investigated in Chapter 4. The band structure of a semiconducting electron acceptor surface allows a multitude of closely spaced acceptor states to exist. These can more easily couple to the reactant surface through its Franck-Condon progression and allow vibrational coherence to be generated in the product. Probing of the vibrational dynamics and coherent states involved throughout the course of the HET process can provide fundamental mechanistic understanding. Probing of transient structural states through XTA offers direct information on the molecular distortions that occur in excited state reactions. This knowledge can inform the design of more efficient systems.

1.4 Objectives

This work is primarily focused on exploring the role of structural dynamics on the excited-state behavior of metalloporphyrins. It also seeks to establish pump-DFWM as an effective tool for measuring excited-state vibrational spectra. This is approached systematically in several steps and from several experimental directions.

First, pump-DFWM is chosen as a particularly suitable technique to probe the vibrational dynamics. Specific excited states can be targeted and the vibrational spectra can be monitored on an ultrafast timescale. Pump-DFWM instrumentation is built to produce tunable sub 10 fs pulses at 10 kHz for efficient data collection. It was used to measure the dynamics of a simple metalloporphyrin in solution. The solutionphase dynamics can then be used as a baseline for more complex variations. Specific vibrational modes that couple to excited states can be identified to inform about the nuclear relaxation coordinate. Vibrational interaction with solvent molecules is also identifiable. Transient absorption measurements can explain electronic effects and define the general relaxation path and kinetics.

The molecule is then bound to a semiconductor surface to investigate the structural dynamics over the course of HET. Experimental methods are developed further to allow the measurement of vibrational dynamics in dye-sensitized films for the first time. Vibrational coherence and reaction-induced vibrational excitation can be identified and distinguished. Differences from the solution measurements can be attributed to HET and surface effects.

Next, the structural dynamics of metalloporphyrins are directly probed by Xray pulses. Transient structures in the excited-state relaxation are identifiable and can be combined with vibrational information from pump-DFWM measurements to form a more complete picture of the structural dynamics. Solvent interactions can also be directly probed and understood, especially since the X-ray absorbing metal acts as the coordination center.

Finally, errant signal contributions must be excluded. Identification and characterization of misleading measurement artifacts is performed. Molecular aggregation or excimer formation is ruled out as a source of apparent concentration-dependent dynamics that would otherwise indicate intermolecular interactions. The deceptive dynamics are corrected for, and the meaningful structural information is preserved.

Chapter 2 EXPERIMENTAL METHODS

2.1 Abstract

This chapter describes the methods used to probe the systems studied in this work. Instrumentation capable of measuring short-lived molecular excited states, as well as sensitivity to structural changes on the ultrafast timescale were required and developed. Raman spectroscopy can probe molecular vibrations in the ground state. Transient absorption is an effective technique for characterizing the general dynamics of excited states, with femtosecond resolution. Pump-degenerate four-wave-mixing provides information on the the vibrational dynamics involved in the ultrafast evolution of excited states. X-ray transient absorption can investigate nuclear reorganization around specific atomic sites of photoexcited molecules. These spectroscopic techniques offer complementary information that provide a detailed picture of the structural dynamics involved in electronic excitation and photochemical reaction paths. A summary of the chemical systems is also provided. The suitability of metalloporphyrins and TiO_2 for photo dynamic studies is explained.

2.2 Raman Spectroscopy

DFWM functions as a time-domain variant of Raman spectroscopy, and therefore a brief discussion of standard Raman methods is necessitated. Raman spectroscopy is a steady-state technique sensitive to vibrational modes of the analyte. Since the identification of the underlying effect in the early 20th century, Raman spectroscopy has grown to become a standard laboratory tool for vibrational analysis. [25, 26, 27, 28] Raman spectroscopy is based on energetic changes of scattered light from the sample. When incident light is scattered of a sample, the vast majority of the scattered light has the same energy. However, a small portion is energetically downshifted. Another small percentage is scattered off at a higher energy. The energy shifts occur discretely, and can produce a spectrum composed of peaks when the shift is plotted against intensity. Furthermore, the energetic shifts directly correspond to the frequencies of the vibrational modes in the scattering sample.



Figure 2.1: Raman Stokes, anti-Stokes, and Rayleigh scattering are the result of vibrational energy level transitions.

The mechanism of this shift can be understood based on the model displayed in Figure 2.1. The scattering process can be described quantum mechanically as a two step process. First, an incident photon promotes the scattering molecule to a virtual energy state from a vibrational ground state. This state is is not an eigenfunction of the system and only serves as an intermediate. Second, radiative relaxation occurs. Relaxation typically occurs to the ground state and the emitted photon is at the same frequency as the incident one. This case is called Rayleigh scattering. Alternatively, relaxation can occur to a higher vibrational energy level, with the scattered photon at a lower frequency. This is refereed to as a Stokes shift. Because the difference in energy is equal to the difference in quantized vibrational states, the frequency shift of the scattered photon corresponds to a vibrational frequency mode in the molecule. Light can scatter at a higher energy in the anti-Stokes case when the initial excitation occurs from a vibrationally excited state and relaxation proceeds to the ground state. This produces the same vibrational spectrum, but occurs less frequently under normal conditions and is correspondingly less intense. The lower occurrence is due to the low fraction of molecules in excited vibrational states at standard temperatures. The ratio of the intensities of the Stokes and anti-Stokes spectra directly follows the Boltzmann distribution. [29] Laser excitation sources are generally used due to their high intensity and narrow linewidth, which allows easy filtering of the Rayleigh contribution to isolate the Stokes and anti-Stokes Raman scattered light.

The light-matter interaction can also be understood classically, with the incident light acting as a perturbation on the electric field of the molecule. An induced dipole moment can then oscillate and radiate. For Raman scattering to occur, the induced dipole must oscillate at a new frequency. The ease of distortion of the dipole is the polarizability. Therefore the magnitude of the Raman effect is dependent on the change in polarizability of the molecular dipole. The selection rule for Raman active transitions is fundamentally that there must be a change in polarizability in the vibrational mode. This can be viewed as a distortion of the electron density in the bonds. Strong Raman active samples are thus usually systems with weakly bound, widely distributed electrons, such as halogenated and conjugated molecules. Highly polar bonds on the other hand are often weak Raman scatterers. Water, for instance, is not Raman active, which makes Raman spectroscopy attractive for biological studies. Because Raman spectroscopy relies on scattering, it is applicable to solid and liquid samples, be they homogeneous or heterogeneous. This in contrast to transmissive methods like IR absorption, where too much absorption or scattering eliminates the signal.

The Raman instrument used for measurements discussed in this work was a HoloLab 5000R spectrometer manufactured by Kaiser Optical Systems. A 785 nm continuous-wave laser was used for sample excitation. Liquid samples were measured in a homemade aluminum well plate, with a 0.5 mL well volume. The depth of the well was verified as sufficient to not produce any signal from the aluminum. The focal length of the excitation beam was 7 mm, resulting in a numerical aperture of ~0.8. An adjustable jack was used for alignment to position the sample plate to a depth that produced maximum signal. A notch filter and transmission grating were in place before detection. The resulting frequency resolution was 0.3 cm^{-1} . A charge-coupled device (CCD) camera with thermoelectric cooling was used as a detector for full spectral acquisition without aperture scanning. The varying sensitivity of the CCD to different wavelengths was corrected for by using a broadband lamp between measurements. The spectral response to the broadband lamp was used as a normalization factor for samples. This correction also addressed nonuniform spatial response from the CCD across its pixel array. Measurements were performed in an enclosed container, so that the optical collection fiber was protected from stray ambient light.

2.3 Ultashort Pulse Generation and Characterization

Laser pulses with durations in the ten to forty femtosecond range were used in the majority of this work. Optical pulses on this timescale are limited in duration by their spectral bandwidth. The relation between duration, Δt , and bandwidth, $\Delta \omega$, of a pulse is referred to as the time-bandwidth product, and is expressed as

$$\Delta t \cdot \Delta \omega \ge C_s \tag{2.1}$$

The value of the constant C_s depends on the shape of the pulse envelope. Commonly encountered values for C_s are 0.441 for the case of a Gaussian pulse profile and 0.315 for the case of a sech² profile. [30] The values of Δt and $\Delta \omega$ are taken from the full-width at half-maximum (FWHM) of the pulse in the time and frequency domains respectively. This relation can be understood from a Fourier analysis perspective. The temporal and spectral characteristics of the electric field are directly related through Fourier transforms, and they cannot be independently modified. This restriction of the minimum achievable pulse length by the available bandwidth is often referred to as a "transform limit" in reference to their Fourier relation. The phase across the pulse must be constant in order to reach the transform limit. An uneven temporal distribution of frequency components in the pulse is caused by travel through media, including air. [31] The frequency dependence of refractive index leads to a dispersion of the spectral components in time. For standard materials, pulses in the visible regime take on a characteristic distribution where the higher frequency components lag after the lower frequencies. This is referred to as a chirped pulse. A pulse with the opposite distribution is referred to as negatively chirped. Pulse compression is usually accomplished by negatively chirping a pulse before it passes through materials in order to perfectly compensate the induced positive chirp. However, compression becomes challenging when the frequency distribution deviates far from linear.

The commercial laser system used in this work to generate femtosecond pulses consists of a Ti:sapphire oscillator (Coherent Mantis) coupled to a regenerative chirped pulse amplifier (Coherent Legend). The amplifier outputs a 6.1 W pulse train of 35 fs pulses centered at 800 nm at a 10 kHz repetition rate. The pulses in the train are split by a series of beamsplitters to accommodate multiple pump-probe experiments across the optical table. Notable allocations include two 110 μ J portions that drive two independent noncollinear optical parametric amplifiers (NOPAs), as well as a 200 nJ portion that generates a white light supercontinuum.

2.3.1 Noncollinear Optical Parametric Amplification

NOPAs are tools to generate ultrashort pulses over a wide tunable range from the near UV to near IR. [32] The optical parametric amplification is accomplished in a nonlinear crystal medium, which mediates transfer of energy from a pump beam to a signal beam. The pump beam effectively amplifies an input lower frequency signal beam, and a third idler beam is produced as a result of momentum and energy conservation. Alignment of the proper momentum conservation conditions is critical to produce a maximally amplified signal. This is tuned by adjusting the angle of the nonlinear crystal, typically β -Barium Borate (BBO), so that the anisotropic polarization of the crystal is along the ideal conditions for the desired amplification frequency. Control of the angle that the signal and pump beams meet inside the crystal can compensate for frequency dispersion. When both conditions are met, broadband pulses can be produced over the visible regime. The broad bandwidth output is necessary to reach a transform limit below 30 fs. [33]



Figure 2.2: The NOPA contains a beamsplitter (BS), concave spherical mirrors (SM), and a lens pair that acts as a telescope. A variable delay stage allows for matching the timing of the pump and supercontinuum pulses in the amplification BBO. The amplification of the green portion of the white light is depicted.

The design of the home-built NOPAs used in this work is schematically depicted in Figure 2.2. Construction and optimization was done to produce suitably broadband and short pulses for use in pump-DFWM. The fundamental input beam is split 98:2 by a beamsplitter, and the lower intensity portion generates a seed pulse while the higher intensity portion goes towards the pump pulse. The seed is generated as a white light supercontinuum by focusing in a 3 mm sapphire. The other path serves as the pump, where a lens pair telescopes the fundamental to a smaller diameter to fit through a 0.5 mm BBO cross-section, creating a frequency-doubled 400 nm pulse. Both pulses are crossed in a 1 mm BBO where parametric amplification occurs. The delay stage facilities matching the arrival times of the two pulses at the BBO. An important parameter in the design is the all-reflective path of the white light. Using curved mirrors rather than lenses reduces chirp, and aids in generating more bandwidth in the output. The sapphire is also carefully positioned such that the point of supercontinuum generation is near the exit side in order to minimize the path length of material that the white light travels through. Additionally, the seed and pump beams are not focused together directly in the amplification BBO. Instead, they are focused ~ 1 inch in front of the crystal to preserve the BBO from damage. However, the divergence cones of the pump and seed must be matched to produce a spatially symmetric amplified beam spot. Alignment is typically focused on adjusting the beam crossing angle, BBO tilt angle, and the pump delay. When all three parameters are properly set, broadband amplification is achieved. The NOPA output is sent through a BK7 prism pair for temporal compression. [34] Figure 2.3 shows an example output spectrum and the pulse measurement in the time domain. The depicted pulse had an energy of 6.5 μ J.



Figure 2.3: At the correct alignment conditions, the NOPA outputs a very broadband amplified spectrum. The measured auto-correlation produces a pulse duration below 10 fs.
2.3.2 Cross-Correlation

Measurement of the temporal width of the optical pulses used cannot be done by simply recording the response of a photodiode on an oscilloscope, because the response times of electronics are not fast enough; instead, the optical pulse can be used to measure itself or other pulses. [35] The characterization of the pulse durations used in measurements is important, as it dictates the time resolution of the experiment. Several styles of cross-correlation and auto-correlation were thus used in this work. Cross-correlation involves the mixing of two different beams in a nonlinear medium to produce a signal. Auto-correlation uses the same beam, split and recombined with itself. In either case, one pulse is swept across the other in time and the intensity of the nonlinear signal is recorded as a function of the relative timing. Most often, second harmonic generation (SHG) between the two pulses is performed in a BBO crystal to produce this correlation trace. The intensity of the SHG signal is a convolution of the two pulse envelopes. The tilt angle of the BBO must be set correctly to produce a SHG signal, and the weak signal may be difficult to work with since it is typically in the UV. Alternatively, a silicon carbide photodiode can be used to perform twophoton absorption based correlation. In this case, the beams are spatially overlapped on the detector. The bandgap of the detector is too large to register wavelengths in the optical range, but a photocurrent is generated when two-photon absorption occurs at double the photon energy. This method is not feasible when using pulses in the UV, which span the bandgap on their own, or for near-IR pulses when the sum of the pulse energies is lower than the silicon carbide bandgap. For autocorrelation traces, the FWHM of the trace can be used to calculate the width of the pulse profile required to produce the recorded convolution with itself. The auto-correlation trace of a 9 fs sech² pulse is shown in Figure 2.3. This output is close to the shortest pulse achievable with conventional NOPA and compression techniques. Three pulse auto-correlations were also be performed, with a different factor used to calculate the input pulse durations. Self-diffraction in this glass produced a convolution signal for three pulse experiments. The width of the cross-correlation between pump and probe pulses was used to define the instrument response function for experiments in this work.

2.4 Transient Absorption Spectroscopy

Transient absorption spectroscopy is used to measure the absorption spectrum of photoexcited species. An overview of the technique can be found in [36]. In brief, a pump pulse promotes the analyte to an excited state, and a probe pulse immediately follows. The spectrum of the probe pulse is recorded after the sample has been photoexcited, and when the sample has not been perturbed by a pump pulse. The difference in absorption of the two spectra is a transient absorption spectrum. This difference spectrum isolates absorption features in the probe pulse induced by the pump pulse. What is produced is a spectrum of the *change* in absorption, reported throughout this work as: ΔA . Unlike absorption from the ground state, the change in absorption can be negative. The delay between the pump and probe pulses can be systematically varied, and the time-dependence of ΔA can be followed on an ultrafast timescale, limited by the pulse durations. Snapshots of ΔA captured by the probe pulse at multiple delay points are presented throughout this work as two-dimensional maps as functions of wavelength and time.

There are four general contributions to ΔA . Perhaps the most intuitive is excited-state absorption. This appears as a positive signal where absorption from the initially prepared excited state can proceed to even higher-lying states. Excited-state absorption can generally appear at spectral locations that differ from ground-state absorption, and is not directly related to the ground-state absorption features. The dynamics in excited-state absorption are related to the relaxation pathway through available electronic states and their vibrational levels. Another prominent signal contribution comes from ground-state bleach. This appears as a negative contribution to ΔA . The ground-state absorption becomes weaker after some sample fraction has been promoted to an excited state. Accordingly, peaks in the ground-state spectrum will appear as negative peaks in the ΔA spectrum since less absorbers are present for that transition. A third signal contribution is from stimulated emission. Based on first order selection rules, transitions from the excited state down to the ground state are also allowed if the reverse transition is allowed. [37] Therefore the probe pulse can stimulate a downward transition when it interacts with the excited state. This appears as a negative signal, since it manifests as an increase light (the opposite of absorption) after excitation. Stimulated emission is often spectrally overlapped with ground-state bleach or is located where the fluorescence emission band is located. The fourth signal contribution is from photoinduced product absorption. If excitation led to the generation of new chemical species, such as excimers, charge-separated states, or any photochemical product, the absorption of the new chromophore will be present as a positive signal contribution. The time delay when the pump and probe pulse overlap is referred to as time-zero. At time-zero, additional signal contributions can be present from undesired nonlinear effects of the coherent pulse interactions beyond the transient absorption. [38] These effects are called a coherent artifact, and do not affect the longer term dynamics. Measurement of the ΔA from a blank solvent can be used to confirm the presence of this artifact, though it cannot be reliably subtracted out from sample measurements.

Transient absorption measurements in this work were carried out using a NOPA as a tunable pump. A broadband supercontinuum was generated in a 3 mm sapphire and compressed using a pair of dispersion compensation mirrors (Laser Quantum, DCM12) to function as the probe. The optical layout is depicted in Figure 2.4. The spectrum of the probe pulse is displayed in Figure 2.5. The pump beam duration was minimized by a prism compressor in the beam path. An off-axis parabolic mirror was used to collimate the white light rather than a lens to avoid dispersion. The chirp of the supercontinuum was reduced through six bounces off of the dispersion compensation mirrors. Each reflection imparts negative chirp on the pulse by effectively providing a longer path length for longer wavelengths using multilayered high reflective dielectric material. These mirrors also compensate for the frequency dependent shift of timezero. In this way, the instrument response function was kept under 35 fs. The pump beam passed through a chopper wheel before incidence on the sample. Pump and probe



Figure 2.4: Transient absorption spectroscopy is performed using a chopped pump beam on a variable delay path, and a supercontinuum probe beam on an all-reflective path. The probe pulse is compressed with a dispersion compensation mirror (DCM) before its focus on the sample by an off-axis parabolic mirror (OAPM).

beams were kept at magic-angle polarization difference of 54.7° to avoid measurement of orientation-dependent dynamics in the samples. Both pulses were focused by the same 200 mm focal-length off-axis parabolic mirror onto the sample. The pulse properties for individual measurements are described in each chapter. For solution measurements, 1 mm path length cuvettes (Starna) were used. The cuvette was mounted on an x-y translation stage to optimize the position of beam overlap and minimize excess sample penetration. Solid-state samples were mounted in a sealed vacuum chamber, built from a modified microscopy cryostat (CIA, RC102-CFM) connected to a turbomolecular pump (Pfieiffer, HiPace80). Pressures of 10^{-7} Pa were typical. The vacuum chamber was mounted on an x-y-z translation stage and equipped with two 0.5 mm fused silica windows spaced 25 mm apart to facilitate alignment and transmission of the optical pulses. The vacuum environment reduces oxidation, sample damage, and any solvent effects.



Figure 2.5: The detected spectrum of the supercontinuum probe pulse is spread across the visible region from 450 nm to 750 nm.

Two different detection schemes were implemented over the course of this work. Originally, the signal was collected through a monochromator (Oriel, CS260) as single

wavelength kinetics. Lock-in amplification (Signal Recovery, 7230) was used with a silicon photodiode (Thorlabs, DET10A). The chopper frequency was set to 337 Hz, and the phase of the lock-in signal was adjusted using a known reference sample's signal (Zn-TPP). Transient absorption spectra were produced by scanning the monochromator at fixed pump delays. The monochromator grating was blazed at 475 nm with 300 lines/mm. This detection method was used for measurements discussed in Chapter 3 and Chapter 6. Later, a multichannel detection scheme was implemented for simultaneous acquisition of spectra at various time points. This method allowed for more rapid data collection, and was used for measurements featured in Chapter 4 and Chapter 5. A 1024 pixel CCD array (e2V, EV71YEM1GE1014) was used for shot-toshot detection. The line scan rate of the camera provided acquisition of spectra from single laser shots at a 10 kHz rate. The chopper was then set at 5 kHz to block every other pump pulse, and difference spectra were calculated from subtraction of subsequent probe pulse spectra from each other. The phase of the chopper was adjusted using the signal from a known reference sample (Zn-TPP). A detailed discussion of both detection methods and alignment procedures for each is provided in [39].

Regardless of detection method, transient absorption signals at individual wavelengths, σ_{λ} , are fit with the expression

$$\sigma_{\lambda} = \sum_{i=0}^{n} A_{i}^{\lambda} N_{i} \tag{2.2}$$

The independent amplitude at each wavelength and the population of each state are represented by A_i^{λ} and N_i respectively. The number of states involved in the dynamics are represented by the *n* terms of the summation in equation (2.2). This parameter is held to the minimum value that allows for fitting the signals at all wavelengths without a systematic deviation of the residuals. Initial fits are performed at spectral peaks in the spectrum and suspected representative wavelengths. The total signal at a given wavelength therefore composed of weighted contributions from the population of each state. The time-dependent population of each state is obtained by solving a set of linear rate equations allowing for parallel and sequential decays which represent the species-associated difference spectra relaxation model, i.e.

$$\frac{dN_0}{dt} = -A \cdot g(t) + \sum_i \frac{1}{\tau_n} N_n \tag{2.3}$$

$$\frac{dN_1}{dt} = A \cdot g(t) - \sum_k \frac{1}{\tau_1} N_1$$
(2.4)

$$\frac{dN_i}{dt} = \sum_{l} \frac{1}{\tau_{i-1}} N_{i-1} - \sum_{m} \frac{1}{\tau_i} N_i$$
(2.5)

Here τ_i denotes the time constant associated with a state's $N_i \to N_{i+1}$ population transitions. The $A \cdot g(t)$ term acts as a population source representing the pump pulse, and is composed of amplitude A and the Gaussian envelope:

$$g(t) = e^{\left[-4\ln(2)\left(\frac{t-t_0}{W}\right)^2\right]}$$
(2.6)

The pulse function considers W as the full width at half maximum of the pumpprobe cross-correlation. The fitting procedure attempts to find a set of global parameters $[A_i^{\lambda}, \tau_i]$ that produce the best fit across all measured wavelengths.

2.5 Pump-Degenerate Four-Wave-Mixing Spectroscopy

Pump-degenerate four-wave-mixing (pump-DFWM) is a vibrationally sensitive ultrafast spectroscopy technique. The physical principles of the method are fully described in reference [40]. Similarly to transient absorption, an initial actinic pump pulse promotes the sample to an excited state as the first step. Instead of a single probe pulse though, a sequence of three degenerate pulses with identical spectra is used to probe the excited state. The three pulse sequence accomplishes degenerate four-wave mixing (DFWM) on the photoexcited sample. The time ordering of the series of pulses is depicted in Figure 2.6.

DFWM can be understood as a form of transient grating spectroscopy, or a broadband stimulated Raman scattering (SRS) method. From the SRS perspective,



Figure 2.6: The time ordering of the pump-DFWM sequence consists of an initial actinic pulse to promote the system, to an electronically excited state, followed by a set of pulses that generate a DFWM signal on the excited state. Evolution of the excited state is tracked by varying 'T', and wavepacket dynamics are followed by scanning 't'. The DFWM pump and Stokes pulses are kept coincident in time.

the initial two pulses in the DFWM sequence act as a Raman pump and Stokes pulse. The bandwidth of the degenerate pulses exceeds the vibrational energy level spacing of the molecular analyte. Therefore, when the Raman pump excites the molecule, the Stokes pulse can immediately stimulate a transition through a resonant vibrational spacing. The energy difference that satisfies the Raman scattering transition is contained in the pulses and thus resonantly enhanced. The third pulse acts as a probe of the scattering transition and takes advantage of momentum conservation when a proper beam geometry is exploited. The directionality of the stimulated signal can be directed along a background-free path. From a transient grating perspective, DFWM operates by inducing a polarization grating in the sample through the pump and Stokes pulses. These two pulses are incident on the sample at an angle to each other, and produce a modulated excitation in the molecular medium. The third probe pulse may then interact with the grating and send a diffracted beam in a new direction. Phase stability of the pulses on the nanometer scale is important to preserve the effective line spacing of the induced grating. Similarly to Raman spectroscopy, the perturbed polarizability leads to a coupling of electronic and vibrational effects, and the modulation of the



Figure 2.7: A vibrational wavepacket is prepared by impulsive excitation in an arbitrary excited state (ES_{α}) . DFWM pulses serve to probe the time-dependent evolution of the packet through resonant absorption to a higher-lying excited state (ES_{β}) .

signal carries information on the vibrational modes. Pump-DFWM can also be viewed from a wavepacket perspective. The initial actinic pump is spectrally broad and acts impulsively on the sample. The pulse impulsively prepares several vibrational eigenstates of the electronic excited state, which coherently form a vibrational wavepacket in the excited state potential energy surface. This is illustrated in Figure 2.7. The DFWM sequence then serves to probe the status of the wavepacket through stimulated Raman transitions. If the DFWM pulses are resonant to an electronic transition to a higher-lying state, the signal is amplified through resonance enhancement. As the wavepacket evolves in its potential, over actinic pump delays, the DFWM probe sequence can follow the Raman active vibrational modes and their coherence. Through resonant enhancement, spectral tuning of the actinic pump can thus prepare a targeted excited state, and spectral tuning of the DFWM sequence can probe vibrational dynamics of targeted excited-states.

Two iterations of DFWM instruments were built and commissioned over the

course of this work. The initial optical setup is depicted in Figure 2.8. Measurements were carried out using two NOPAs. The output of one NOPA was split into three pulses forming a DFWM probe sequence in a BOXCARS phase matching geometry, generating a spatially separated signal through momentum conservation. The probe delay was varied by a fast scanning piezo stage (Piezosystem Jena, PX-400-SG). The actinic pump pulse travels through an independent delay stage. All beams were aligned to be parallel and then focused by a shared off-axis parabolic mirror onto the sample. The generated DFWM signal beam was directed to the monochromator described in section 2.4 and detected by a photomultiplier tube (Hamamatsu, H7827-012). A chopper wheel blocked every other pump pulse, allowing for shot-to-shot subtraction and removal of signal contributions not induced by the pump pulse. This setup was used to collect the data discussed in Chapter 3.

The second iteration of pump-DFWM instrument is depicted in Figure 2.9. The same vacuum chamber described in section 2.4 was used to measure solid-state samples. This setup featured the same piezo delay controller and independent delay of the actinic pump that was chopped at 5 kHz. The main advantage gained from the newer design is its inherent phase-stability. The design was based on two-dimensional spectroscopy instruments. [41, 42] The beam paths are distributed such that any induced phase disturbances at each reflection are canceled out by the other beams. The passively phase-stable setup eliminates low-frequency noise caused by mechanical vibrations and increases the beam pointing stability of the probe sequence. This stability leads to a reduction in optical scattering from the sample. This setup was used to collect the results discussed in Chapter 4. The improved setup was critical for measurement of colloidal, highly scattering, thin film samples. After the sample, a 200 μ m pinhole was mounted on a xy translation stage and placed in the path of the signal beam in order to spatially filter out scattered contributions. Careful vertical and horizontal alignment of the pinhole was performed to optimize the spatial filtering and retain maximum signal. The beam was then recollimated and traveled 1 m before entering the monochromator. An attempt was made to directly place an optical fiber with the same diameter in lieu



Figure 2.8: In the initial setup, two beamsplitters (BS) separated an input pulse into three spots for the DFWM sequence. The beams were arranged into the corners of a square (BOXCAR geometry) and focused onto the sample solution by a shared off-axis parabolic mirror (OAPM). The actinic pump pulse was independently delayed, and focused by the same mirror.

of the pinhole; however, this did not lead to an increase in signal-to-noise. The 1 m beam path instead effectively served to eliminate nearly collinear scattered light and allow it to diverge away from the signal before entering the monochromator.



Figure 2.9: The second pump-DFWM instrument utilized three beamsplitters (BS) to create the three pulse DFWM sequence. A fourth pulse is also created, but was blocked and not used. The shared reflective surfaces provide a passively phase stable setup. The actinic pump is focused along with the DFWM beams by a spherical mirror, redirected towards the sample. A vacuum chamber was used for solid-state samples, and a pinhole spatially selected the signal beam.

The DFWM signal is produced as an oscillating time-domain plot. The amplitude of the modulations is related to the induced polarizability grating, and the frequency of the modulations directly corresponds to the Raman-active vibrational modes of the sample. The time-domain signal can be put through a Fourier transform to reproduce Raman spectra. The general data treatment process is summarized in Figure 2.10 for an arbitrary signal. Population dynamics can be superimposed on the signal and are removed by exponential fitting and subtraction. During data acquisition, the piezo stage is left free-running to follow a 10 Hz sinusoidal voltage. Due to the 10 kHz repetition rate of the laser system, 1000 data points are thus collected for every time trace sweep. The rapid free-running nature of the DFWM delay allows for real-time alignment of the instrument on the frequency spectrum. A constantly updated fast-Fourier transform is displayed on acquisition software, and the visible vibrational modes can be used as a target to maximize. This process is more straightforward than optimizing on the time-domain signal, which can offer deceptive results and has a more difficult to identify signal maximum. Furthermore, the accessible frequencies can indicate the lower bound of the pulse duration; if known high frequency peaks are not detected, the probing pulses may not be short enough to sample their vibrational periods. The specific resolutions, pulse properties, and time-windows used varies for each experiment, and these parameters are discussed in their respective chapters. For collection of excited-state vibrational dynamics, shot-to-shot subtraction was used. Alternating pump pulse shots were blocked by the chopper wheel, and the data acquisition software organized each measurement as 'pump-on' or 'pump-off'. The organized time-domain signals were then subtracted. The difference signal was verified as flat for all measurements before time-zero. An additional photodiode was placed in the path of the pump beam prior to the sample to verify that the pump pulse maintained a consistent 5 kHz repetition. If the diode received an errant pulse, or missed a pulse, the data collection software recorded an error message. In this way, vibrational dynamics induced by the pump pulse can be isolated.



Figure 2.10: The raw oscillatory data of the DFWM pulse intensity is collected in the time domain over a time window scanned up to 2 ps (a). The first 100 fs are removed to avoid coherent artifact contributions. The signal is fit with a single exponential decay (b). The fit is subtracted from the signal in order to remove the non-oscillatory component (c). The data is then zero-padded and put through a discrete Fourier transform using a Hanning window to produce a frequency spectrum (d).

2.6 X-Ray Transient Absorption Spectroscopy

X-ray transient absorption (XTA) is a pump-probe pulse technique, analogous to optical transient absorption described in section 2.4. An optical laser pulse is used to pump the sample, and the induced dynamics are probed by an X-ray pulse. Using an X-ray probe allows transient structures associated with reaction dynamics to be accessed by X-ray absorption spectroscopy (XAS). [43, 2, 44] Unlike optical absorption, which is sensitive to electronic transitions, the XAS spectrum is sensitive to atomic transitions from inner-shell orbitals to unoccupied orbitals and to the continuum. [45] The spectrum is divided into two main regions: the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The XANES energy region includes the region of onset of the absorption edge, as the name indicates. This includes the pre-edge and edge shapes. The EXAFS portion on the other hand is at energies above the transition edge. XANES spectra can report on the transitions from core levels to vacant states. This can provide information on the local coordination environment near the absorbing atom. With XTA, changes in coordination can be directly investigated in photoexcited species. [46] The transition edge of the XANES region is often composed of multiple entangled scattering signals and becomes difficult to interpret, although some metals have structural signatures that can be identified for specific transitions. [47] The EXAFS region is sensitive to scattering of the photoelectron wave originating from the absorbing atom. Interference from neighboring atoms produces characteristic wavy EXAFS spectra. The complex EXAFS scattering signal can be modeled by the following equation:

$$\chi(k) = \sum_{j} \frac{N_{j} F_{j}(k) e^{-2k^{2} \sigma_{j}^{2}}}{k R_{j}^{2}} sin(2k R_{j} + \delta_{j}(k))$$
(2.7)

Here j is the index of the local atomic shells around the scattering atom, N is the coordination number, f(k) is the amplitude of the backscatter, σ^2 is the thermal disorder in the distances, k is the wave-vector, R is the average distance, and δ is the phase shift. Using this model along with an estimated input structure, the EXAFS signal can experimentally identify the measured molecular structure within hundredths of Ångströms. A transient EXAFS signal can thus provide detailed information on non-equilibrium structural states.

XTA experiments discussed in Chapter 5 were performed at beamline 11-ID-D at the Advanced Photon Source of Argonne National Laboratory. The X-ray pulses were generated from synchrotron radiation. A detailed description of the beamline parameters and capabilities can be found in reference [3]. The pulse scheme is depicted in Figure 2.11. Measurements were carried out in 24 electron bunch mode, where 24 evenly distributed electron bunches are circulated in the storage ring and produce radiation at the sample at a rate of 6.5 MHz. The laser pump pulse was 1 ps in duration, and the X-ray probe pulse was 80 ps. The excitation energy was 50 μ J. The excited-state lifetime of the samples measured was verified to be on the nanosecond timescale so that they could be probed by the relatively long X-ray pulses. Time-zero is defined at a delay of 120 ps after photoexcitation, because that is the time point when the maximum excited-state fraction can initially be probed. Experiments were carried out at 1 kHZ based on the laser repetition rate. Multiple X-ray pulses probe the sample before the next excitation pulse arrives, and any long-lived dynamics could be investigated. The time between X-ray probes was 154 ns. The laser was electronically gated to record ground-state spectra throughout the experiment from the same electron bunch.

The sample chamber and beam paths are displayed in Figure 2.12. Pump and probe beams meet at 20° in the sample. Concentrations of 20 mM in ethanol were used. The sample was recirculated through a flowing liquid jet using a peristaltic pump. A heart chamber reservoir was continuously bubbled with nitrogen and the system was largely sealed from atmosphere to minimize oxidation. The emitted fluorescence is proportional to the amount of absorbed X-ray radiation. Soller slits with glued-on Z-1 filters were in place in front of the photodiodes. Two avalanche photodiodes on either side of the chamber collect X-ray fluorescence from the chamber. Two detectors are used in order to double the collected signal. Additionally, if the signal from one



Figure 2.11: The laser pump generates an excited state probed by X-ray pulses. Pulse timing is described in the text. Adapted with permission from [2]. Copyright 2013 American Chemical Society.

photodiode begins to differ from the other, it can indicate that an issue has arisen with that detector. A separate avalanche photodiode is upstream of the sample. This detector serves as a reference to adjust for pulse-to-pulse intensity fluctuations. The intensities of the two diodes collecting sample fluorescence were normalized to the intensity of the reference detector for each pulse. The recirculating sample jet was carefully adjusted to maintain laminar flow in the chamber in order to avoid noise from density fluctuations in the beam path. The flow was constantly monitored over video camera to ensure no deviations occurred.



Figure 2.12: The sample chamber utilized a recirculating flowing jet. Two detectors on the sides of the sample chamber collect emitted X-ray fluorescence. A normalization detector collects X-ray emission from air before the sample. Reprinted with permission from [3]. Copyright 2013 American Chemical Society.

2.7 Materials

The materials chosen for investigation satisfy two fundamental conditions. First, they must be scientifically relevant. Their properties may not be fully understood or they may provide new information towards a meaningful topic. Secondly, they need to be experimentally accessible. The properties of the materials must be suitable for investigation by the methods available. Metalloporphyrins and substrates studied in this work meet both of these critical criteria.

2.7.1 Metalloporphyrins

To study the dynamics of nuclear motion in molecular excited states, different metalloporphyrins were used. This class of molecules exhibits strong absorption in the visible region, making them relevant for practical light-driven photochemical applications. This also makes them accessible for investigation by standard light sources. The basic metalloporphyrin structure is a set of four pyrrrole groups linked together at their α carbons by methine connections to form a single ring, with a single metal atom bound at the center by the inward-facing nitrogens. The conjugated ring contains 18 π electrons, and the planar structure has D_{4h} symmetry. These molecules are commonly modified by adding substituents and changing the central metal ion. Functionalization can alter the electronic structure and available transitions, to effectively enhance the light absorption properties, reactivity, or physical behavior of the system. [48] Some naturally occurring metalloporphyrins are famously found in chlorophyll, hemoglobin, and the mitochondrial electron transport chain. Synthetic porphyrins are used in a wide range of applications, from medicinal chemistry to materials science.

The majority of this work used zinc-tetraphenylporphyrin (Zn-TPP) and variations. The Zn-TPP skeletal structure is shown in Figure 2.13. Zn-TPP was purchased from Sigma-Aldrich. A common modification, present in Chapters 4 and 5, was the addition of a carboxylic acid group on the exterior by synthetic collaborators in the Galoppini group. [49] The carboxylic acid facilitates chemisorption to TiO_2 surfaces and allows efficient electron transfer through the linker. [50] This metalloporphyrin variation serves as a prototypical system, and its behavior is often taken as representative of a wide range of similar systems. [51] Because it as among the most well-studied porphyrins, new information on vibrational and structural effects in the behavior of photoexcited Zn-TPP is informative to a broad community. Solution phase studies in this work used tetrahdrofuran (THF) as a solvent. Zn-TPP is highly soluble and weakly coordinating in this solvent. THF also has minimal overlapping vibrational modes with Zn-TPP, which simplifies pump-DFWM spectra. The molar absorptivity (ε) of Zn-TPP in THF was found to be 5.71 × 10⁶ M⁻¹ cm⁻¹.



Figure 2.13: The structure of Zn-tetraphenylporphyrin consists of a porphyrin ring with phenyl groups at the *meso* positions.

The characteristic UV-Vis absorption spectrum of metalloporphyrins consists of two major bands. The complex electronic structure of the aromatic system allows multiple transitions between various molecular orbitals. The first absorption band, called the Q band, corresponds to excitation to the first excited singlet state, S_1 . This band is typically in the visible region, and can be quite broad. The high degree of symmetry in metalloporphyrins leads to splitting of the Q band, which widens the absorption features. Modifications to the molecular symmetry by additional substituents accordingly alters the shape and position of the Q band. The second absorption band is from the transition to a second excited singlet state, S_2 , and is called the Soret band. This band is typically more intense and more narrow than the Q band. Typically the Soret band absorbs in the near UV region.

The optical absorption transitions are often explained by the "Gouterman four orbital model". [52] This model describes the degeneracy of several molecular orbitals as the origin of the Soret and Q bands. Two degenerate HOMOs can transition to two degenerate LUMOs. These degeneracies are a natural consequence of the D_{4h} symmetry and aromaticity of the porphyrin system, and are altered by structural modifications. This simple model is sufficient to approximate basic metalloporphyrin transitions, but more accurate models have been developed through density functional theory (DFT) methods. [53] The extensive overlap of HOMOs and LUMOs complicates interpretation of electronic spectroscopy results, as discussed in Chapter 3.

2.7.2 TiO₂

For experiments on heterogeneous electron transfer, TiO_2 was used as the electron acceptor substrate. TiO_2 is an extensively studied, well-understood, and commonly used material for photoinduced HET. [54, 55, 56, 57, 58, 59, 60, 61, 62] TiO₂ is a cheap and nontoxic material. Films of TiO₂ on thin glass were prepared for molecular sensitization. The films were composed of colloidal nanoparticles of anatase TiO₂. The anatase phase unit cell is octahedral, with a central titanium atom surrounded by six oxygens. [63] The band gap of 3.2 eV for anatase TiO₂ films makes it suitable for dye-sensitized solar applications. The UV band gap will not be spanned by visible energy photons. However, an attached dye can absorb visible light and transfer electrons into the TiO₂ conduction band. Nanoporous films offer a high surface area for dye coverage.

Thin films used in this work were prepared by spreading a solution of colloidal TiO_2 nanoparticles onto 50 µm thin AF45 Schott glass. The solution was spread onto the glass by sliding a filled reservoir with an angled razor blade opening on its edge across the surface, in the so called "doctor blade" method. [64] The colloidal sol-gel solution was synthesized through hydrolosis of Ti(IV)-isopropylate with aqueous nitric acid and autoclaving, as described in reference [65]. The alkali-free glass eliminates

the possibility of diffusion of alkali atoms into the TiO_2 lattice, which can degrade the material and alter measured dynamics. [66] The thickness of the glass is small in order to reduce coherent artifact contributions in ultrafast measurements. The resulting films had a TiO₂ layer of ~10 µm thickness. The effective surface area of the film was 140 m²/g. [67] The nanoparticles had an average diameter of 15 nm, as shown by scanning electron microscopy in Figure 2.14. Prepared films were stored in a desiccator under vacuum at 10^{-3} Pa prior to dye-sensitization.



Figure 2.14: A scanning electron microscope image of the colloidal TiO_2 shows the size of the individual nanoparticles.

Sensitization of the films with metalloporphyrin dyes was performed in several steps. First, the film was heated in a tube furnace for 45 minutes at 450° C. This removes any residual oxidized species from the preparation process. The film was then immediately transferred to soak in a solution of dye molecules. Solution concentrations were on the order of 100 μ M, and the film was left to soak for 30 minutes. Next, the film was blown dry with argon gas and rinsed several times with solvent to remove any unbound molecules. The solvent rinse was taken in aliquots, which were later measured for fluorescence. A loss of fluorescence in the later aliquots validated complete rinsing of the film. The dye adsorption occurs from the carboxylic acid linker on the molecules to the TiO₂. Binding is accomplished from chemical attachment of the oxygen atoms in

the linker group to titanium atoms on the surface. Monodentate and bidentate ligation are possible. $\left[68,\,69\right]$

Chapter 3

ZINC PORPHYRIN VIBRATIONAL DYNAMICS IN SOLUTION

3.1 Abstract

In this chapter, results from pump-DFWM on Zn-TPP in solution are presented that clarify information gained from transient experiments. The vibrational modes of the Zn-TPP molecule are observed from DFWM measurements on varying prepared states and compared. The electronic ground state, a vibrationally hot electronic excited state, and a vibrationally cold electronic excited state are independently prepared by varying the excitation energy of the pump laser pulse. The vibrational spectra produced and their dynamics are analyzed and discussed. Taken alongside complementary transient absorption measurements, the DFWM results establish vibrational relaxation as physical mechanism responsible for often-observed ultrafast relaxation kinetics that immediately follow photoexcitation of the Soret band of Zn-TPP, which has been a source of debate in previous literature. This chapter is largely adapted with permission from reference [70]. Copyright 2016 American Chemical Society.

3.2 Background and Motivation

While many aspects of Zn-TPP excited-state dynamics are well understood, one remaining question concerns the initial relaxation in the S_2 state. Although Zn-TPP is one of the most extensively studied metalloporphyrins, and its excited-state dynamics frequently serve as a reference for other more complex systems such as aggregated and substituted porphyrins, [71, 72, 73, 74, 75] a remaining question exists concerning the initial relaxation in the S_2 state. A characteristic rate constant on the order of 100 fs has been consistently observed for early dynamics in this representative porphyrin by multiple research groups, and some controversy exists whether this process can be attributed to vibrational relaxation in the S_2 state or if a second excited state, S'_2 , is responsible. [76, 77, 72] The rapidity and antecedence of the dynamics has led to a general assumption that some type of vibrational relaxation is involved. [78, 72] However, no direct measurement has been previously presented to confirm this assertion. Difficulty in pinpointing the mechanism has likely stemmed from the need for high time resolution required to observe sub-100 fs dynamics, and the need for tunable excitation in to order prepare initial states of slightly different energies. Furthermore, TA results are complicated by the broad and overlapping spectral features of Zn-TPP.

This initial ultrafast decay process was first reported by Gustavson's group through a time resolved fluorescence study, and was assigned to vibrational relaxation (IVR). [78] Zewail's group later observed this fast time constant in transient absorption measurements and assigned it to a distinct higher lying electronic state above the S_2 energy surface. [76] Enescu et al. further confirmed the existence of fast dynamics in or above the S_2 state and assigned it to a relaxation of the coherently excited degenerate S_2 state. [77] The Steer group has discussed both possibilities without giving an unambiguous assignment. [79, 80] Apart from the fundamental aspect of expanding the understanding of porphyrin photophysics, the identification of this process serves as an important input for theoretical models which fail in many cases to accurately predict the complex degeneracy of states in metalloporphyrins. [81, 82, 83, 84] Additionally, applications such solar energy conversion and photocatalysis rely on excitedstate processes occurring on the femtosecond timescale which may compete with the intramolecular dynamics under investigation. [85] Focus in the following sections is thus placed on unequivocal assignment of the initial relaxation dynamics of Zn-TPP. Pump-degenerate four-wave mixing is used to study vibrational dynamics over the first several hundred femtoseconds occurring after excitation.

3.3 Steady State Results

Prior to performing ultrafast experiments, steady-state absorption and fluorescence measurements were carried out to ensure the integrity of prepared Zn-TPP solutions and verify that sample degradation or molecular aggregation did not influence the dynamics. It is known that the dynamics of porphyrin excited states are particularly susceptible to aggregation induced complications, including $\pi - \pi$ stacking, metal ligation, and exciton coupling. [86, 87, 88, 89] A series of solutions was therefore prepared in a wide range of concentrations to investigate possible changes of the electronic spectrum of the sample. Solutions of Zn-TPP dissolved in tetrahydrofuran (THF) from 0.1 μ M to 100 μ M were analyzed using UV-Vis absorption and fluorescence spectroscopy. This concentration range was chosen to span the range typically chosen for ultrafast measurements, and to reach relatively high and low values between which J-aggregation would be expected to appear. [90] The concentrations were also kept within the linear response range of the instrumentation used. Solutions of 1 μ M and below are thought to be below the threshold for molecular aggregation, which is thoroughly encompassed by the range investigated. [91]

The normalized absorption spectra of the Soret band for Zn-TPP samples of 1 μ M and above are shown in Figure 3.1. A 1 mm path length cuvette was used. No broadening of the absorption profile or shifting of the peak was observed in the overlayed spectra. No evidence of J-aggregation or other distortions of the electronic spectrum was exhibited across this range of THF based solutions.

Fluorescence excitation-emission spectra are displayed in Figure 3.2. Solutions were contained in a 10 mm square cuvette. The concentrations accessible extend one order of magnitude below those in UV-Vis absorption. No change in the fluorescence profiles was observed from 0.1 μ M to 5 μ M, providing further assurance of sample purity. Since 0.1 μ M solutions are well below the expected aggregation threshold, the unchanging fluorescence matrices show that Zn-TPP exists primarily as a monomer at concentrations up to 5 μ M. The concentration range overlaps between the fluorescence



Figure 3.1: The normalized Soret absorption profile of Zn-TPP in THF is unaltered over a broad range of concentrations. There is no signature of J-aggregation at concentrations up to 100 μ M.

and absorption measurements. Therefore the lack of aggregation signature in the fluorescence data is taken together with the unchanging absorption spectra in Figure 3.1 to conclude that no appreciable aggregation occurs in THF based Zn-TPP solutions up to 100 μ M. Zn-TPP has a relatively high solubility in THF, which helps mitigate aggregation. [92] The spectral features of the Zn-TPP electronic structure are consistent over the range of concentrations investigated, including the 50 μ M and 100 μ M concentrations used in the transient absorption and pump-DFWM experiments discussed in sections 3.4 and 3.5.

To further check for sample purity and degradation, liquid injection field desorption ionization (LIFDI) mass spectrometry (MS) was carried out on the 100 μ M sample after optical measurements were performed. The results are presented in Figure 3.3. This soft ionization technique induces minimal fragmentation of the analyte and signal is readily obtained from molecular ions. [93] No peaks were present in the



Figure 3.2: The normalized fluorescence excitation-emission spectra of low concentration Zn-TPP solutions in THF do not show signs of broadening in either the Soret or Q bands over a 50 fold concentration change.

calculated m/z region for demetallated Zn-TPP, suggesting that the molecules in solution did not suffer from loss of the central zinc atom to any significant degree. Only one isotopic pattern was predominantly detected, which is attributed to the Zn-TPP molecular ion, and no patterns from expected photoproducts or molecular substructures were found. These qualitative results provide evidence that the sample did not undergo any appreciable chemical degradation which would influence measurements of the dynamics.



Figure 3.3: The LIFDI-MS spectrum of the sample shows that the isotopic pattern obtained over the course of the measurement (a) was identical to the calculated pattern for the Zn-TPP (b). Monitoring the field desorption spectrum (c) for demetallated Zn-TPP as current was increased did not produce any ion peaks (d).

3.4 Transient Absorption Results

Two transient absorption experiments were performed on 50 μ M Zn-TPP THF solution, using the methodology described in section 2.4. One using a pump pulse centered at 420 nm, corresponding to excitation of on the high energy side of the ground-state absorption maximum, and another using a pump pulse centered at 430 nm, slightly lower energy than the Soret peak. The overlap of the excitation pulses spectra with the Zn-TPP ground-state absorption spectrum is shown in Figure 3.4.



Figure 3.4: The overlap of normalized spectra of the pump pulses used in this chapter with the absorption of Zn-TPP in THF illustrates the difference in excitation towards the high or low energy side of the Soret band.

The transient absorption map recorded after 420 nm excitation is shown in Figure 3.5. This map of ultrafast dynamics in the first picosecond of relaxation reproduces and confirms data presented previously in reference [72]. Across the visible spectrum, broad excited-state absorption is observed as a positive signal. Negative contributions from ground-state bleach of the Q band are observed in the regions around 560 nm and 600 nm.

The kinetics were fit by the global fitting procedure described in section 2.4, resulting in a rate model of five time constants as shown in Figure 3.6. The contributing



Figure 3.5: The transient absorption map collected after 420 nm excitation shows dynamic features throughout the visible spectrum within the first picosecond.

processes are as follows: $\tau_1 = 70$ fs, initial relaxation in or above S_2 ; $\tau_2 = 1.8$ ps, $S_2 \rightarrow S_1$ internal conversion (IC) predominantly around 650 nm; $\tau_3 = 10$ ps and $\tau_4 = 100$ ps, vibrational relaxation in S_1 ; $\tau_5 = 1.8$ ns intersystem crossing to T_1 . These measurements are in very good agreement with recent literature values, and individual kinetic traces at representative wavelengths and fits of the contributions to the data are displayed in Figure 3.7.



Figure 3.6: The relaxation path for Zn-TPP following excitation of the Soret band involves multiple steps and electronic states. The initial component is thought to be either IVR or conversion through a nearly degenerate dark state. Internal conversion to S_1 follows, wherein further IVR occurs in two steps, before crossover to the long lived triplet state.

The fastest component, τ_1 , has been assigned based on order of magnitude arguments only. [72] This component has been reported several times with time constants of around 100 fs. It contributes to the dynamics broadly across the probe spectrum, as seen in its species-associated difference spectrum shown in Figure 3.8. There are negative dips corresponding to regions of ground-state bleach in the transient absorption spectra. The component was attributed to S₂ population dynamics, because it was not present after excitation the Q band and it was not observed in stimulated emission from the Q band. Direct S₂ \rightarrow S₀ relaxation can also be ruled out for assignment, because ground-state bleach recovery was not observed on this timescale.



Figure 3.7: Selected kinetic traces from transient absorption at 420 nm are fit with contributions from a minimum of six states. Each component contributes to the signal across the spectrum to a varying degree, including a fast 70 fs relaxation from an unclear state.



Figure 3.8: Species-associated decay shows the spectral distribution of the 70 fs τ_1 contribution to the overall transient absorption dynamics that follow excitation at 420 nm.

Because IC from S_2 to S_1 occurs on a 1 ps timescale, the positive signal between 500 nm and 540 nm in the first few hundred femtoseconds predominantly originates from S_2 absorption. Internal conversion from a dark S'_2 state above S_2 , or relaxation inside the S_2 energy surface have consequently been discussed as possible explanations. The latter explanation raises the question of how vibrational relaxation manifests as a delayed rise time in the TA signal. It is not obvious why a cold S_2 state should have stronger excited-state absorption compared its vibrationally hot state. A peak shift is generally a more expected observation for cooling dynamics. The fact that the τ_1 component is observed specifically as rise of the TA signal is often neglected. Excitation on the low energy side of the absorption maximum can probe how the τ_1 process depends on the presence of excess energy.

The transient absorption map resulting from 430 nm excitation is presented in Figure 3.9. This map is very similar to the one in Figure 3.5, with the noticeable differences at very early delays. Fitting the data reveals that the signal rise is instantaneous within the instrument response of 25 fs, in contrast to measurements at higher pump energy. Comparison of kinetic traces and fits at representative wavelengths are shown



Figure 3.9: The transient absorption map of the first picosecond of relaxation after excitation at 430 nm contains positive and negative features across the spectrum.

in Figure 3.10.

For further comparison, the transient absorption difference map that results from subtracting measurement at 420 nm excitation from measurement at 430 nm excitation is shown in Figure 3.11. The difference map results most noticeably in a negative contribution across the majority of the probe spectrum from the missing 70 fs component. A positive contribution on the same timescale is present in the region where ground-state bleach spectrally overlaps with the τ_1 rise.

This positive region could possibly be explained by the difference between a vibrationally hot and cold S_2 state. In that case, the excited-state absorption of the hot S_2 would be initially red-shifted, causing a positive signal at 570 nm missing from the cold state. As vibrational cooling occurs, the signal would shift towards 550 nm and both contributing maps would become identical, leading to zero in the difference. This scenario of a red-shifted peak moving towards overlap of a cold state at a constant wavelength is simulated in Figure 3.12.

Based on the simple simulation, IVR is predicted to be observed as a blueshifting crossing point at zero on the difference map. Unfortunately, the experimental data is not conclusive in this regard. The negative contribution in the region of interest does shift towards lower wavelengths, but the positive contribution on the other side of the peak remains at a constant position. These dynamics are highlighted by the dashed white lines in Figure 3.11. Instead of a cooling process, a static zero-crossing line is indicative of a population between two states. This could be interpreted as an isosbestic point between states S'_2 at 570 nm and S_2 at 550 nm. Furthermore, the true dynamics of the possible spectral shift are not known, and are not necessarily linear. The difference map is also built from two normalized transient absorption spectra, which can introduce artifacts into the subtraction. Therefore, clear assignment of the physical process responsible for τ_1 is not possible from only these transient absorption measurements.


Figure 3.10: Normalized kinetic traces from the transient absorption maps and their fits at selected wavelengths highlight the difference in early dynamics from excitation at 430 nm (black) versus 420 nm (blue). A slower rise is exhibited from higher energy excitation, while traces produced using a lower photon energy pump rise within the instrument response time. The data from 430 nm excitation can thus be fit with one fewer components.



Figure 3.11: The map produced by normalizing and subtracting the data in Figure 3.5 from the data in Figure 3.9 shows major differences within the earliest dynamics. Dashed white lines highlight the region where positive crosses over to negative and shifting between vibrational or electronic states could be observed.



Figure 3.12: Subtraction of a stationary peak from a peak that is blue-shifting towards the same position produces a diagonal zero line. This simple simulation is representative of the expected result for Figure 3.11 in the event of vibrational relaxation, particularly at the area of its dashed lines.

3.5 Pump-DFWM Results

Pump-DFWM is well suited to investigate the vibrational dynamics of Zn-TPP on the timescale of the contentious time constant. Measurements were carried out using the method described in section 2.5 on Zn-TPP dissolved in THF at 100 μ M in a 1 mm path length cuvette. The instrument depicted in Figure 2.8 was used. The technique is sensitive to the vibrational modes coupled to electronic excitation, and can identify the relaxation of individual modes of the molecular excited state. The relaxation of modes coupled to the S₀ \rightarrow S₂ transition were examined by using the same pump pulses as in section 3.4 and a degenerate probing pulse sequence energetically resonant to the excited-state absorption of Zn-TPP at 510 nm. The overlap of the DFWM pulses and the absorption from the Zn-TPP excited state are shown in Figure 3.13. The monochromator after the sample was set at 510 nm. Vibrational modes specifically coupled to the S₂ state were selectively measured by removing ground state contributions through shot-to-shot subtraction, and by virtue of recording a time range before S₂ \rightarrow S₁ internal conversion occurs. Pulse energies of 50 nJ were used, and pulse lengths were measured to be 12 fs by autocorrelation. Optical alignment was performed to maximize the amplitude of the peak at 1352 cm^{-1} at an actinic pump delay of 1 ps.



Figure 3.13: The spectrum of the pulse centered at 510 nm used for the DFWM probing pulse sequence overlaps with the positive absorption in the Zn-TPP excited state. This region is also far from the ground-state absorption transition, allowing the excited state to be singled out for resonant enhancement.

The background-free nature of DFWM measurement in the time domain eliminates the influence of fluorescence that typically obfuscates Raman spectra of solutionphase Zn-TPP. Figure 3.14 presents a comparison between a ground-state spectrum vibrational spectrum collected on resonance with ground-state absorption and an excitedstate spectrum collected shortly after excitation of the Soret band at 420 nm. The Raman active modes present in the ground state are in good agreement with published results. [94, 95] Peaks attributable to Zn-TPP are observed at 195, 385, 629, 1001, 1078, 1236, 1352, 1492, and 1550 cm⁻¹ in the DFWWM spectrum of the ground state. An additional peak at 910 cm⁻¹ is a vibrational mode of the THF solvent. [96] The spectrum of the excited state exhibits two major vibrational modes at 385 cm⁻¹ and 1352 cm⁻¹, as well as the peak from THF, while the rest of the molecular modes are no longer present. The two peaks preserved in the excited-state spectrum are therefore coupled to the S₂ state. These vibrational modes on photoexcited Zn-TPP correspond to a Zn-pyrrole stretch and a stretch of the interior porphyrin ring, as depicted in Figure 3.15. [97, 98]



Figure 3.14: Excited-state resonant pump-DFWM spectra at T=500 fs (a) and ground state resonant DFWM spectrum (b) show multiple peaks. Dominant features are a 385 cm⁻¹ metal-pyrrole stretch, 1352 cm⁻¹ inner ring stretch, and a 910 cm cm⁻¹ solvent mode denoted by an asterisk, which are preserved after photoexcitation to S_2 .



Figure 3.15: The major vibrational modes appearing in the pump-DFWM spectra are stretching of the Zn-N bond (a), which appears at 385 cm⁻¹, and stretching within the porphyrin interior across the *meso* carbon and pyrrrole nitrogen atoms (b) that appears at 1352 cm⁻¹.

Figure 3.16 shows the vibrational spectrum produced by Fourier transformation as a function of 420 nm actinic pump delay (T). On close inspection, the mode centered around 1350 cm⁻¹ shows a time-dependent shift towards higher vibrational frequencies, while no shift is observed for the lower frequency mode at 385 cm⁻¹. The solvent mode at 910 cm⁻¹ blue-shifts by 3 cm⁻¹, which is just within the instrumental resolution. The absence of a shift at 385 cm⁻¹ rules out systematic error for this solvent peak shift. Additionally, phase information from the purely time domain measurements reveals that the two vibrational peaks of Zn-TPP are in phase with each other, while the solvent peak is out of phase. The amplitude of the higher frequency peak rises over time and the lower frequency peak does not exhibit any significant amplitude change. The intensity of the peak maxima over the course of relaxation are shown in Figure 3.17 for the two prominent molecular vibrations. A magnification of the 1350 cm⁻¹ region is presented in Figure 3.18, where it can be seen that a frequency shift from 1340 to 1352 cm⁻¹ occurs at a rate fit with an 85 fs time constant.



Figure 3.16: The pump-DFWM map produced after excitation at 420 nm shows three major peaks and their behavior over the first several hundred femtoseconds following S_2 activation. The peaks in the 1350 cm⁻¹ and 380 cm⁻¹ regions share the same phase, while the peak at 910 cm⁻¹ was found to have π phase difference.



Figure 3.17: The magnitude of the two molecular vibrational modes detected after 420 nm excitation shows an increase of the higher frequency peak, and an indiscernible change at the lower frequency over the first 600 fs of dynamics.



Figure 3.18: The peak in the 1350 cm⁻¹ region of the pump-DFWM map in Figure 3.16 increases in frequency by 13 cm⁻¹ and magnitude over time. A rate of 85 fs is fit to the frequency shift by tracking the position of the maximum of the peak, which is displayed by the dashed line.

The pump-DFWM map produced after 430 nm excitation is displayed in Figure 3.19. The same 430 nm centered actinic pump shown in Figure 3.4 was used. The higher signal-to-noise is a result of increased excited state population at this excitation energy. The same vibrational features exhibited in Figure 3.16 are present, including the two major molecular modes at 1352 cm^{-1} and 385 cm^{-1} as well as the THF peak at 910 cm^{-1} . However, the time-dependence of the peaks differs at this excitation energy. The map retains its shape over the initial 600 fs of S₂ relaxation, and no frequency shifts are observed. Figure 3.20 shows a magnification of the 1350 cm⁻¹ area. In contrast to Figure 3.18, there is no blue-shift of the high frequency Zn-TPP vibrational mode.



Figure 3.19: The pump-DFWM map acquired after excitation at 430 nm shows nearly identical features to Figure 3.16. Peaks at 1352, 910, and 385 cm⁻¹ are prominent, and features remain static over the time range measured.



Figure 3.20: Magnification of the 1350 cm⁻¹ region of Figure 3.19 shows an absence of peak shifting. In contrast to Figure 3.18, this high frequency vibration does not change over time when a 430 nm pump pulse is employed.

3.6 Discussion

The smooth frequency shift evident in Figure 3.18 towards higher vibrational energy can be explained by vibrational relaxation within an anharmonic energy surface of S₂. [99, 100, 101] The vibrational energy increases as the spacing of vibrational energy levels increases towards the bottom of the potential, which is approached over the course of relaxation. The frequency shift is best fit by a second-order polynomial function, indicating a third-order perturbation to the harmonicity of the surface. [102] A similar ring stretching mode in molecular benzene at 1494 cm⁻¹ has an anharmonic correction of 10 cm⁻¹, which is on the same scale as the 13 cm⁻¹ shift observed for the 1350 cm⁻¹ stretch of Zn-TPP. [103] The timescale of the shift is consistent with the τ_1 dynamics observed in transient absorption, and offers strong evidence that vibrational relaxation in S₂ is the mechanism responsible for the presence of the time constant.

The alternative explanation for the source of the rapid initial dynamics, IC from a dark S'_2 state to S_2 , would not produce the continuous shift in frequency observed. Instead, the frequency would be expected to jump between values if each state is coupled to distinct vibrational modes. [99, 104] The frequency peak could possibly stay at one position over time if each state happens to couple to the same mode. In either case the smooth shift that was measured would not result, offering strong evidence that vibrational cooling in S_2 is the source of τ_1 . The data in Figure 3.20 provides further evidence for the IVR assignment. At the lower pump energy of 430 nm, the vibrational ground state of S_2 is prepared. In this case no vibrational cooling is expected within the potential, and no frequency shift should be observed. The constant signal measured offers just that.

The rise of the signal amplitude in Figure 3.17 is on the same timescale of a rise in excited-state absorption of the transient absorption signal. [77, 72] The increase in peak amplitude is attributed to relaxation into greater resonance with S_2 excited-state absorption, especially because this is the condition for which the instrument was initially aligned.

The preservation of signal attribute to the solvent in the pump-DFWM spectra

is unexpected, because contributions not induced by the actinic pump are subtracted out of the measurement. Its presence could be attributed to energy transfer from the Zn-TPP chromophore to its solvent shell. After the Zn-TPP molecule has been imbued with excess electronic and vibrational energy, it can be redistributed within a few vibrational periods into the surrounding THF shell. This interpretation is supported by the phase shift of π between vibrations on the chromophore compared to the solvent associated peaks, as labeled in Figure 3.16. The large number of solvent species relative to chromophores is responsible for the large change in polarizability evidenced by the 910 $\rm cm^{-1}$ peak. The enhancement of Raman modes in solvating molecules has been reported before. [105, 106] These results would thus indicate that a vibrational wavepacket is prepared in the solvent coordinate in order to stabilize the redistributed electron density of the photoexcited chromophore. Alternatively, the peak could be a result from oversubtraction of the DFWM measurements before and after Soret excitation due to the induced changes in sample absorbance. However, rescaling the intensity of the time domain signal with pump pulse energy did not remove the THF peak or affect the phase shift.

3.7 Conclusion

In summary, pump-DFWM and transient absorption results have elucidated the origin of dynamics in Zn-TPP which have been reported in numerous studies with contradicting assignments. Transient absorption maps produced with different excitation energies showed that the roughly 100 fs rise time is due to some type of population shift from 550 nm to 570 nm, but did not provide enough evidence to conclusively assign the dynamics to vibrational relaxation or to IC through a dark state above S_2 . Additional information available from Pump-DFWM results showed that two vibrational modes predominately couple to S_2 excitation. A stretch of the porphyrin ring was identified to undergo a frequency increase on the 100 fs timescale. The smooth frequency shift could not be readily explained by internal conversion, and is highly compatible with a vibrational relaxation model in an anharmonic S_2 potential. With all the results taken

together, the physical process behind the fast dynamics could be definitively assigned as IVR. These results are applicable to a broad class of metalloporphyrins which share similarities in nuclear and electronic structure.

Chapter 4

VIBRATIONAL DYNAMICS IN A HETEROGENEOUS ELECTRON TRANSFER SYSTEM

4.1 Abstract

The focus of this chapter is placed on pump-DFWM data collected from zinc porphyrin bound to a thin film of TiO_2 nanoparticles. Electron transfer is induced by a pump pulse, and the vibrational modes of the system are examined. This chapter is a natural continuation of the work in Chapter 3, where the same ZnTPP chromophore is now part of a more complex system. Vibrational spectra of the short lived molecular cation are compared to the neutral porphyrin, and the dynamics after photoexcitation are investigated. The fate of vibrational modes observed in the oxidized state offers insight into the role of electronic-vibrational coupling and coherence in HET. A major accomplishment of this chapter is the experimental achievement in measuring the ultrafast vibrational dynamics of a complex heterogeneous solid-state system. The work presented herein is adapted with permission from reference [107]. Copyright 2018 American Chemical Society.

4.2 Background and Motivation

Investigation of the dynamic response of solar energy conversion systems to photoexcitation is necessary to fully understand their behavior and functionality. [108, 109, 110, 111, 112] However, important systems such as dye-sensitized films and perovskites are complex and present experimental challenges in their study. [113, 114, 115] Dye-sensitized films are of particular interest due to their importance for a multitude of photo-driven applications, including photocatalysis, water purification, and solar energy conversion. [116, 117, 118, 119] The heterogeneity of dye-sensitized films composed of colloidal semiconductor nanoparticles for instance offers increased difficulty of study relative to homogenous solutions. Scattering of light off the colloid can lead to a dramatic decrease in signal-to-noise ratios. [120] Additionally, electron transfer at the interface is a critical process in the behavior of the system, and it typically occurs very rapidly on a sub-picosecond timescale. [121, 122, 123, 124] Femtosecond time resolution is therefore required. The system investigated in this chapter consists of a modified zinc porphyrin, dubbed Zn-PE-(COOH)₂, chemically bound to a thin film of colloidal TiO₂ nanoparticles. Zn-PE-(COOH)₂ offers typical porphyrin dynamics that can be representative of similar systems, and the chromophore has been previously investigated in Chapter 3. The TiO₂ film can be specially prepared to minimize optical scattering. [125] The functionalized porphyrin, depicted in Figure 4.1, acts as a light absorber, which then transfers an electron into the TiO₂ through the molecule-semiconductor interface.

The effect of coupling between electronic and vibrational dynamics has recently come to light as an important factor in many excited-state driven processes, and the role of coherent nuclear motion is not currently well-understood. [20, 126, 127, 128, 129, 130] Accordingly, several ultrafast nonlinear spectroscopic methods have been recently developed to attempt to address these issues. A comparison of the strengths and limitations of several burgeoning spectroscopies that are sensitive to electronic-vibrational effects has been summarized in reference [131]. Transient IR [132, 133, 134] and 2D-IR [135, 136, 137] spectroscopy have been successfully employed as vibrational probes of HET systems. However, IR-based methods are typically used to probe the broad spectrum of the injected electron rather than the direct response of the dye molecule. Femtosecond stimulated Raman scattering (FSRS) [138, 139] has been used to measure dye-sensitized colloidal suspensions. Measurements in suspensions are complicated by solvent effects and signal from unbound dye molecules in the solution. Scattering of light off of nonuniform particles in suspension can lead to increased noise, and solvated oxygen and water can lead to photodegradation or oxidation of the molecule at the



Figure 4.1: The Zn-PE-(COOH)₂ molecular structure contains of an alkyl bridge terminating in two carboxylic acid linkers that facilitate binding to the TiO2 surface. The porphyrin *meso*, α , and β carbons are labeled, as well as the three phenyl bridging groups.

surface. Measurements on films in vacuum are more ideal. Solid-state systems under vacuum have the advantage that they are more directly comparable to quantum mechanical simulations that are mostly performed assuming a vacuum environment. Quantum dynamics simulations that include effects of nuclear motion and coherence on the dynamics of the electronic states involved in HET are currently being developed. [140, 141, 142, 143] Pump-DFWM was implemented for this study to overcome these issues.

One advantage of pump-DFWM is the ability to measure at resonance with targeted transitions of the species of interest for signal enhancement. [144] In electron transfer systems, the DFWM probe pulses can be tuned to resonance with the chromophore excited-state or cation absorption to selectively probe the vibrational dynamics of each. The time window measured is also fully adjustable down to the femtosecond pulse duration, allowing selective measurement of the structural dynamics before and after electron transfer occurs. In contrast, resonant FSRS experiments introduce some issues. [100] The Raman pump used for FSRS requires a relatively high pulse energy. When on resonance, this high intensity pulse stimulates multiple nonlinear signals in the sample, complicating interpretation of the data. [145] The resonant Raman pump is also more likely to photobleach the sample. This problem is exacerbated in solid-state samples, because new chromophores are not constantly flowing into the beam path.



Figure 4.2: The S₂ electronic state of Zn-PE-(COOH)₂ is impulsively populated by an actinic pulse, preparing a vibrational wavepacket on the energy surface. The fate of the wavepacket is probed after electron transfer by employing a DFWM pulse sequence at an appropriate delay.

The spectroscopic scheme for the pump-DFWM experiments of this study is illustrated in Figure 4.2. The actinic pump pulse promotes the dye molecule to an excited state, where HET is then energetically favorable. After electron transfer, DFWM is used to probe the condition of the vibrational wavepacket in the potential energy surface of the oxidized state. By restricting the DFWM acquisition to times after HET has occurred, the vibrational modes on the cation can be isolated. Spectral tuning of the probe pulses to the absorption of the cation further targets the post-HET species. This pump-DFWM experiment is summarized by the cartoon in Figure 4.3.



Figure 4.3: The experimental scheme involves Zn-TPP chromophore molecules modified with bridge groups attached to a film of TiO_2 nanoparticles. Electron transfer is induced from the chromophore by an actinic pump pulse and occurs through the bridge group into the colloid. Vibrational dynamics of the molecule are then probed by a DFWM sequence.

4.3 Transient Absorption Results

Transient absorption spectra were collected using the method described in section 2.4. A pump pulse centered at 420 nm was used to achieve resonance with excitation in the porphyrin Soret band. Measurements were carried out on the Zn-PE- $(COOH)_2$ sensitized TiO₂ film to characterize the electron injection time. The pump and probe pulses had pulse energies of 300 nJ and 20 nJ respectively. The duration of the pump pulse was determined to be 25 fs by cross-correlation. The spot sizes of the pump and probe beams at the sample were 300 µm and 80 µm. The large area of the pump beam reduces photodegradation and nonlinear signal contributions due to the decreased fluence. The solid-state sample was kept under vacuum at 10^{-7} Pa.



Figure 4.4: The transient absorption map of Zn-PE-(COOH)_2 bound to a colloidal TiO_2 film produced after 420 nm excitation to S_2 exhibits both rapid and slow dynamics throughout the probed spectral region.

The resulting transient absorption map is presented in Figure 4.4. The maximum excited-state absorption is found at 480 nm and rapidly decays as the excited state is lost to HET. Ground-state bleach from the lowest singlet excited state dominates the signal around 555 nm. The signal is otherwise positive with a decay toward zero across the visible spectrum. Global fitting produced three time constants for the dynamics. These are assigned to the lifetime of the Zn-PE-(COOH)₂ excited state and of the Zn-PE-(COOH)₂⁺ cation based on previous analysis documented in reference [85]. The lifetime of the excited state was found to be 85 fs as it undergoes HET. Contrary to solution-phase measurements, the cation is the only absorbing species present on the sample after HET. The transient absorption spectrum of the cation on the surface is displayed in Figure 4.5 where the broad and overlapping peaks can be seen. The generated Zn-PE-(COOH)₂⁺ cation exhibits a lifetime with two components, one of 3.1 ps and another of over 25 ps. Kinetic traces at selected wavelengths displayed in Figure 4.6 show the fast electron injection time followed by the slower biexponential decay of the oxidized state.



Figure 4.5: The transient absorption spectrum of Zn-PE-(COOH)_2 chemisorbed to TiO_2 at a delay of 5 ps after excitation of the Soret band shows characteristic broad porphyrin features across the visible region.



Figure 4.6: Kinetic traces of Zn-PE-(COOH)₂ bound to TiO_2 following S₂ excitation are displayed. The traces are extracted from the data in Figure 4.4 at representative wavelengths of 480 nm (a) and 690 nm (b). The 85 fs injection time is evident as a rapid decay, followed by a slower decay of the post-injection species.

4.4 DFWM Results

DFWM measurements were performed on the solid-state system using the procedure described in section 2.5. The DFWM pulse sequence was centered at 580 nm, and the duration of the pulses was determined to be 15 fs by autocorrelation. Careful alignment of the beams in tandem with the pinhole placement was necessary to record the first signal from a colloidal film. The sample was also translated around the focal plane as part of the alignment procedure in order to find a spot with minimal scattering and maximal chromophore density. The unpumped ground-state DFWM spectrum of a clean TiO₂ thin film that was not sensitized with dye molecules is displayed in Figure 4.7. A steady-state Raman spectrum of the same film is also shown for comparison. All of the Raman-active vibrational modes of the film were successfully collected through DFWM. The signature Raman peak structure of anatase TiO₂ from 148 to 640 cm^{-1} was accurately reproduced by DFWM spectroscopy on the colloidal film in both energies and intensities, confirming the efficacy of the technique for measuring nanostructured solid-state samples.



Figure 4.7: The DFWM spectrum of a thin film of anatase TiO_2 nanoparticles (a) reproduces the features found in its steady-state Raman spectrum (b).

The blank TiO₂ spectrum can then be compared with ground-state DFWM results from the film after it was sensitized with Zn-PE-(COOH)₂. As described in section 2.5, the periodic time domain signal is collected, and an exponential fit is then subtracted to remove the population dynamics and isolate the oscillatory contributions before a Fourier transform is then performed. Figure 4.8(a) shows the resultant ground-state DFWM spectrum of the dye-sensitized film. The intense 148 cm⁻¹ peak is still present from the TiO₂. The rest of the features can be attributed to vibrations within the porphyrin molecule. Figure 4.8(b) shows the DFWM spectrum of Zn-TPP in THF for reference. All of the major features in the solution phase are present in the vibrational spectrum of the down molecule, albeit with a decreased signal to noise ratio. Small peak shifts in the adsorbed molecule spectrum are attributed to the presence of the anchor group for surface attachment and the lack of solvent environment.



Figure 4.8: The DFWM spectra of a colloidal TiO_2 thin film features peaks attributable to Zn-PE-(COOH)₂ sensitization with the dye (a). The peak at 148 cm⁻¹ is from TiO₂. The DFWM spectrum of Zn-TPP in THF solution (b) displays similar peaks. The peak at 910 cm⁻¹ is from the solvent.

4.5 Pump-DFWM Results

Pump-DFWM measurements were performed using an 300 nJ actinic pump pulse centered at 420 nm, with the same probing pulse sequence from section 4.4. Pump-DFWM spectra of the Zn-PE-(COOH)₂ sensitized film at delays of 5, 8, and 12 ps are presented in Figure 4.9. The peaks in Table 4.1 for the neutral and cation form of the porphyrin have been assigned following Raman measurements of Zn-TPP in methylene chloride solution at 80 K by Yamaguchi et al. and according to DFT calculations performed. [146] The ground-state spectrum of $Zn-PE-(COOH)_2$ on the film was found to be very similar to that of the chromophore in solution. Our assignments agree well with Yamaguchi et al., and slight shifts can be attributed to the different environment. Modes below 400 $\rm cm^{-1}$ can be assigned to wagging and bending modes of the Zn-TPP macrocycle. [147] Interestingly, the cation spectrum on the film is dominated by modes that can be attributed to the phenyl rings in the bridge, labeled phb1-3 in Figure 4.1. Accordingly, these modes have not been observed by Yamaguchi et al. in their measurements. The 1380 $\rm cm^{-1}$ mode of the Zn-PE-(COOH)₂⁺ cation has been observed by Yamaguchi and can be assigned following DFT calculations to a C-H bending mode at the β positions on the porphyrin ring. It is closely connected to the 1347 cm⁻¹ mode observed in the ground state that arises from $\nu(C_{\alpha}-N)$, as well as contributions from $\delta(C_{\beta}-H)$ as labeled in Figure 4.1.

It should be noted that the measured signal is recorded as a shot-to-shot difference between measurements of the pumped and unpumped sample and the observed bands in the cation are therefore restricted to those triggered by the optical excitation. The molecular vibrations observed on the cation must either be initiated by or survive the HET process. It is then expected that only selected bands relevant to the HET should be observed in the pump-DFWM measurements. The dominant modes appearing in the cation spectrum are modes between phenyl groups in the bridge and C–H bending modes on the circumference of the macrocycle. DFT calculations performed using the B3LYP functional and 6-31G* basis set confirm that the oxidized Zn-PE- $(COOH)_2^+$ should exhibit more intense vibrational modes in the region between 700



Figure 4.9: Pump-DFWM spectra of Zn-PE-(COOH)₂ chemisorbed to TiO_2 shows several consistent peaks, highlighted by dashed red lines. At delays of 5, 8, and 12 ps following excitation of S₂ the cation is the primary species.

$Zn-PE-(COOH)_2^+$	$Assignments^{\dagger}$
-	$\nu(C_{\beta}-C_{\beta}) + \delta(C_{\beta}-H)$
1380	$\delta(\mathrm{C}_{eta} ext{-}\mathrm{H})$
-	$\nu(C_{\alpha}-N) + \delta(C_{\beta}-H)$
-	$ u(\mathrm{C}_m ext{-}\mathrm{C}_\phi)$
-	$\delta(C_{\beta}-H)$
-	Ph
953	$\nu(\text{phb2-phb3})$
885	phb1 wagging
765	phb2 twisting

Table 4.1: Table of Vibrational Mode Assignments for Raman-Active Frequencies (cm^{-1}) Observed in Zn-PE-(COOH)₂ and Zn-PE-(COOH)₂⁺ Bound to TiO₂

[†] Ph, phb, ν , and δ are *meso*-phenyl modes, bridge-phenyl modes, stretching modes, and bending modes, respectively.

and 1000 cm⁻¹, which are assigned to the phenyl groups in the bridge and are not observed in its neutrally charged form. The calculated Raman spectra for the ground state and cation of Zn-PE-(COOH)₂ are displayed in Figure 4.10. The calculated Zn-PE-(COOH)₂⁺ spectrum can be compared to the pump-DFWM results, in which the cation produced after HET was isolated. Because pump-DFWM only reports specifically on the Raman-active modes that are triggered by photoexcitation with the actinic pump, not all calculated vibrational modes for the cation would be expected to appear in the measurement. The evolution of the major peaks in the cation spectrum are shown in Figure 4.11. However, because only three time points were recorded, the significance of the decay of two of the bridge modes is not clear.



Figure 4.10: DFT calculated Raman spectra of the neutral and oxidized form of $Zn-PE-(COOH)_2$ predict differences in the accessible vibrational modes. The cation exhibits more modes of more even intensity below 1200 cm⁻¹



Figure 4.11: Evolution of the amplitude of the four major vibrational peaks observed in the cation at 765 cm⁻¹, 885 cm⁻¹, 953 cm⁻¹, and 1380 cm⁻¹ shows a slight decay of two modes associated with the bridge groups.

4.6 Discussion

It appears reasonable that the 1380 cm^{-1} vibrational mode is connected to the π -excited state, while the vibrations in the bridge are connected to the electron transfer process. This assignment is also supported by the pump-DFWM measurements in Chapter 3 of the Zn-TPP chromophore in solution where a mode at 1352 cm^{-1} was found to strongly couple to excitation in the S_2 band. These measurements show the potential of pump-DFWM for investigating HET systems. By following the evolution of the Raman modes, crucial information about HET can be gained. For example, pump-DFWM can allow through-bond and through-space HET to be distinguished. In addition to following the dynamics of the bands, measurements with different actinic pump photon energies can give important information about the nature of the HET process. In the event of adiabatic electron transfer from a vibrationally hot prepared donor state, it could be expected for excess vibrational energy to flow coherently into the oxidized acceptor state. [148] Alternatively, a nonadiabtic HET could induce vibrations as a result of weakly coupled surface crossing leading to a hot state in the cation. [24] The fact that in the present measurement $Zn-PE-(COOH)_2^+$ was excited at its absorption maximum to a Franck-Condon state preceding HET suggests that the 1380 cm^{-1} mode located on the chromophore is indeed triggered by the actinic pump pulse and survives HET, while the lower-lying bridge modes are triggered by HET. Selection of different dye molecules specifically designed for resonant enhancement could lead to a factor of 10^4 increase in signal-to-noise for the experiment and offer more information addressing these questions. [149]

4.7 Conclusion

Pump-DFWM has been successfully applied to nanostructured solid-state samples for the first time. This allows measurement of vibrational-electronic coupling and coherence in HET systems. High-quality samples and minimized scattering were critical experimental parameters to consider. Interfacial charge transfer was monitored on an ultrafast time scale while identifying contributions from vibrational and electronic state dynamics. Vibrations have been observed on the molecular side of the post-injection cation state directly following HET. The vibrational features observed in Chapter 3 are not found to be the same predominant modes in the porphyrin after HET. Assignment of the modes observed in the cation and comparison to measurements of the Zn-TPP chromophore suggest that pump-DFWM can distinguish between vibrational modes that are triggered by photoexcitation and those that are triggered by nonadiabatic surface crossing in the HET process.

Chapter 5

NICKEL PORPHYRIN EXCITED-STATE LIGATION

5.1 Abstract

This chapter describes the excited-state dynamics of a nickel metalloporphyrin. The mechanism responsible for the dynamics is revealed by X-ray transient absorption to be a ligation of solvent molecules to the central metal atom. Occupation of the nickel $4p_z$ orbital is specifically evidenced by a time-dependent change in its signature X-ray absorption peak. Both association and dissociation of the solvent occurs in the excited state, accompanied by a shift between square-planar and octahedral geometry around the porphyrin center. These structural changes are observable as an additional time constant in optical transient absorption dynamics in coordinating solvent. The dynamics disappear accordingly in a non-coordinating environment. Structural dynamics measured with atomic specificity are complementary to broader scale vibrational modes of the molecule accessible by pump-DFWM. The understanding of optically-induced ligation is important for the design of photocatalytic systems and light-driven chemical reactions.

5.2 Background and Motivation

The electronic configuration of molecular excited states can provide information about transient nuclear configurations. The orbital occupation of atoms can be probed by X-ray pulses to inform on the structure of photo-activated species. The driving force and the paths of chemical reactions can be understood by studying transient structures and bond formation. For instance, the binding of ligands to the Fe atom in heme porphyrins has been well studied and revealed multi-step reaction paths based on varying ligation states of the metal atom, which dictated the function and efficacy of oxygen uptake. [150, 151, 152, 153, 154] Absorption of X-ray pulses by the metal center of the porphyrin offers information on the occupancy of the orbitals and the local bonding environment. [155, 156, 157] Nickel porphyrins have also been surmised to undergo ligand association and dissociation in photoexcited states, as well as flexing of the nonplanar porphyrin ring. [158, 159, 160, 161, 162] The $3d^8$ valence configuration of Ni(II) makes it suitable for ligation if electron density is directed away from the metal and into the conjugated π system. [163, 164] This condition can be satisfied in the excited state of properly tailored molecules.



Figure 5.1: Ni-TPPF-Ac consists of a Ni-tetraphenylporphyrin substituted with fluorine atoms across the phenyl moieties. A carboxylic acid group is present to allow chemisorption to TiO_2 for HET experiments.

The ultrafast dynamics are challenging to understand through optical transient absorption, as the electronic structure is not clearly defined from information gained by probing molecular orbitals. For porphyrins especially the optical spectra are complicated by multiple overlapping features. While this property makes them desirable for many light-driven applications, it complicates understanding of the specific processes and dynamics that underlie their excited-state functionality. Furthermore, optically dark states that arise from metal-centered transitions cannot be easily accessed. Xray transient absorption can directly probe the status of the atomic orbitals of nickel. Transient orbital configurations can be observed through changes in the absorption of the metal atom. The time resolution in XTA is limited by electron bunching in the synchrotron storage ring, and the measurements are thus restricted to the picosecond regime. Optical studies can be used to complement X-ray results and access femtosecond dynamics. Pump-DFWM can address vibrational modes that can be confirmed by XTA to play a role in chemical reaction coordinates. The metalloporphyrin studied in this chapter, designated Ni-TPPF-Ac is depicted in Figure 5.1. The addition of fluorinated phenyl rings provides broader visible absorption and electron withdrawal into the π system. [165, 166, 167] A carboxylic acid group is also present to facilitate binding to TiO₂, a vestige of attempted HET experiments.

DFT calculations were performed at the camb3lyp-631d level using Gaussian 09 software to confirm the involvement of the nickel atom in the excited states and the transitions involved in excitation. The calculated molecular orbitals are shown in Figure 5.2 to illustrate the engagement of the metal. XTA on Ni-TPPF-Ac in solution can investigate possible changes in the ligation state of the molecule and deviations from the ground-state structure. Direct probing of the nickel atom provides evidence of its orbital occupancy status and elucidates transient structural states much more clearly than optical transient absorption. Understanding these molecular changes can inform control of chemical reactions that are thermodynamically or kinetically driven by photoexcited states. Measuring the XTA dynamics in a solvent capable of coordination to the metal can monitor its ligation or deligation. Bond making or breaking in the excited state is at the heart of photochemistry, which can be probed at the nickel center of Ni-TPPF-Ac through XTA.



Figure 5.2: The DFT calculated major molecular orbitals involved in transition to the excited state of Ni-TPPF-Ac show inclusion of the central nickel atom. Compared to the HOMO of the ground state, electron density increases at the metal in the LUMO and LUMO+1 states that are populated after photoexcitation.

5.3 Optical Results

The ground-state absorption spectrum of Ni-TPPF-Ac is presented in Figure 5.3. A 15 μ M concentration in ethanol was used in a 1 mm path length quartz cuvette. An intense Soret band is centered at 400 nm. A dual-peaked Q band is found with maxima at 520 and 555 nm. The spectral shape is typical for a Nitetraphenylporphyrin. [168] The excitation laser pulse used for time-resolved measurements is set at 400 nm to overlap with the Soret absorption peak and maximize the excited state population. Optical transient absorption was performed as described in section 2.4, and the resulting map is displayed in Figure 5.4. A double pass delay line was used to measure dynamics on a longer timescale. The Ni-TPPF-Ac in ethanol was diluted until the OD was 1 at the Soret maximum. The pump pulse was kept at 150 nJ. The map exhibits long-lived features centralized in the 500 to 550 nm region. Alternating peaks of positive and negative intensity survive for several nanoseconds. The nanosecond-scale lifetime of Ni-TPPF-Ac confirms its suitability for XTA measurements, where the probe pulse length is around 150 ps.

Traces of the transient absorption spectra are displayed in Figure 5.5. The observed features are assigned to a single excited state absorption band that directly overlaps with negative GSB dips from the Q band in the 500 nm area. There is a shift of the peaks at 1 ns after excitation relative to 100 ps. This shift hints at the presence of two distinct excited states with slightly different excited-state absorption energies that are populated at different times. At 1 ns the excited-absorption at 440 nm has fully relaxed. Global fitting of the kinetics confirms multiple relaxation steps, and $S_2 \rightarrow S_1$ internal conversion is assigned as the source of the shift.

Kinetic traces of the dynamics at two representative wavelengths are presented in Figure 5.6. Slower dynamics are observed at 530 nm, and a rapid decay component is apparent at 560 nm. Three time constants produced from global fitting are adequate to reproduce the dynamics. The fastest process, $\tau_1 = 22$ ps, is assigned to internal conversion to S₁ from S₂. Intersystem crossing to T₁ is assigned to $\tau_2 = 612$ ps. The triplet lifetime of $\tau_3 = 2.7$ ns is responsible for the slowest dynamics. The fast decay of



Figure 5.3: The ground-state absorption spectrum of Ni-TPPF-Ac shows an intense Soret peak and a split Q band at lower energy (inset). Pump-probe measurements are performed with a pump pulse centered at 400 nm to achieve S_2 excitation.

transient absorption at 560 nm is matched by a rise at 530 nm at the same rate, which confirms the assignment of internal conversion for τ_1 . Excited-state absorption from S₁ is more prominent at 530 nm, while S₂ absorption is observed as a decay at higher energies.

The transient absorption dynamics were measured in different solvents. Ethanol and toluene solution environments produced different dynamics at early times, as shown in Figure 5.7. The rise time at 530 nm is slowed in ethanol compared to toluene. Additional dynamics are therefore indicated in the more polar solution. Fitting of the dynamics from toluene measurements results in a near-instantaneous time constant for τ_1 . The dissapearance of the fast component is further investigated by XTA.



Figure 5.4: The optical transient absorption map produced after 400 nm excitation exhibits centralized features in the 500 nm region. Ground-state bleach overlaps with excited-state absorption that persists for several nanoseconds.


Figure 5.5: Alternating positive and negative peaks are observed in the optical transient absorption spectrum of Ni-TPPF-Ac. Excited-state absorption overlaps with bleach from the Q band. A slight red-shift of the peaks occurs over the course of excited-state relaxation.



Figure 5.6: Kinetic traces at 530 nm and 560 nm show differing dynamics. Three time constants fit both signals. The initial rise at 530 nm is matched by the fast decay at 560 nm.



Figure 5.7: The rise of the Ni-TPPF-Ac optical transient absorption signal at 530 nm is affected by solvent. An additional time constant is observed in toluene relative to ethanol based experiments.

5.4 X-Ray Transient Absorption Results



Figure 5.8: X-ray absorption spectra of Ni-TPPF-Ac were collected for the ground state and at two time points after laser excitation. Slight differences are noticeable in the EXAFS, XANES, and pre-edge regions.

The X-ray absorption signals collected at three different time delays are displayed in Figure 5.8. Data collection is performed as described in section 2.6. The laser pump power was 518mW with a 1 kHz repetition rate. EXAFS spectra are a result of 32 averaged scans at each time delay. The EXAFS spectra show a peak at the nickel K-edge of 8.35 keV. A pre-edge feature is observed around 8.34 kEV. Differences between the X-ray absorption are observed across the EXAFS spectrum at different times, and are apparent in the pre-edge region, as shown in Figure 5.9. Measurements at 120 ps serve to probe as near to time-zero as possible, limited by the duration of the probe pulse.

This pre-edge peak is known to be due to absorption at the $1s \rightarrow 4p$ transition for nickel(II). [169] The pre-edge is shifted to higher energies and decreases in the excited



Figure 5.9: A peak in the pre-edge absorption region decreases in magnitude and blue-shifts after photoexcitation.

state measurements. As the molecule relaxes, the peak moves back towards its groundstate position, away from its initial perturbed energy. Assuming that the red-shifted pre-edge peak is a pure ground-state feature, it can be carefully subtracted to produce excited-state EXAFS curves. The resulting subtraction is presented in Figure 5.10. The pre-edge region produced for the 120 ps and 1 ns excited state contributions appear similar. Only a loss of intensity occurs as Ni-TPPF-Ac relaxes back to the ground state.

After subtraction of the ground-state contribution, the EXAFS curves are put through a Fourier transform to produce Figure 5.11. A Hanning window was used and set to an appropriate width to envelop the primary oscillatory features of the EXAFS signal. The R-space plot informs on the differences in bond lengths and X-ray scattering paths between the time-dependent measurements. From FEFF analysis, the peak at 1.3 Å is assigned to scattering from the four Ni–N bonds. Scattering at 2.5 Å is attributed to the α -carbons, and contributions from *meso*- and β -carbons contribute to



Figure 5.10: Subtraction of the ground state spectrum from the excited-state spectra is performed after rescaling to the pre-edge peak absorption in order to isolate absorption features induced by optical excitation. The pre-edge absorption peak is due to a $1s \rightarrow 4p$ transition.

the peak at 3.6 Å. It can be seen that the porphyrin ring slightly expands in the excited state based on the increased radial distances of the carbon atoms away from the nickel center. After 1 ns, the molecule appears to recover close to its initial ground-state configuration.



Figure 5.11: The Fourier transform of the data in Figure 5.10 shows slight differences in X-ray scattering paths of the atoms at different following photoexcitation. The large deviation at 120 ps returns towards the ground state structure by 1 ns.

The transient X-ray absorption difference signal is shown in Figure 5.12. These EXAFS spectra are the result of pump-on minus pump-off recordings and isolate the difference in X-ray absorption when the molecule has been photoexcited. Difference spectra recorded at 120 ps and 1 ns show that there is a significant change in the photoexcited Ni-TPPF-Ac relative to its ground state.

Magnification of the K-edge region shows large differences in the XTA signal at different times in the relaxation process. The pre-edge difference appears initially blue-shifted, and then moves to higher energy after 1 ns. The XANES region takes



Figure 5.12: EXAFS difference spectra at pump delays of 120 ps and 1 ns display a change in the Ni absorption after photoexcitation. The magnitude of the XTA signal decreases as the ground state recovers.

on a different shape at different delay times, hinting that two distinct structural conformations may be contributing to the signal. To attempt to confirm this assignment, kinetic measurements were performed at the two energies indicated by dashed blue lines. In the event of a difference in structures, the two energies would be expected to present different dynamics since the XANES and pre-edge regions probe different inner-shell atomic transitions. [170] The resulting kinetic scans are displayed in Figure 5.13. Both energies relax towards zero, albeit with from opposite directions, on a nanosecond timescale. Biexponential relaxation dynamics are observed at both energies monitored. For comparison of the dynamics, the traces are normalized and overlayed in Figure 5.14. The normalized dynamics are identical within experimental error. Multiple transient structures are thus not confirmed, although kinetic scans at other energies may reveal more information. The long measurement time required for collection of each trace prohibited further time scans in the present study. Fitting of the kinetic scans the τ_1 and τ_2 time constants collected from optical measurements produces a good fit. This indicates that the dynamics measured in optical transient absorption can be attributed to the same physical phenomena responsible for the XTA dynamics.



Figure 5.13: The XANES region of Ni-TPPF-Ac is altered after photoexcitation. There is a significant change in the structure of the pre-edge peak and broad XANES absorption. Blue dashed lines indicate energy positions where kinetic scans are performed.

Comparison of the ground-state EXAFS signal from the initial and final scans indicates that the sample did not undergo any significant degradation. Identical structures are produced, shown in Figure 5.16. This signal preservation discounts contributions from irreversible damaging processes to the transient signals such as interactions with solvated electrons or demetallation of the porphyrin that might be expected. [171] A shift in the baseline fit by the automated software is observed, likely due to a slight bleach in the sample and reduction in overall intensity.



Figure 5.14: The raw XTA kinetics recorded at the pre-edge and XANES peak regions show similar biexponential relaxation dynamics and opposite signs.



Figure 5.15: Normalization of the XTA kinetics highlights the similar dynamics at both energies monitored.



Figure 5.16: Identical X-ray absorption signals recorded before and after hours of irradiation verify the integrity of the sample throughout data collection.

5.5 Discussion

The X-ray absorption results point towards occupation of the $4p_z$ orbital of the porphyrin's nickel center. The negative change in absorption at the pre-edge peak indicates a loss in the $3d \rightarrow 4p$ transition. The p_z orbital is vacant in the ground state, but can experience occupancy by ligation of the metal. Coordination of solvent molecules along the axial plane is the strongest possibility of bonding orbital occupation offered. As this axial p orbital decreases in vacancy, absorption to that state is diminished. Furthermore, an increase in the transition energy is expected as the molecule goes from a square planar towards octahedral geometry, which was also observed. This 4pz occupation was observed as a time-dependent feature. Therefore solvent binding can be taken to occur as a light-driven process. In the excited state, the coordinating ethanol can ligate to the sterically accessible p_z orbital, as illustrated in Figure 5.17. This ligation is facilitated by a shift in electron density from anti-bonding to bonding orbitals in the excited state. This interpretation is supported by similar results reported by Chen et al. [172, 173] As the excited state evolves, the pre-edge feature returns towards the ground state location. This can be understood by loss of the ligation as triplet state relaxes and the ground-state nuclear configuration is recovered.

The changes in nuclear geometry local to the nickel atom are also reported in the Fourier transform spectra shown in Figure 5.11. The immediate $\pi \to \pi^*$ transition achieved by the optical pump pulse results in an expansion of the conjugated porphyrin ring. This is evidenced by the decrease in distance of the innermost nitrogen atoms and an increase in distance of the outer carbon atoms from the nickel center in the excited state.

In the optical transient absorption spectra, solvent dependent dynamics can then be understood more clearly based on the XTA results. The same dynamics were observed in the optical and X-ray transient absorption kinetics in ethanol-based solutions. Since the physical process responsible for the time constant can be assigned as axial solvent ligation from XTA results, the same time constant measured in optical



Figure 5.17: After photoexcitation, the axial $4p_z$ orbital of Ni(II) is occupied by coordinating solvent molecule ligands.

spectra can also be attributed to the same phenomenon. The optically recorded dynamics shown in Figure 5.7 provide further evidence for excited-state solvent coordination. Measurements in non-coordinating toluene did not exhibit the same dynamics. Therefore the ligation mechanism responsible for the observed time constant does not occur in those conditions, as would be expected. Further optical measurements can clarify if ligation occurs singly, doubly, or sequentially. Kinetic measurements at additional X-ray absorption energies may also reveal different states of ligation. Limitations in measurement time for XTA experiments restricted solvent-dependent measurements.

5.6 Conclusions

X-ray transient absorption spectra have elucidated excited-state dynamics of Ni-TPPF-Ac in solution. The central nickel atom of the porphyrin was probed by picosecond X-ray pulses after visible excitation to show that axial ligation of the solvent occurs in the excited state. Transient occupation of the $4p_z$ orbital was observed by XTA. The same dynamics present in optical transient absorption measurements show a disappearance of the ligation time kinetics when a non-coordinating solvent is used. The clarification of the mechanism responsible for optical transient absorption results is demonstrated as structural and geometric reorganization of the porphyrin. This optically-induced ligation process can be used to drive photo-catalysis reactions, where the excited metalloporphyrin can react with desired reactants tailored for the bondmaking process.

Chapter 6

CHARACTERIZATION OF AN INHERENT TRANSIENT ABSORPTION ARTIFACT

6.1 Abstract

This chapter details an experimental artifact that can emerge in transient absorption measurements performed with femtosecond pulses. The effect was observed over the course of experiments described in previous chapters, and necessitated further investigation to fully understand some anomalous results. It was found that absorption of the excitation pulse by the sample can severely alter the spectrum and consequently the temporal pulse shape. This spectral self-filtering effect from the interaction of the sample with the pulse can lead to systematic errors and misinterpretation of data, most notably in concentration dependent measurements. Alterations of dynamics data can be misattributed to intermolecular interactions rather than an experimental artifact. The combination of narrow absorption peaks in the sample with broadband transformlimited excitation pulses is especially prone to this effect. The effect is characterized here by analyzing sample-induced changes in pulse spectra and resulting changes in pulse durations and transient absorption kinetics. The work presented is adapted with permission from reference [174]. Copyright 2017 Elsevier.

6.2 Background and Motivation

The increasing availability of commercial femtosecond laser systems has made transient absorption spectroscopy accessible to researchers with a wide variety of backgrounds other than nonlinear optics. The technique has been established as a useful research tool by thousands of scientists from almost all fields of natural sciences. [175, 176, 177, 178, 179, 180, 181, 182, 183] Techniques using ultrashort laser pulses range from pH perturbations to rapid-release RNA delivery. [184, 185, 186] Using non-collinear parametric amplifiers, time resolution below 30 fs can be achieved with standard Ti:Sapphire based setups. This high time resolution requires sufficient bandwidth in the excitation (pump) pulse. For transient absorption spectroscopy, the pump pulse is typically tuned to overlap with the ground-state absorption spectrum of the sample. If the absorbance peak is narrow compared to the pulse spectrum, then spectral components will be removed from the pulse non-uniformly and the frequency spectrum will be altered. Absorption spectra with narrow lines are found in many bio-molecular systems; for example in proteins like rhodopsin that are responsible for vision processes, and in porphyrins involved in photosynthesis. [187, 188] Narrow absorption features are also common in photochemical systems like transition metal complexes used for photocatalysis and solar cells, [189, 190, 191, 192, 193] and have been reported for semiconductor bulk materials and nanostructures as well. [194, 195, 196, 197] Transient absorption measurements on semiconductors at the band edge are another example affected, since partial pulse overlap with a sharp absorption edge will lead to a similar effect. A series of controlled measurements can demonstrate that the combination of a broadband pump pulse with a narrow ground-state absorption band in the sample can lead to strong distortions in the pump pulse spectrum and alter its time profile. This can lead to systematic errors and misinterpretation of experimental data. Consideration of this effect becomes increasingly important as near-transform-limited pulses on the ten femtosecond timescale with appropriately broad spectra become ever more accessible. Transient absorption experiments dependent on sample concentration or thickness thickness are especially prone to this effect. Because the time profile of the pulse will depend on the optical density (concentration or thickness), measurements on different samples cannot easily be compared to each other.

The "spectral self-filtering" effect was initially observed for a set of transient absorption measurements that were performed on solutions of increasing concentration of Zn-TPP in tetrahydrofuran. Zn-TPP is a prototypical chromophore that has been used in numerous studies ranging from medicinal chemistry [198] to materials science, [199] and serves as a representative sample for typical transient absorption studies. Measurements performed have showed an apparent concentration dependence of the excited-state relaxation dynamics in the first 100 fs. In the study discussed in Chapter 3 a rise time of the transient absorption signal at 520 nm of 120 ±10 fs after excitation with a pump pulse centered at 420 nm was scrutinized. This process was assigned to relaxation in the S₂ state. [70, 72] However, The rise of the signal appeared to slow down by nearly a factor of two as the concentration was increased by two orders of magnitude. After verifying that concentrations as high as 100 μ M were below the point of aggregation of Zn-TPP in THF [200] and that neither demetallated porphyrin nor any other impurities were responsible for the ostensible concentration dependence, it was concluded that the effect must be attributed to a change in the instrument response function, warranting a controlled study. The temporal stretching of a broadband laser pulse as it travels through absorptive media is depicted by the cartoon in Figure 6.1.



Figure 6.1: A near-transform-limited femtosecond laser pulse is stretched in time after losing spectral components due to nonuniform absorption in the sample. Zn-TPP solution absorbs the middle portion of the pulse spectrum, causing a decrease in the spectral components of the pulse in the sample. The initial transform limit is no longer achieved, resulting in an inconspicuous loss of experimental time resolution.

6.3 Experimental Design

The transient absorption setup described in section 2.4 was used to investigate the effect of sample concentration on pulse width and observed signal dynamics. A NOPA output in the near-IR was frequency doubled, resulting in a pump pulse centered at 422 nm with a FWHM of 13 nm. The spectrum of the pulse overlaps almost completely with the Soret absorption band of Zn-TPP, as shown in Figure 6.5. The white light supercontinuum probe was compressed to a minimum using a pair of BK7 prisms and not adjusted throughout the experiment. The 520 nm component was isolated by a monochromator before detection to analyze the kinetics measured at a single representative wavelength for all measurements. This wavelength provides a strong excited-state absorption signal for Zn-TPP, as shown in Figure 3.13, and it is a bright and stable portion of the supercontinuum as can be seen in Figure 2.5. Pump and probe beams were focused to 300 μ m and 100 μ m diameters respectively at their intersection. The relative polarization was set at magic angle. The pulse energy of the pump is 200 nJ before incidence on the sample, corresponding to an energy regime in which the sample exhibits a linear transient absorption response. 1 mm path length quartz cuvettes were used for transient absorption measurements. Cross-correlation measurements were performed using type-I SHG in a 200 μ m thick BBO crystal. To facilitate a well defined change in concentration, careful optical alignment of the setup was performed such that the path length of the pump pulse inside the cuvette was minimized before overlapping with the probe pulse. The angle between the pump and probe pulse was set to 15° and their focal points were set at the very front of a 1 mm cuvette filled with 17 μ M Zn-TPP solution in THF, possessing an optical density of 1 at 422 nm. Finally, an additional 1 mm cuvette was placed in the path of the pump beam path before the first cuvette and filled with varying concentrations of Zn-TPP solution.

6.4 Time-Domain Results

The transient absorption signal of the measured Zn-TPP dynamics are displayed in Figure 6.2 for the time zero region. The rising edge of the signal for Zn-TPP concentrations ranging from 0 μ M to 25 μ M can be compared in these kinetic traces. The slope of the recorded signal noticeably decreases with increasing analyte concentration. The decrease of the signal-to-noise ratio is due to an overall reduction of the signal caused by the decrease in pump energy.



Figure 6.2: Kinetic traces of Zn-TPP transient absorption signals at 520 nm show apparent concentration-dependent dynamics when normalized and overlayed. The excitation pulse travels through solutions of increasing concentration before interacting with probe pulse.

Fitting of the data shows an apparent increase of the rate constant by a factor of two. The fitted rise times corresponding to each sample concentration are presented in Table 6.1. Global fitting at each probe wavelength employed the sequential-state rate model that has been described in section 2.4. The resulting fit lines for each concentration are displayed over the experimental data in Figure 6.3. Each data set contains 400 points. The fit was allowed to converge by allowing only the rise time to change, while holding all other dynamics constant at known values, along with a fixed pulse length. The plots have been normalized for ease of comparison. The apparent rise time of the transient absorption signal is given by a convolution of the initial excited-state absorption dynamics with the Gaussian IRF, which is dependent on the durations of the pulses used in the experiment. These measurements were performed under realistic experimental conditions with a moderately short IRF of 40 fs, and the IRF used for fitting was fixed to 40 fs for all measurements in Fig. 6.2 to demonstrate how spectral filtering can lead to misinterpretation of data. The apparent increase in rise time can be shown to be caused by an increase of the IRF due to spectral selffiltering rather than any physical changes in dynamics of the sample by monitoring accompanying increases in pulse durations.



Figure 6.3: The lines of best fit generated by a global fitting routine, from which the rise times reported in Table 6.1 were extracted, are displayed. Transient absorption at 520 nm is delayed as the concentration of Zn-TPP in the path of the pump beam increases from 0 to 25 μ M. The observed slope of the blue fit lines decreases as the optical density increases.

6.5 Frequency-Domain Results

To further investigate the effect of analyte-induced spectral filtering, the cuvette where the pump and probe beams interacted was replaced with a BBO crystal in order to measure the cross-correlation between the 422 nm pump and the 520 nm portion of the supercontinuum. The cuvette containing the concentration dependent Zn-TPP solution was kept in the path of the excitation beam before the nonlinear crystal. By changing the Zn-TPP concentration in the second cuvette, the effect of spectral filtering on the cross-correlation was measured. The results displayed in Figure 6.4 reveal that as the concentration of the analyte was increased, the measured cross-correlation increased as well. The cross-correlation trace is strongly distorted and quickly loses its Gaussian shape. The FWHM reported in Table 6.1 assumes a Gaussian pulse shape and should be taken with care at concentrations higher than 5 μ M.



Figure 6.4: The SHG cross-correlation of the pump and probe pulses shows a distortion and increase in temporal width as the pump passes through Zn-TPP solutions of increasing concentration.

The distortion of the pulse shape in time should be reflected in the spectrum of the pulse. Figure 6.5 shows the spectrum of the 422 nm pump pulse after passing through the cuvette with Zn-TPP solutions of increasing concentrations together with the spectrum of the Soret band absorption spectrum of Zn-TPP. It can be seen how the sample alters the spectrum by predominantly reducing the intensity at the center wavelength to the point were the central region is completely absorbed. The pulse spectrum shows two peaks in the most egregious case at 25 μ M concentration. Reconstruction of the cross-corrrelation by Fourier transformation of the measured spectrum and subsequent convolution with a 20 fs FWHM Gaussian pulse to account for the probe pulse results in a temporal profile that resembles the width and the structure of the measured cross-correlation, as displayed in Figure 6.6.



Figure 6.5: The spectrum of the pump pulse is altered in shape after passing through a cuvette of Zn-TPP solution. Distortions are more pronounced at higher concentration. The bandwidth of the excitation pulse slightly exceeds the Soret absorption peak width of the porphyrin, indicated by the red dashed curve.



Figure 6.6: A measured cross-correlation from Figure 6.4, in blue, can be qualitatively reproduced based on the spectrum of the pump pulse contributing to it. Converting the spectral measurement to the frequency domain and then performing a convolution with a 20 fs assumed Gaussian pulse representing the probe contribution produces the red curve.

6.6 Discussion

Taking the results from sections 6.4 and 6.5 together, the relation between distortion in pulse spectra and time-domain measurements becomes evident. Furthermore, the combined measurements show that the sample itself is a source of spectral distortion of the pump pulse. This is problematic since the pump pulse is typically tuned to spectrally overlap with an absorption peak in the system under study in order to efficiently access excited states. However, the magnitude of the self-filtering effect can be reduced in a measurement by using thin samples and by placing the region where pump and probe pulse overlap as close to the front surface of the sample as possible. Doing so minimizes absorption of the pump pulse as it travels through the sample prior to the region of spatial overlap with the probe pulse. In addition, a large crossing angle between pump and probe pulse is desirable in reducing the amount of sample penetration prior to their overlap. Using a sample with thickness approaching the order of the interaction volume would be advantageous, such as the thin film produced by a flowing liquid jet. [201, 202]

The effect of filtering within the sample can be reduced by more than a factor of ten in the setup used in this study through careful adjustment of the experiment.

Zn-TPP	Cross	Rise
Concentration	-Correlation	Time
(μM)	FWHM (fs)	τ_{rise} (fs)
0	40.8	108
1	41.2	113
2.5	42.1	132
5	44.1	151
7.5	44.3	162
10	51.9	186
15	70.3	211
25	73.5	243

 Table 6.1: FWHM of Cross-Correlations and Transient Absorption Rise

 Times at Different Concentrations.

Figure 6.7 shows transient absorption measurements on Zn-TPP with increasing analyte concentration taken after meticulous beam alignment on the sample cell. The effect of spectral filtering was minimized after deliberate effort to overlap the pump and probe beams in an optimal position. It is therefore demonstrated possible to take measurements with high time resolution, even at high optical densities. The extreme case of a 500 M solution corresponds to a calculated absorbance of 28.5 through a 1 mm cuvette, although the pulse interaction region was placed only a fraction of that distance into the sample. However, dependence on the alignment makes it difficult to quantify the effect in a real experiment where the exact amount of spectral filtering at the interaction region is unknown and challenging to measure. The effect is therefore difficult to correct mathematically *post hoc*. These results also suggest that the common practice of deconvoluting time-dependent measurements with a previously measured cross-correlation is not necessarily accurate, as the actual IRF can considerably differ from the cross-correlation measured without the sample.



Figure 6.7: Transient absorption kinetic traces on high concentration samples, when recorded after deliberate optical alignment, exhibit minimal distortion of the initial dynamics by spectral filtering.

6.7 Conclusions

The contribution of a spectral self-filtering effect to the pump pulse within the sample in transient absorption measurements has been investigated. The effect is most pronounced in systems where the pump pulse is non-uniformly absorbed by the analyte. Spectral self-filtering was found to alter the temporal profile of the pulse, leading to a reduction in time resolution and thus provides the risk of systematic errors and data misinterpretation. An unaccounted for decrease in the IRF as a result of differences in sample absorbance can easily allow variations in results to be misattributed to changes in excited-state dynamics. Experiments focused on concentration dependence are particularly vulnerable to this inconspicuous pulse distortion between samples. Furthermore, a dependence on pulse interaction region indicates that comparison of measurements between different samples requires meticulous alignment and should be taken with care. Recognition of this measurement artifact becomes increasingly relevant as femtosecond transient absorption experiments with resolution limited by pulse bandwidth reach widespread availability.

Chapter 7 SUMMARY

The structural dynamics of metalloporphyrin systems were successfully measured using transient absorption, pump-DFWM, and XTA spectroscopies on the ultrafast timescale. Pump-DFWM methods in particular were extended to allow the first measurements on a heterogeneous colloidal sample. Successful pump-DFWM measurements in solution and solid-state samples have helped to establish the technique as a powerful tool for ultrafast vibrational spectroscopy.

Pump-DFWM allowed recording of the vibrational dynamics over 1 ps of relaxation following independent excitation to a vibrationally hot and cold singlet excited state of Zn-TPP in THF solution. The role of vibrational relaxation along a specific 1350 cm⁻¹ ring stretching mode was elucidated in the excited-state dynamics of Zn-TPP. The vibrational frequency was found to increase by 13 cm^{-1} within 400 fs, indicating the relaxation of the vibrational mode within an anharmonic potential energy surface. This clarified a longstanding question regarding the overall relaxation dynamics. Another mode at 350 cm^{-1} was also identified to couple to electronic excitation, attributed to stretching at the Zn-N bonds. Transient absorption measurements alone were not sufficient to isolate the mechanism responsible for the observed dynamics. Additionally, vibrational interaction with the surrounding solvent was observed in the photoexcited metalloporphyrin. This interaction was evidenced as an intense peak in the photoinduced vibrational spectrum. It was further indicated by a phase-shift of the solvent frequency relative to the metalloporphyrin, accessible in this pure time-domain measurement. When Zn-TPP was modified with a bridging linker group and bound to TiO_2 , similar ground state vibrational features were measured as in solution. After photoexcitation though, the spectrum differed significantly. HET from the Zn-TPP chromophore into the semiconductor was found to induce multiple new vibrational modes in the oxidized product state of the molecule. The electron transfer time was identified with transient absorption at 85 fs. Pump-DFWM spectra produced after that time showed enhanced peaks at vibrational modes assigned to the bridge group through which electron transfer occurred. The HET induced peaks decayed on a different timescale than vibrations induced on the chromophore by the pump pulse. The triggered bridge group vibrations of the cation indicate that HET from the metalloporphyrin occurs as a largely nonadiabatic process, with vibrational excitation of the product state generated by Franck-Condon factors at the surface crossing.

The metalloporphyrin had its metal substituted from Zn(II) to Ni(II) to accommodate XTA measurements. Rather than measure distributed vibrational features of the molecule, XTA directly reported on the local structure around the metal center and its dynamics. Following photoexcitation, the porphyrin ring was found to expand. Significant changes were observed across the transient X-ray absorption due to photoexcitation. A 0.6 Å increase in the Ni- C_{α} distance was found from analysis of the EXAFS signal at 120 ps, the earliest available time point. This complemented the vibrational data from pump-DFWM measurements on Zn-TPP, where ring expansion was a dominant mode coupled to the excited state transition. Furthermore, the XTA data showed a transient occupancy of the Ni $4p_z$ orbital, strongly indicating axial ligation of solvent molecules triggered by photoexcitation. This data supplements the photoinduced vibrational interaction of Zn-TPP with solvent observed through pump-DFWM. The clear excited state ligation of the Ni atom has implications for photoinduced chemical reactivity involving porphyrins. The dynamics attributed to solvent ligation were observed in optical transient absorption, and disappeared when a non-coordinating solvent was used. Assignment of the dynamics to structural reorganization due to solvent attachment is not possible solely through optical measurements,

but was informed by direct XTA measurements. Optical experiments can more easily investigate ligation parameters and conditions.

When different concentration samples were used, transient absorption measurements showed changes in the dynamics of Zn-TPP at early times. The dynamics were assigned by pump-DFWM and XTA to vibrational relaxation in the exterior ring stretch. These dynamics were initially perplexing. Intermolecular interactions between metalloporphyrins was thought to be the cause, but this could not be confirmed by steady-state optical measurements. A series of carefully prepared measurements revealed the apparent dynamics to be an experimental artifact. Absorption from the sample distorted the spectral properties of the pump pulse, and therefore its time duration. The smeared time resolution causes a change in the instrument response function that must be accounted for. This effect is inherent to any concentration-dependent femtosecond transient absorption measurement. The effect was characterized, and careful optical alignment minimized the contribution to further measurements. Awareness of the effect is important to not misattribute a shifting time resolution to a physical molecular response, such as intermolecular interactions.

Future work involving combined pump-DFWM and XTA measurements on more similar systems could fully characterize structural effects in molecular excited states, as evidenced by these early results. Selection of materials for HET studies that are both suitable for pump-DFWM and can survive intense X-ray irradiation would offer unprecedented insight into the role of coherent nuclear motion and transient states in interfacial electron transfer.

117

BIBLIOGRAPHY

- J. W. Lichtman and J.-A. Conchello. Fluorescence Microscopy. Nature Methods, 2:910–919, 2005.
- [2] L. X. Chen, X. Zhang, E. C. Wasinger, K. Attenkofer, G. Jennings, A. Z. Muresan, and J. S. Lindsey. Tracking Electrons and Atoms in a Photoexcited Metalloporphyrin by X-Ray Transient Absorption Spectroscopy. *Journal of the American Chemical Society*, 129(31):9616–9618, 2007.
- [3] L. X. Chen and X. Zhang. Photochemical Processes Revealed by X-Ray Transient Absorption Spectroscopy. *The Journal of Physical Chemistry Letters*, 4(22):4000– 4013, 2013.
- [4] G. Ciamician. The Photochemistry of the Future. Science, 36(926):385–394, 1912.
- [5] M. Grätzel. Molecular Engineering in Photoconversion Systems. In Energy Resources through Photochemistry and Catalysis, chapter 3, pages 71–98. Academic Press, 1983.
- [6] V. Balzani. Supramolecular Photochemistry. Pure and Applied Chemistry, 6(62):1099–1102, 2009.
- [7] A. P. Castano, T. N. Demidova, and M. R. Hamblin. Mechanisms in Photodynamic Therapy: Part One: Photosensitizers, Photochemistry and Cellular Localization. *Photodiagnosis and Photodynamic Therapy*, 1(4):279–293, 2004.
- [8] H. Sato. Photodissociation Reactions Mediated by Solid Surfaces. In Progress in Photochemistry and Photophysics, chapter 5, pages 135–167. CRC Press, 1992.
- [9] A. E. O'Connor, W. M. Gallagher, and A. T. Byrne. Porphyrin and Nonporphyrin Photosensitizers in Oncology: Preclinical and Clinical Advances in Photodynamic Therapy. *Photochemistry and Photobiology*, 85(5):1053–1074, 2009.
- [10] N. J. Turro. Organic Photochemistry: an Overview. In Modern Molecular Photochemistry, chapter 1, pages 1–17. University Science Books, 1991.
- [11] S. L. Murov, I. Carmichael, and G. L. Hug. Photophysics of Organic Molecules in Solution. In *Handbook of Photochemistry*, chapter 1, pages 1–54. Marcel Dekker, 1993.

- [12] J. Franck and E. G. Dymond. Elementary Processes of Photochemical Reactions. Transactions of the Faraday Society, 21:536–542, 1926.
- [13] B. M. and O. R. Zur Quantentheorie der Molekeln. Annalen der Physik, 389(20):457–484, 1927.
- [14] T. S. Rose, M. J. Rosker, and A. H. Zewail. Femtosecond Real-Time Observation of Wave Packet Oscillations (Resonance) in Dissociation Reactions. *The Journal* of Chemical Physics, 88(10):6672–6673, 1988.
- [15] A. H. Zewail. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. The Journal of Physical Chemistry A, 104(24):5660–5694, 2000.
- [16] M. H. Vos, J. C. Lambry, S. J. Robles, D. C. Youvan, J. Breton, and J. L. Martin. Direct Observation of Vibrational Coherence in Bacterial Reaction Centers using Femtosecond Absorption Spectroscopy. *Proceedings of the National Academy of Sciences*, 88(20):8885–8889, 1991.
- [17] Q. Wang, R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank. Vibrationally Coherent Photochemistry in the Femtosecond Primary Event of Vision. *Science*, 266(5184):422–424, 1994.
- [18] C. Chudoba, E. Riedle, M. Pfeiffer, and T. Elsaesser. Vibrational Coherence in Ultrafast Excited State Proton Transfer. *Chemical Physics Letters*, 263(5):622– 628, 1996.
- [19] B. Wolfseder, L. Seidner, W. Domcke, G. Stock, M. Seel, S. Engleitner, and W. Zinth. Vibrational Coherence in Ultrafast Electron-Transfer Dynamics of Oxazine 1 in N,N-dimethylaniline: Simulation of a Femtosecond Pump-Probe Experiment. *Chemical Physics*, 233(2):323–334, 1998.
- [20] D. B. Turner, K. E. Wilk, P. M. G. Curmi, and G. D. Scholes. Comparison of Electronic and Vibrational Coherence Measured by Two-Dimensional Electronic Spectroscopy. *The Journal of Physical Chemistry Letters*, 2(15):1904–1911, 2011.
- [21] S. Ramakrishna, F. Willig, and V. May. Theory of Ultrafast Photoinduced Heterogeneous Electron Transfer: Decay of Vibrational Coherence into a Finite ElectronicVibrational Quasicontinuum. *The Journal of Chemical Physics*, 115(6):2743–2756, 2001.
- [22] A. Z. Szarka, N. Pugliano, D. K. Palit, and R. M. Hochstrasser. Vibrational Coherence in the Solution Phase Photoisomerization Reaction of Cis-Stilbene. *Chemical Physics Letters*, 240(1):25–0, 1995.
- [23] S. A. Trushin, W. Fuss, W. E. Schmid, and K. L. Kompa. Femtosecond Dynamics and Vibrational Coherence in Gas-Phase Ultraviolet Photodecomposition of Cr(CO)₆. The Journal of Physical Chemistry A, 102(23):4129–4137, 1998.

- [24] M. Bixon and J. Jortner. Vibrational Coherence in Nonadiabatic Dynamics. The Journal of Chemical Physics, 107(5):1470–1482, 1997.
- [25] C. V. Raman and K. S. Krishnan. A New Type of Secondary Radiation. Nature, 121:501–502, 1928.
- [26] P. Renate, S. Michael, and P. Jürgen. Raman Spectroscopy-A Prospective Tool in the Life Sciences. *ChemPhysChem*, 4(1):14–30, 2002.
- [27] Z. Movasaghi, S. Rehman, and I. U. Rehman. Raman Spectroscopy of Biological Tissues. Applied Spectroscopy Reviews, 42(5):493–541, 2007.
- [28] E. Smith and G. Dent. Applications. In Modern Raman Spectroscopy A Practical Approach, chapter 6, pages 135–179. John Wiley & Sons, 2005.
- [29] F. Moya, S. Druet, and J. Taran. Gas Spectroscopy and Temperature Measurement by Coherent Raman Anti-Stokes Scattering. Optics Communications, 13(2):169–174, 1975.
- [30] P. Lazaridis, G. Debarge, and P. Gallion. Time-Bandwidth Product of Chirped sech² Pulses: Application to Phase-Amplitude-Coupling Factor Measurement. *Optics Letters*, 20(10):1160–1162, 1995.
- [31] B. Proctor, E. Westwig, and F. Wise. Characterization of a Kerr-Lens Mode-Locked Ti:Sapphire Laser with Positive Group-Velocity Dispersion. Optics Letters, 18(19):1654–1656, 1993.
- [32] E. Riedle, M. Beutter, S. Lochbrunner, J. Piel, S. Schenkl, S. Spörlein, and W. Zinth. Generation of 10 to 50 fs Pulses Tunable through all of the Visible and the NIR. *Applied Physics B*, 71:457–465, 2000.
- [33] T. Kobayashi and A. Baltuska. Sub-5 fs Pulse Generation from a Noncollinear Optical Parametric Amplifier. *Measurement Science and Technology*, 13(11):1671, 2002.
- [34] B. Kohler, V. V. Yakovlev, J. Che, J. L. Krause, M. Messina, K. R. Wilson, N. Schwentner, R. M. Whitnell, and Y. Yan. Quantum Control of Wave Packet Evolution with Tailored Femtosecond Pulses. *Physical Review Letters*, 74:3360– 3363, 1995.
- [35] R. Trebino. Ultrashort Laser Pulses. In Frequency-Resolved Optical Gating: The Measurement of Ultrashort Laser Pulses, chapter 2, pages 11–35. Springer, 2000.
- [36] R. Berera, R. van Grondelle, and J. T. Kennis. Ultrafast Transient Absorption Spectroscopy: Principles and Application to Photosynthetic Systems. *Photosyn*thesis Research, 101(2-3):105–118, 2009.

- [37] A. Einstein. Zur Quantentheorie der Strahlung. Physikalische Zeitschrift, 18, 1917.
- [38] Y. J. Yan and S. Mukamel. Femtosecond Pump-Probe Spectroscopy of Polyatomic Molecules in Condensed Phases. *Physical Review A*, 41:6485–6504, 1990.
- [39] J. S. Nieto-Pescador. Photoinduced Electron Transfer at the Tetrapyrrole-TiO₂ Interface: Effect of the Energy Alignment. PhD thesis, University of Delaware, 2017.
- [40] S. Mukamel. Wavepacket Analysis of Nonimpulsive Measurements. In Principles of Nonlinear Optics and Spectroscopy, chapter 13, pages 369–411. Oxford University Press, 1995.
- [41] U. Selig, F. Langhojer, F. Dimler, T. Löhrig, C. Schwarz, B. Gieseking, and T. Brixner. Inherently Phase-Stable Coherent Two-Dimensional Spectroscopy Using Only Conventional Optics. *Optics Letters*, 33:2851–2853, 2008.
- [42] I. A. Heisler, R. Moca, F. V. A. Camargo, and S. R. Meech. Two-Dimensional Electronic Spectroscopy Based on Conventional Optics and Fast Dual Chopper Data Acquisition. *Review of Scientific Instruments*, 85:063103, 2014.
- [43] L. X. Chen. Probing Transient Molecular Strictures in Photochemical Processes Using Laser-Initiated Time-Resolved X-Ray Absorption Spectroscopy. Annual Review of Physical Chemistry, 56(1):221–254, 2005.
- [44] L. X. Chen, X. Zhang, J. V. Lockard, A. B. Stickrath, K. Attenkofer, G. Jennings, and D.-J. Liu. Excited-State Molecular Structures Captured by X-Ray Transient Absorption Spectroscopy: a Decade and Beyond. Acta Crystallographica Section A, 66(2):240–251, 2010.
- [45] J. Yano and V. K. Yachandra. X-Ray Absorption Spectroscopy. *Photosynthesis Research*, 102(2):241, 2009.
- [46] J. V. Lockard, S. Kabehie, J. I. Zink, G. Smolentsev, A. Soldatov, and L. X. Chen. Influence of Ligand Substitution on Excited State Structural Dynamics in Cu(I) Bisphenanthroline Complexes. *The Journal of Physical Chemistry B*, 114(45):14521–14527, 2010.
- [47] J. Marco, J. Gancedo, M. Gracia, J. Gautier, E. Ros, and F. Berry. Characterization of the Nickel Cobaltite, NiCo₂O₄, Prepared by Several Methods: An XRD, XANES, EXAFS, and XPS Study. *Journal of Solid State Chemistry*, 153(1):74– 81, 2000.
- [48] D. G. Johnson, M. P. Niemczyk, D. W. Minsek, G. P. Wiederrecht, W. A. Svec, G. L. Gaines, and M. R. Wasielewski. Photochemical Electron Transfer

in Chlorophyll-Porphyrin-Quinone Triads: the Role of the Porphyrin-Bridging Molecule. *Journal of the American Chemical Society*, 115(13):5692–5701, 1993.

- [49] K. Chitre, A. Batarseh, A. Kopecky, H. Fan, H. Tang, R. Lalancette, R. A. Bartynski, and E. Galoppini. Synthesis of Zinc Tetraphenylporphyrin Rigid Rods with a Built-In Dipole. *The Journal of Physical Chemistry B*, 119(24):7522–7530, 2015.
- [50] W. M. Campbell, A. K. Burrell, D. L. Officer, and K. W. Jolley. Porphyrins as Light Harvesters in the Dye-Sensitised TiO₂ Solar Cell. *Coordination Chemistry Reviews*, 248(13):1363–1379, 2004.
- [51] D. Chen, D. Yang, J. Geng, J. Zhu, and Z. Jiang. Improving Visible-Light Photocatalytic Activity of N-doped TiO₂ Nanoparticles via Sensitization by Zn Porphyrin. *Applied Surface Science*, 255(5):2879–2884, 2008.
- [52] M. Gouterman, G. H. Wagnière, and L. C. Snyder. Spectra of Porphyrins: Part II. Four Orbital Model. *Journal of Molecular Spectroscopy*, 11(1-6):108–127, 1963.
- [53] E. Baerends, G. Ricciardi, A. Rosa, and S. van Gisbergen. A DFT/TDDFT Interpretation of the Ground and Excited States of Porphyrin and Porphyrazine Complexes. *Coordination Chemistry Reviews*, 230(12):5–27, 2002.
- [54] S. Y. Huang, G. Schlichthrl, A. J. Nozik, M. Grätzel, and A. J. Frank. Charge Recombination in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells. *The Journal* of Physical Chemistry B, 101(14):2576–2582, 1997.
- [55] P. Yu, K. Zhu, A. G. Norman, S. Ferrere, A. J. Frank, and A. J. Nozik. Nanocrystalline TiO₂ Solar Cells Sensitized with InAs Quantum Dots. *The Journal of Physical Chemistry B*, 110(50):25451–25454, 2006.
- [56] T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Lian, and S. Yanagida. Phenyl-Conjugated Oligoene Sensitizers for TiO₂ Solar Cells. *Chemistry of Materials*, 16(9):1806–1812, 2004.
- [57] A. C. Fisher, L. M. Peter, E. A. Ponomarev, A. B. Walker, and K. G. U. Wijayantha. Intensity Dependence of the Back Reaction and Transport of Electrons in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells. *The Journal of Physical Chemistry B*, 104(5):949–958, 2000.
- [58] M. K. Nazeeruddin, R. Humphry-Baker, P. Liska, and M. Grätzel. Investigation of Sensitizer Adsorption and the Influence of Protons on Current and Voltage of a Dye-Sensitized Nanocrystalline TiO₂ Solar Cell. *The Journal of Physical Chemistry B*, 107(34):8981–8987, 2003.

- [59] J. van de Lagemaat, N.-G. Park, and A. J. Frank. Influence of Electrical Potential Distribution, Charge Transport, and Recombination on the Photopotential and Photocurrent Conversion Efficiency of Dye-Sensitized Nanocrystalline TiO₂ Solar Cells: A Study by Electrical Impedance and Optical Modulation Techniques. *The Journal of Physical Chemistry B*, 104(9):2044–2052, 2000.
- [60] G. Schlichthörl, S. Y. Huang, J. Sprague, and A. J. Frank. Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells: A Study by Intensity Modulated Photovoltage Spectroscopy. *The Journal of Physical Chemistry B*, 101(41):8141–8155, 1997.
- [61] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, and H. Arakawa. A Coumarin-Derivative Dye Sensitized Nanocrystalline TiO₂ Solar Cell Having a High Solar-Energy Conversion Efficiency up to 5.6%. *Chemical Communications*, 0:569–570, 2001.
- [62] N.-G. Park, J. van de Lagemaat, and A. J. Frank. Comparison of Dye-Sensitized Rutile- and Anatase-Based TiO₂ Solar Cells. *The Journal of Physical Chemistry* B, 104(38):8989–8994, 2000.
- [63] T. Ohsaka, F. Izumi, and Y. Fujiki. Raman Spectrum of Anatase, TiO₂. Journal of Raman Spectroscopy, 7(6):321–324, 1978.
- [64] G. N. Howatt, R. G. Breckenridge, and J. M. Brownlow. Fabrication of Thin Ceramic Sheets for Capacitors. *Journal of the American Ceramic Society*, 30(8):237–242, 1947.
- [65] J. Rochford, D. Chu, A. Hagfeldt, and E. Galoppini. Tetrachelate Porphyrin Chromophores for Metal Oxide Semiconductor Sensitization: Effect of the Spacer Length and Anchoring Group Position. *Journal of the American Chemical Soci*ety, 129(15):4655–4665, 2007.
- [66] R. Ernstorfer. Spectroscopic Investigation of Photoinduced Heterogeneous Electron Transfer. PhD thesis, Freie Universität Berlin, 2004.
- [67] R. Rossmanith, C. K. Weiss, J. Geserick, N. Hsing, U. Hörmann, U. Kaiser, and K. Landfester. Porous Anatase Nanoparticles with High Specific Surface Area Prepared by Miniemulsion Technique. *Chemistry of Materials*, 20(18):5768–5780, 2008.
- [68] K. S. Kim and M. A. Barteau. Pathways for Carboxylic Acid Decomposition on Titania. *Langmuir*, 4(4):945–953, 1988.
- [69] Q. Qu, H. Geng, R. Peng, Q. Cui, X. Gu, F. Li, and M. Wang. Chemically Binding Carboxylic Acids onto TiO₂ Nanoparticles with Adjustable Coverage by Solvothermal Strategy. *Langmuir*, 26(12):9539–9546, 2010.

- [70] B. Abraham, J. Nieto-Pescador, and L. Gundlach. Ultrafast Relaxation Dynamics of Photoexcited Zinc-Porphyrin: Electronic-Vibrational Coupling. *The Journal of Physical Chemistry Letters*, 7(16):3151–3156, 2016.
- [71] R. Kumble, S. Palese, V. S.-Y. Lin, M. J. Therien, and R. M. Hochstrasser. Ultrafast Dynamics of Highly Conjugated Porphyrin Arrays. *Journal of the American Chemical Society*, 120(44):11489–11498, 1998.
- [72] M. Kullmann, A. Hipke, P. Nuernberger, T. Bruhn, D. C. G. Gotz, M. Sekita, D. M. Guldi, G. Bringmann, and T. Brixner. Ultrafast Exciton Dynamics After Soret- or Q-band Excitation of a Directly β, β'-linked Bisporphyrin. *Physical Chemistry Chemical Physics*, 14:8038–8050, 2012.
- [73] A. Perdomo-Ortiz, J. R. Widom, G. A. Lott, A. Aspuru-Guzik, and A. H. Marcus. Conformation and Electronic Population Transfer in Membrane-Supported Self-Assembled Porphyrin Dimers by 2D Fluorescence Spectroscopy. *The Journal of Physical Chemistry B*, 116(35):10757–10770, 2012.
- [74] M. T. Colvin, A. L. Smeigh, E. M. Giacobbe, S. M. M. Conron, A. B. Ricks, and M. R. Wasielewski. Ultrafast Intersystem Crossing and Spin Dynamics of Zinc meso-Tetraphenylporphyrin Covalently Bound to Stable Radicals. *The Journal* of Physical Chemistry A, 115(26):7538–7549, 2011.
- [75] H.-J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht, and J. T. Hupp. Light-Harvesting and Ultrafast Energy Migration in Porphyrin-Based Metal-Organic Frameworks. *Journal of the American Chemical Society*, 135(2):862–869, 2013.
- [76] H.-Z. Yu, J. S. Baskin, and A. H. Zewail. Ultrafast Dynamics of Porphyrins in the Condensed Phase: II. Zinc Tetraphenylporphyrin. *The Journal of Physical Chemistry A*, 106(42):9845–9854, 2002.
- [77] M. Enescu, K. Steenkeste, F. Tfibel, and M.-P. Fontaine-Aupart. Femtosecond Relaxation Processes from Upper Excited States of Tetrakis(N-methyl-4pyridyl)porphyrins Studied by Transient Absorption Spectroscopy. *Physical Chemistry Chemical Physics*, 4:6092–6099, 2002.
- [78] G. G. Gurzadyan, T.-H. Tran-Thi, and T. Gustavsson. Time-resolved Fluorescence Spectroscopy of High-Lying Electronic States of Zn-Tetraphenylporphyrin. *The Journal of Chemical Physics*, 108(2):385–388, 1998.
- [79] X. Liu, U. Tripathy, S. V. Bhosale, S. J. Langford, and R. P. Steer. Photophysics of Soret-Excited Tetrapyrroles in Solution. II. Effects of Perdeuteration, Substituent Nature and Position, and Macrocycle Structure and Conformation in Zinc(II) Porphyrins. *The Journal of Physical Chemistry A*, 112(38):8986–8998, 2008.
- [80] A. Lukaszewicz, J. Karolczak, D. Kowalska, A. Maciejewski, M. Ziolek, and R. P. Steer. Photophysical Processes in Electronic States of Zinc Tetraphenyl Porphyrin Accessed on One- and Two-Photon Excitation in the Soret Region. *Chemical Physics*, 331:359–372, 2007.
- [81] G. A. Peralta, M. Seth, and T. Ziegler. Magnetic Circular Dichroism of Porphyrins Containing M = Ca, Ni, and Zn. A Computational Study Based on Time-Dependent Density Functional Theory. *Inorganic Chemistry*, 46(22):9111– 9125, 2007.
- [82] H. Solheim, K. Ruud, S. Coriani, and P. Norman. The A and B Terms of Magnetic Circular Dichroism Revisited. *The Journal of Physical Chemistry A*, 112(40):9615–9618, 2008.
- [83] K. Falahati, C. Hamerla, M. Huix-Rotllant, and I. Burghardt. Ultrafast Photochemistry of Free-Base Porphyrin: a Theoretical Investigation of B → Q Internal Conversion Mediated by Dark States. *Physical Chemistry Chemical Physics*, 20:12483–12492, 2018.
- [84] K. A. Nguyen, P. N. Day, R. Pachter, S. Tretiak, V. Chernyak, and S. Mukamel. Analysis of Absorption Spectra of Zinc Porphyrin, Zinc meso-Tetraphenylporphyrin, and Halogenated Derivatives. *The Journal of Physical Chemistry A*, 106(43):10285–10293, 2002.
- [85] J. Nieto-Pescador, B. Abraham, J. Li, A. Batarseh, R. A. Bartynski, E. Galoppini, and L. Gundlach. Heterogeneous Electron-Transfer Dynamics through Dipole-Bridge Groups. *The Journal of Physical Chemistry C*, 120:48–55, 2016.
- [86] U. Tripathy, D. Kowalska, X. Liu, S. Velate, and R. P. Steer. Photophysics of Soret-Excited Tetrapyrroles in Solution. I. Metalloporphyrins: MgTPP, ZnTPP, and CdTPP. *The Journal of Physical Chemistry A*, 112(26):5824–5833, 2008.
- [87] B. Moore and J. Autschbach. Density Functional Study of Tetraphenylporphyrin Long-Range Exciton Coupling. *ChemistryOpen*, 1(4):184–194, 2012.
- [88] R. Nozawa, W.-Y. C. Hiroko Tanaka, Y. Hong, I. Hisaki, S. Shimizu, J.-Y. Shin, T. Kowalczyk, S. Irle, D. Kim, and H. Shinokubo. Stacked Antiaromatic Porphyrins. *Nature Communications*, 7:13620, 2016.
- [89] R. F. Khairutdinov and N. Serpone. Photoluminescence and Transient Spectroscopy of Free Base Porphyrin Aggregates. *The Journal of Physical Chemistry* B, 103(5):761–769, 1999.
- [90] Y. Li, W.-W. Han, and M.-X. Liao. Spectroscopic and Crystal Structural Analyses of Zinc (II) Tetraphenylporphyrin J-aggregates. Acta Physico-Chimica Sinica, 25(12):2493, 2009.

- [91] Y. Li and R. P. Steer. Kinetics of Disaggregation of a Non-covalent Zinc Tetraphenylporphyrin Dimer in Solution. *Chemical Physics Letters*, 373(12):94– 99, 2003.
- [92] J. Karolczak, D. Kowalska, A. Lukaszewicz, A. Maciejewski, and R. P. Steer. Photophysical Studies of Porphyrins and Metalloporphyrins: Accurate Measurements of Fluorescence Spectra and Fluorescence Quantum Yields for Soret Band Excitation of Zinc Tetraphenylporphyrin. *The Journal of Physical Chemistry A*, 108(21):4570–4575, 2004.
- [93] J. H. Gross, N. Nieth, H. B. Linden, U. Blumbach, F. J. Richter, M. E. Tauchert, R. Tompers, and P. Hofmann. Liquid Injection Field Desorption/Ionization of Reactive Transition Metal Complexes. *Analytical and Bioanalytical Chemistry*, 386:52, 2006.
- [94] A. P. Hard, U. A. Jayasooriya, and A. N. Cammidge. Molecular Sensors Using a Resonance Raman Template. Analyst, 128:70–74, 2003.
- [95] Y.-H. Zhang, W. Zhao, P. Jiang, L.-J. Zhang, T. Zhang, and J. Wang. Structural Parameters and Vibrational Spectra of a Series of Zinc meso-Phenylporphyrins: A DFT and Experimental Study. *Spectrochimica Acta Part A*, 75(2):880–890, 2010.
- [96] J. Hauer, T. Buckup, and M. Motzkus. Pump-Degenerate Four Wave Mixing as a Technique for Analyzing Structural and Electronic Evolution: Multidimensional Time-Resolved Dynamics Near a Conical Intersection. *The Journal of Physical Chemistry A*, 111:10517–10529, 2007.
- [97] U. Even, J. Magen, J. Jortner, J. Friedman, and H. Levanon. Isolated Ultracold Porphyrins in Supersonic Expansions. I. Free-Base Tetraphenylporphyrin and Zn-tetraphenylporphyrin. *The Journal of Chemical Physics*, 77(9):4374–4383, 1982.
- [98] T. G. Spiro, R. S. Czernuszewicz, and X.-Y. Li. Metalloporphyrin Structure and Dynamics from Resonance Raman Spectroscopy. *Coordination Chemistry Reviews*, 100:541–571, 1990.
- [99] M. S. Marek, T. Buckup, and M. Motzkus. Direct Observation of a Dark State in Lycopene Using Pump-DFWM. *The Journal of Physical Chemistry B*, 115:8328– 8337, 2011.
- [100] J. Zhou, W. Yu, and A. E. Bragg. Structural Relaxation of Photoexcited Quaterthiophenes Probed with Vibrational Specificity. *The Journal of Physi*cal Chemistry Letters, 6(17):3496–3502, 2015.

- [101] T. A. A. Oliver, N. H. C. Lewis, and G. R. Fleming. Correlating the Motion of Electrons and Nuclei with Two-Dimensional ElectronicVibrational Spectroscopy. *Proceedings of the National Academy of Sciences*, 111:10061–10066, 2014.
- [102] C. M. Bender and T. T. Wu. Anharmonic Oscillator. Physical Review, 184:1231– 1260, 1969.
- [103] L. Goodman, A. G. Ozkabak, and S. N. Thakur. A Benchmark Vibrational Potential Surface: Ground-State Benzene. *The Journal of Physical Chemistry*, 95(23):9044–9058, 1991.
- [104] J. Brazard, L. A. Bizimana, T. Gellen, W. P. Carbery, and D. B. Turner. Experimental Detection of Branching at a Conical Intersection in a Highly Fluorescent Molecule. *The Journal of Physical Chemistry Letters*, 7(1):14–19, 2016.
- [105] R. Shimada, H. Kano, and H. Hamaguchi. Molecular Near-Field Effect and Intensity Enhancement of Solvent Modes in Resonance Hyper-Raman Scattering. *Journal of Raman Spectroscopy*, 37(4):469–471, 2006.
- [106] R. Shimada, H. Kano, and H. Hamaguchi. Intensity Enhancement and Selective Detection of Proximate Solvent Molecules by Molecular Near-Field Effect in Resonance Hyper-Raman Scattering. *The Journal of Chemical Physics*, 129(2):024505, 2008.
- [107] B. Abraham, H. Fan, E. Galoppini, and L. Gundlach. Vibrational Spectroscopy on Photoexcited Dye-Sensitized Films via Pump-Degenerate Four-Wave Mixing. *The Journal of Physical Chemistry A*, 122(8):2039–2045, 2018.
- [108] C. S. Ponseca, P. Chábera, J. Uhlig, P. Persson, and V. Sundström. Ultrafast Electron Dynamics in Solar Energy Conversion. *Chemical Reviews*, 117(16):10940–11024, 2017.
- [109] M. Grätzel. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. Inorganic Chemistry, 44(20):6841–6851, 2005.
- [110] C. C. Gradinaru, J. T. M. Kennis, E. Papagiannakis, I. H. M. van Stokkum, R. J. Cogdell, G. R. Fleming, R. A. Niederman, and R. van Grondelle. An Unusual Pathway of Excitation Energy Deactivation in Carotenoids: Singlet-to-Triplet Conversion on an Ultrafast Timescale in a Photosynthetic Antenna. *Proceedings of the National Academy of Sciences*, 98(5):2364–2369, 2001.
- [111] W. Zinth and J. Wachtveitl. The First Picoseconds in Bacterial PhotosynthesisUltrafast Electron Transfer for the Efficient Conversion of Light Energy. *ChemPhysChem*, 6(5):871–880, 2005.

- [112] E. Romero, R. Augulis, V. I. Novoderezhkin, M. Ferretti, J. Thieme, D. Zigmantas, and R. van Grondelle. Quantum Coherence in Photosynthesis for Efficient Solar-Energy Conversion. *Nature Physics*, 10:676–682, 2014.
- [113] N. A. Anderson and T. Lian. Ultrafast Electron Transfer at the Moleculesemiconductor Nanoparticle Interface. Annual Review of Physical Chemistry, 56(1):491–519, 2005.
- [114] A. Furube, R. Katoh, T. Yoshihara, K. Hara, S. Murata, H. Arakawa, and M. Tachiya. Ultrafast Direct and Indirect Electron-Injection Processes in a Photoexcited Dye-Sensitized Nanocrystalline Zinc Oxide Film: The Importance of Exciplex Intermediates at the Surface. *The Journal of Physical Chemistry B*, 108(33):12583–12592, 2004.
- [115] J. Nieto-Pescador, B. Abraham, and L. Gundlach. Photoinduced Ultrafast Heterogeneous Electron Transfer at Molecule-Semiconductor Interfaces. *The Journal* of Physical Chemistry Letters, 5:3498–3507, 2014.
- [116] A. Pérez-Larios, A. Hernndez-Gordillo, G. Morales-Mendoza, L. Lartundo-Rojas, Á. Mantilla, and R. Gómez. Enhancing the H₂ Evolution from WaterMethanol Solution using Mn²⁺-Mn³⁺-Mn⁴⁺ Redox Species of Mn-Doped TiO₂ SolGel Photocatalysts. *Catalysis Today*, 266:9–16, 2016.
- [117] S. Gelover, L. A. Gmez, K. Reyes, and M. T. Leal. A Practical Demonstration of Water Disinfection using TiO₂ Films and Sunlight. *Water Research*, 40(17):3274– 3280, 2006.
- [118] S. K. Deb. Dye-Sensitized TiO₂ Thin-Film Solar Cell Research at the National Renewable Energy Laboratory (NREL). Solar Energy Materials and Solar Cells, 88(1):1–10, 2005.
- [119] J. Zhang, Y. Lou, M. Liu, H. Zhou, Y. Zhao, Z. Wang, L. Shi, D. Li, and S. Yuan. High-Performance Dye-Sensitized Solar Cells Based on ColloidSolution Deposition Planarized Fluorine-Doped Tin Oxide Substrates. ACS Applied Materials & Interfaces, 10(18):15697–15703, 2018.
- [120] Y. S. Kaganovskii, V. D. Freilikher, E. Kanzieper, Y. Nafcha, M. Rosenbluh, and I. M. Fuks. Light Scattering from Slightly Rough Dielectric Films. *Journal of the Optical Society of America A*, 16(2):331–338, 1999.
- [121] J. M. Rehm, G. L. McLendon, Y. Nagasawa, J. Moser, and M. Grätzel. Femtosecond Electron-Transfer Dynamics at a Sensitizing Dye-Semiconductor (TiO₂) Interface. *The Journal of Physical Chemistry*, 100:9577–9578, 1996.
- [122] N. J. Cherepy, G. P. Smestad, M. Grätzel, and J. Z. Zhang. Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin

Dye-Sensitized TiO₂ Nanocrystalline Electrode. The Journal of Physical Chemistry B, 101(45):9342–9351, 1997.

- [123] J. Nieto-Pescador, B. Abraham, A. J. Pistner, J. Rosenthal, and L. Gundlach. Electronic State Dependence of Heterogeneous Electron Transfer: Injection from the S₁ and S₂ State of Phlorin Into TiO₂. *Physical Chemistry Chemical Physics*, 17:7914–7923, 2015.
- [124] A. Morandeira, G. Boschloo, A. Hagfeldt, and L. Hammarström. Photoinduced Ultrafast Dynamics of Coumarin 343 Sensitized p-Type-Nanostructured NiO Films. *The Journal of Physical Chemistry B*, 109(41):19403–19410, 2005.
- [125] C. Zimmermann, F. Willig, S. S. Ramakrishna, B. Burfeindt, B. Pettinger, R. Eichberger, and W. Storck. Experimental Fingerprints of Vibrational Wave-Packet Motion during Ultrafast Heterogeneous Electron Transfer. *The Journal* of Physical Chemistry B, 105:9245–9253, 2001.
- [126] M. Plenio, J. Almeida, and S. Huelga. Origin of Long-Lived Oscillations in 2D-Spectra of a Quantum Vibronic Model: Electronic Versus Vibrational Coherence. *The Journal of Chemical Physics*, 139:235102, 2013.
- [127] V. Tiwari, W. K. Peters, and D. M. Jonas. Electronic Resonance with Anticorrelated Pigment Vibrations Drives Photosynthetic Energy Transfer Outside the Adiabatic Framework. *Proceedings of the National Academy of Sciences*, 110(4):1203–1208, 2013.
- [128] N. Christensson, H. F. Kauffmann, T. Pullerits, and T. Mančal. Origin of Long-Lived Coherences in Light-Harvesting Complexes. *The Journal of Physical Chemistry B*, 116(25):7449–7454, 2012.
- [129] E. Romero, R. Augulis, V. I. Novoderezhkin, M. Ferretti, J. Thieme, D. Zigmantas, and R. Van Grondelle. Quantum Coherence in Photosynthesis for Efficient Solar-Energy Conversion. *Nature Physics*, 10(9):676–682, 2014.
- [130] S. Chaudhuri, S. Hedström, D. D. Méndez-Hernández, H. P. Hendrickson, K. A. Jung, J. Ho, and V. S. Batista. Electron Transfer Assisted by Vibronic Coupling from Multiple Modes. *Journal of Chemical Theory and Computation*, 13(12):6000–6009, 2017.
- [131] J. P. Kraack, A. Wand, T. Buckup, M. Motzkus, and S. Ruhman. Mapping Multidimensional Excited State Dynamics Using Pump-Impulsive-Vibrational-Spectroscopy and Pump-Degenerate-Four-Wave-Mixing. *Physical Chemistry Chemical Physics*, 15:14487–14501, 2013.
- [132] J. B. Asbury, T. Wang, H. N. Ghosh, and T. Lian. Ultrafast Electron Transfer Dynamics from Molecular Adsorbates to Semiconductor Nanocrystalline Thin Films. *The Journal of Physical Chemistry B*, 105:4545–4557, 2001.

- [133] C. She, J. Guo, S. Irle, K. Morokuma, D. L. Mohler, H. Zabri, F. Odobel, K.-T. Youm, F. Liu, J. T. Hupp, and T. Lian. Comparison of Interfacial Electron Transfer through Carboxylate and Phosphonate Anchoring Groups. *The Journal* of Physical Chemistry A, 111(29):6832–6842, 2007.
- [134] M. Abdellah, A. M. El-Zohry, L. J. Antila, C. D. Windle, E. Reisner, and L. Hammarstrm. Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO₂ as a Reversible Electron Acceptor in a TiO₂ Re Catalyst System for CO₂ Photoreduction. Journal of the American Chemical Society, 139(3):1226–1232, 2017.
- [135] W. Xiong, J. E. Laaser, P. Paoprasert, R. A. Franking, R. J. Hamers, P. Gopalan, and M. T. Zanni. Transient 2D IR Spectroscopy of Charge Injection in Dye-Sensitized Nanocrystalline Thin Films. *Journal of the American Chemical Soci*ety, 131:18040–18041, 2009.
- [136] W. Chen, C. Qian, X.-Y. Liu, and H.-Q. Yu. Two-Dimensional Correlation Spectroscopic Analysis on the Interaction between Humic Acids and TiO₂ Nanoparticles. *Environmental Science & Technology*, 48:11119–11126, 2014.
- [137] T. A. Oudenhoven, Y. Joo, J. E. Laaser, P. Gopalan, and M. T. Zanni. Dye Aggregation Identified by Vibrational Coupling Using 2D IR Spectroscopy. *The Journal of Chemical Physics*, 142:212449, 2015.
- [138] R. R. Frontiera, J. Dasgupta, and R. A. Mathies. Probing Interfacial Electron Transfer in Coumarin 343 Sensitized TiO₂ Nanoparticles with Femtosecond Stimulated Raman. *Journal of the American Chemical Society*, 131:15630–15632, 2009.
- [139] D. P. Hoffman, O. P. Lee, J. E. Millstone, M. S. Chen, T. A. Su, M. Creelman, J. M. J. Fréchet, and R. A. Mathies. Electron Transfer Dynamics of Triphenylamine Dyes Bound to TiO₂ Nanoparticles from Femtosecond Stimulated Raman Spectroscopy. *The Journal of Physical Chemistry C*, 117:6990–6997, 2013.
- [140] L. G. C. Rego and V. S. Batista. Quantum Dynamics Simulations of Interfacial Electron Transfer in Sensitized TiO₂ Semiconductors. *Journal of the American Chemical Society*, 125:7989–7997, 2003.
- [141] S. G. Abuabara, L. G. C. Rego, and V. S. Batista. Influence of Thermal Fluctuations on Interfacial Electron Transfer in Functionalized TiO₂ Semiconductors. *Journal of the American Chemical Society*, 127:18234–18242, 2005.
- [142] J. Li, I. Kondov, H. Wang, and M. Thoss. Theoretical Study of Photoinduced Electron-Transfer Processes in the Dye-Semiconductor System Alizarin-TiO₂. *The Journal of Physical Chemistry C*, 114:18481–18493, 2010.

- [143] A. Torres, R. S. Oliboni, and L. G. C. Rego. Vibronic and Coherent Effects on Interfacial Electron Transfer Dynamics. *The Journal of Physical Chemistry Letters*, 6(24):4927–4935, 2015.
- [144] M. Motzkus, S. Pedersen, and A. H. Zewail. Femtosecond Real-Time Probing of Reactions. 19. Nonlinear (DFWM) Techniques for Probing Transition States of Uni- and Bimolecular Reactions. *The Journal of Physical Chemistry*, 100:5620– 5633, 1996.
- [145] P. Kukura, D. W. McCamant, and R. A. Mathies. Femtosecond Time-Resolved Stimulated Raman Spectroscopy of the S₂ $(1B_u^+)$ Excited State of β -Carotene. *The Journal of Physical Chemistry A*, 108(28):5921–5925, 2004.
- [146] H. Yamaguchi, M. Nakano, and K. Itoh. Resonance Raman Scattering Study on the π-Cation Radicals Of Magnesium, Zinc, and Copper Tetraphenylpoprhines. *Chemistry Letters*, 11(9):1397–1400, 1982.
- [147] M. Aydin and D. L. Akins. Infrared and Raman Spectroscopic Characterization of Porphyrin and its Derivatives. In Applications of Molecular Spectroscopy to Current Research in the Chemical and Biological Sciences, chapter 7, pages 142– 162. IntechOpen, 2016.
- [148] K. Wynne, G. D. Reid, and R. M. Hochstrasser. Vibrational Coherence in Electron Transfer: The Tetracyanoethylene-Pyrene Complex. *The Journal of Chemical Physics*, 105:2287–2297, 1996.
- [149] C. L. Evans and X. S. Xie. Coherent Anti-Stokes Raman Scattering Microscopy: Chemical Imaging for Biology and Medicine. Annual Review of Analytical Chemistry, 1(1):883–909, 2008.
- [150] H. Wang, G. Peng, and S. P. Cramer. X-Ray Absorption Spectroscopy of Biological Photolysis Products: Kilohertz Photolysis and Soft X-Ray Applications. *Journal of Electron Spectroscopy and Related Phenomena*, 143(1):1–7, 2005.
- [151] D. M. Mills, A. Lewis, A. Harootunian, J. Huang, and B. Smith. Time-Resolved X-Ray Absorption Spectroscopy of Carbon Monoxide-Myoglobin Recombination after Laser Photolysis. *Science*, 223(4638):811–813, 1984.
- [152] A. B. Stickrath, M. W. Mara, J. V. Lockard, M. R. Harpham, J. Huang, X. Zhang, K. Attenkofer, and L. X. Chen. Detailed Transient Heme Structures of Mb-CO in Solution after CO Dissociation: An X-Ray Transient Absorption Spectroscopic Study. *The Journal of Physical Chemistry B*, 117(16):4705–4712, 2013.
- [153] M. W. Mara, M. Shelby, A. Stickrath, M. Harpham, J. Huang, X. Zhang, B. M. Hoffman, and L. X. Chen. Electronic and Nuclear Structural Snapshots in Ligand Dissociation and Recombination Processes of Iron Porphyrin in Solution:

A Combined Optical/ X-Ray Approach. The Journal of Physical Chemistry B, 117(45):14089–14098, 2013.

- [154] S. A. Wilson, T. Kroll, R. A. Decreau, R. K. Hocking, M. Lundberg, B. Hedman, K. O. Hodgson, and E. I. Solomon. Iron L-Edge X-Ray Absorption Spectroscopy of Oxy-Picket Fence Porphyrin: Experimental Insight into Fe-O₂ Bonding. *Journal of the American Chemical Society*, 135(3):1124–1136, 2013.
- [155] J. E. Penner-Hahn, T. J. McMurry, M. Renner, L. Latos-Grazynsky, K. S. Eble, I. M. Davis, A. L. Balch, J. T. Groves, J. H. Dawson, and K. O. Hodgson. X-Ray Absorption Spectroscopic Studies of High Valent Iron Porphyrins. Horseradish Peroxidase Compounds I and II and Synthetic Models. *The Journal of Biological Chemistry*, 258(21):12761–12764, 1983.
- [156] S. A. Krasnikov, N. N. Sergeeva, M. M. Brzhezinskaya, A. B. Preobrajenski, Y. N. Sergeeva, N. A. Vinogradov, A. A. Cafolla, M. O. Senge, and A. S. Vinogradov. An X-Ray Absorption and Photoemission Study of the Electronic Structure of Ni Porphyrins and Ni N-Confused Porphyrin. *Journal of Physics: Condensed Matter*, 20:235207, 2008.
- [157] R. K. Hocking, E. C. Wasinger, Y.-L. Yan, F. M. F. deGroot, F. A. Walker, K. O. Hodgson, B. Hedman, and E. I. Solomon. Fe L-Edge X-Ray Absorption Spectroscopy of Low-Spin Heme Relative to Non-Heme Fe Complexes: Delocalization of Fe d-Electrons into the Porphyrin Ligand. *Journal of the American Chemical Society*, 129(1):113–125, 2007.
- [158] D. Kim, C. Kirmaier, and D. Holten. Nickel Porphyrin Photophysics and Photochemistry. A Picosecond Investigation of Ligand Binding and Release in the Excited State. *Chemical Physics*, 75(3):305–322, 1983.
- [159] C. M. Drain, S. Gentemann, J. A. Roberts, N. Y. Nelson, C. J. Medforth, S. Jia, M. C. Simpson, K. M. Smith, J. Fajer, J. A. Shelnutt, and D. Holten. Picosecond to Microsecond Photodynamics of a Nonplanar Nickel Porphyrin: Solvent Dielectric and Temperature Effects. *Journal of the American Chemical Society*, 120(15):3781–3791, 1998.
- [160] J. Rodriguez and D. Holten. Ultrafast Vibrational Dynamics of a Photoexcited Metalloporphyrin. *The Journal of Chemical Physics*, 91(6):3525–3531, 1989.
- [161] J. L. Retsek, C. M. Drain, C. Kirmaier, D. J. Nurco, C. J. Medforth, K. M. Smith, I. V. Sazanovich, V. S. Chirvony, J. Fajer, and D. Holten. Photoinduced Axial Ligation and Deligation Dynamics of Nonplanar Nickel Dodecaarylporphyrins. *Journal of the American Chemical Society*, 125(32):9787–9800, 2003.
- [162] C. M. Drain, C. Kirmaier, C. J. Medforth, D. J. Nurco, K. M. Smith, and D. Holten. Dynamic Photophysical Properties of Conformationally Distorted

Nickel Porphyrins. 1. Nickel(II) Dodecaphenylporphyrin. *The Journal of Physical Chemistry*, 100(29):11984–11993, 1996.

- [163] D. Kim and D. Holten. Picosecond Measurements on the Binding and Release of Basic Ligands by Excited States of Ni(II) Porphyrins. *Chemical Physics Letters*, 98(6):584–589, 1983.
- [164] J. Rodriguez and D. Holten. Ultrafast Photodissociation of a Metalloporphyrin in the Condensed Phase. The Journal of Chemical Physics, 92(10):5944–5950, 1990.
- [165] A. J. Pistner, D. A. Lutterman, M. J. Ghidiu, Y.-Z. Ma, and J. Rosenthal. Synthesis, Electrochemistry, and Photophysics of a Family of Phlorin Macrocycles That Display Cooperative Fluoride Binding. *Journal of the American Chemical Society*, 135:6601–6607, 2013.
- [166] A. J. Pistner, G. P. A. Yap, and J. Rosenthal. A Tetrapyrrole Macrocycle Displaying a Multielectron Redox Chemistry and Tunable Absorbance Profile. *The Journal of Physical Chemistry C*, 116(32):16918–16924, 2012.
- [167] A. J. Pistner, D. A. Lutterman, M. J. Ghidiu, E. Walker, G. P. A. Yap, and J. Rosenthal. Factors Controlling the Spectroscopic Properties and Supramolecular Chemistry of an Electron Deficient 5,5-Dimethylphlorin Architecture. *The Journal of Physical Chemistry C*, 118(26):14124–14132, 2014.
- [168] T. S. Rush, P. M. Kozlowski, C. A. Piffat, R. Kumble, M. Z. Zgierski, and T. G. Spiro. Computational Modeling of Metalloporphyrin Structure and Vibrational Spectra: Porphyrin Ruffling in NiTPP. *The Journal of Physical Chemistry B*, 104(20):5020–5034, 2000.
- [169] F. de Groot, G. Vankó, and P. Glatzel. The 1s X-Ray Absorption Pre-Edge Structures in Transition Metal Oxides. *Journal of Physics: Condensed Matter*, 21(10):104207, 2009.
- [170] F. Babonneau, S. Doeuff, A. Leaustic, C. Sanchez, C. Cartier, and M. Verdaguer. XANES and EXAFS Study of Titanium Alkoxides. *Inorganic Chemistry*, 27(18):3166–3172, 1988.
- [171] M. L. Shelby, P. J. Lestrange, N. E. Jackson, K. Haldrup, M. W. Mara, A. B. Stickrath, D. Zhu, H. T. Lemke, M. Chollet, B. M. Hoffman, X. Li, and L. X. Chen. Ultrafast Excited State Relaxation of a Metalloporphyrin Revealed by Femtosecond X-Ray Absorption Spectroscopy. *Journal of the American Chemical Society*, 138(28):8752–8764, 2016.
- [172] L. X. Chen, W. J. H. Jäger, G. Jennings, D. J. Gosztola, A. Munkholm, and J. P. Hessler. Capturing a Photoexcited Molecular Structure Through Time-Domain X-Ray Absorption Fine Structure. *Science*, 292(5515):262–264, 2001.

- [173] L. X. Chen, X. Zhang, E. C. Wasinger, J. V. Lockard, A. B. Stickrath, M. W. Mara, K. Attenkofer, G. Jennings, G. Smolentsev, and A. Soldatov. X-Ray Snapshots for Metalloporphyrin Axial Ligation. *Chemical Science*, 1:642–650, 2010.
- [174] B. Abraham, J. Nieto-Pescador, and L. Gundlach. Analyte-Induced Spectral Filtering in Femtosecond Transient Absorption Spectroscopy. *Journal of Luminescence*, 187:92–95, 2017.
- [175] G. Auböck, C. Consani, F. van Mourik, and M. Chergui. Ultrabroadband Femtosecond Two-Dimensional Ultraviolet Transient Absorption. Optics Letters, 37(12):2337–2339, 2012.
- [176] T. Koyama, T. Tsunekawa, T. Saito, K. Asaka, Y. Saito, H. Kishida, and A. Nakamura. Ultrafast Excitation Energy Transfer from Encapsulated Quaterrylene to Single-Walled Carbon Nanotube. *Journal of Luminescence*, 169:645–648, 2016.
- [177] A. Blättermann, C. Ott, A. Kaldun, T. Ding, V. Stooß, M. Laux, M. Rebholz, and T. Pfeifer. In Situ Characterization of Few-Cycle Laser Pulses in Transient Absorption Spectroscopy. *Optics Letters*, 40(15):3464–3467, 2015.
- [178] S. D. Dimitrov, S. Wheeler, D. Niedzialek, B. C. Schroeder, H. Utzat, J. M. Frost, J. Yao, A. Gillett, P. S. Tuladhar, I. McCulloch, J. Nelson, and J. R. Durrant. Polaron Pair Mediated Triplet Generation in Polymer/Fullerene Blends. *Nature Communications*, 6:6501, 2015.
- [179] Z. Li, M. Jia, B. Abraham, J. C. Blake, D. Bodine, J. T. Newberg, and L. Gundlach. Synthesis and Characterization of ZnO/CuO Vertically Aligned Hierarchical Tree-like Nanostructure. *Langmuir*, 34(3):961–969, 2018.
- [180] S. Schenkl, F. van Mourik, N. Friedman, M. Sheves, R. Schlesinger, S. Haacke, and M. Chergui. Insights into Excited-State and Isomerization Dynamics of Bacteriorhodopsin from Ultrafast Transient UV Absorption. *Proceedings of the National Academy of Sciences*, 103(11):4101–4106, 2006.
- [181] V. Sundström. Femtobiology. Annual Review of Physical Chemistry, 59:53–77, 2008.
- [182] C. He, B. Abraham, H. Fan, R. Harmer, Z. Li, E. Galoppini, L. Gundlach, and A. V. Teplyakov. Morphology-Preserving Sensitization of ZnO Nanorod Surfaces via Click-Chemistry. *The Journal of Physical Chemistry Letters*, 9(4):768–772, 2018.

- [183] G. Cerullo, C. Manzoni, L. Luer, and D. Polli. Time-Resolved Methods in Biophysics. 4. Broadband Pump-Probe Spectroscopy System with Sub-20 fs Temporal Resolution for the Study of Energy Transfer Processes in Photosynthesis. *Photochemical & Photobiological Sciences*, 6:135–144, 2007.
- [184] D. Rimmerman, D. Leshchev, D. J. Hsu, J. Hong, B. Abraham, R. W. Henning, I. Kosheleva, and L. X. Chen. Probing Cytochrome c Folding Transitions Upon Photo-Triggered Environmental Perturbations Using Time-Resolved X-Ray Scattering. *The Journal of Physical Chemistry B*, Article ASAP(DOI: 10.1021/acs.jpcb.8b03354), 2018.
- [185] R. S. Riley, M. N. Dang, M. M. Billingsley, B. Abraham, L. Gundlach, and E. S. Day. Evaluating the Mechanisms of Light-Triggered siRNA Release from Nanoshells for Temporal Control Over Gene Regulation. *Nano Letters*, Article ASAP(DOI: 10.1021/acs.nanolett.8b00681), 2018.
- [186] D. Rimmerman, D. Leshchev, D. J. Hsu, J. Hong, B. Abraham, R. W. Henning, I. Kosheleva, and L. X. Chen. Insulin Hexamer Dissociation Dynamics Revealed by Photoinduced T-jumps and Time-Resolved X-Ray Solution Scattering. *Photochemical & Photobiological Sciences*, Article ASAP(DOI: 10.1039/C8PP00034D), 2018.
- [187] A. Kay and M. Graetzel. Artificial Photosynthesis. 1. Photosensitization of Titania Solar Cells with Chlorophyll Derivatives and Related Natural Porphyrins. *The Journal of Physical Chemistry*, 97(23):6272–6277, 1993.
- [188] O. P. Ernst, V. Gramse, M. Kolbe, K. P. Hofmann, and M. Heck. Monomeric G Protein-Coupled Receptor Rhodopsin in Solution Activates its G Protein Transducin at the Diffusion Limit. *Proceedings of the National Academy of Sciences*, 104(26):10859–10864, 2007.
- [189] J. J. Teesdale, A. J. Pistner, G. P. Yap, Y.-Z. Ma, D. A. Lutterman, and J. Rosenthal. Reduction of CO₂ Using a Rhenium Bipyridine Complex Containing Ancillary BODIPY Moieties. *Catalysis Today*, 225:149–157, 2014.
- [190] S. Aoi, K. Mase, K. Ohkubo, and S. Fukuzumi. Mechanism of a One-Photon Two-Electron Process in Photocatalytic Hydrogen Evolution from Ascorbic Acid with a Cobalt Chlorin Complex. *Chemical Communications*, 51:15145–15148, 2015.
- [191] M. G. Walter, A. B. Rudine, and C. C. Wamser. Porphyrins and Phthalocyanines in Solar Photovoltaic Cells. *Journal of Porphyrins and Phthalocyanines*, 14(09):759–792, 2010.

- [192] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, and M. Grtzel. Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. *Nature Chemistry*, 6:242–247, 2014.
- [193] J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. D. Cola, and L. Flamigni. Ruthenium(II) and Osmium(II) Bis(terpyridine) Complexes in Covalently-Linked Multicomponent Systems: Synthesis, Electrochemical Behavior, Absorption Spectra, and Photochemical and Photophysical Properties. *Chemical Reviews*, 94(4):993–1019, 1994.
- [194] T. V. Shubina, M. M. Glazov, N. A. Gippius, A. A. Toropov, D. Lagarde, P. Disseix, J. Leymarie, B. Gil, G. Pozina, J. P. Bergman, and B. Monemar. Delay and Distortion of Slow Light Pulses by Excitons in ZnO. *Physical Review B*, 84:075202–4, 2011.
- [195] G. Boobalan, P. M. Imran, S. Ramkumar, and S. Nagarajan. Fabrication of Luminescent Perylene Bisimide Nanorods. *Journal of Luminescence*, 146:387– 393, 2014.
- [196] E. Garnett and P. Yang. Light Trapping in Silicon Nanowire Solar Cells. Nano Letters, 10:1082–1087, 2010.
- [197] S. Li, M. Chen, and X. Liu. Zinc Oxide Porous Nano-Cages Fabricated by Laser Ablation of Zn in Ammonium Hydroxide. *Optics Express*, 22(15):18707–18714, 2014.
- [198] K. Lu, C. He, and W. Lin. A Chlorin-Based Nanoscale Metal-Organic Framework for Photodynamic Therapy of Colon Cancers. *Journal of the American Chemical Society*, 137(24):7600–7603, 2015.
- [199] D. E. Williams, J. A. Rietman, J. M. Maier, R. Tan, A. B. Greytak, M. D. Smith, J. A. Krause, and N. B. Shustova. Energy Transfer on Demand: Photoswitch-Directed Behavior of Metal-Porphyrin Frameworks. *Journal of the American Chemical Society*, 136(34):11886–11889, 2014.
- [200] M. Ringuet and J. Gagnon. Synthesis and Protonation Studies of a meso-Unsubstituted Surfactant Porphyrin. *Canadian Journal of Chemistry*, 63:2420– 2424, 1985.
- [201] M. J. Tauber, R. A. Mathies, X. Chen, and S. E. Bradforth. Flowing Liquid Sample Jet for Resonance Raman and Ultrafast Optical Spectroscopy. *Review of Scientific Instruments*, 74(11):4958–4960, 2003.
- [202] A. Picchiotti, V. I. Prokhorenko, and R. J. D. Miller. A Closed-Loop Pump-Driven Wire-Guided Flow Jet for Ultrafast Spectroscopy of Liquid Samples. *Re*view of Scientific Instruments, 86:093105, 2015.

Appendix A COPYRIGHT PERMISSIONS



Quick Price Estimate

Adaptations/modifications - Springer Nature allows adaptation of figures for style and formatting purposes under this license under the condition that this does not alter the meaning of the content.

I would like to 🛛	reuse in a dissertation/thesis	This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving RightsLink.
I am a/an 🛛	academic/university or research institute V	
My format is 🕐	print and electronic 🔻	
I would like to use 🛛	figures/tables/illustrations 🔻	
Number of figures/tables 📀	1	
Circulation/distribution 📀	<501 🔻	
High-res required 📀	no 🔻	
Are you the author of this Springer Nature content? 0	no 🔻	
I will be translating 🞯	no	
My currency is	USD - \$ 🔻	
Quick Price	Click Quick Price	
	QUICK PRICE CONTINUE	

Copyright © 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>. <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

https://s100.copyright.com/AppDispatchServlet#formTop

1/1



by X-ray Transient Absorption

Lin X. Chen, Xiaoyi Zhang, Erik



Author:

Date:



a Photoexcited Metalloporphyrin If you're a copyright.com usar, you can login to RightsLink using your copyright.com credentials. Already a RightsLink user o want to learn more?

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

Spectroscopy

Publication: Journal of the American Chemical Society Publisher: American Chemical Society Aug 1, 2007

Copyright @ 2007, American Chemical Society

C. Wasinger, et al

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.



Copyright © 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>, <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

https://s100.copyright.com/AppDispatchServiet

1/1

Figure A.2: Copyright permission for Figure 2.11



PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional
 uses are granted (such as derivative works or other editions). For any other uses, please
 submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.



Copyright © 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>, <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

https://s100.copyright.com/AppDispatchServlet

Figure A.3: Copyright permission for Figure 2.12

1/1



PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional
 uses are granted (such as derivative works or other editions). For any other uses, please
 submit a new request.



Copyright © 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>, <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

https://s100.copyright.com/AppDispatchServlet

1/1

Figure A.4: Copyright permission for material in Chapter 3



PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional
 uses are granted (such as derivative works or other editions). For any other uses, please
 submit a new request.

CLOSE WINDOW

Copyright © 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>, <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

BACK

https://s100.copyright.com/AppDispatchServlet

1/1

Figure A.5: Copyright permission for material in Chapter 4

Rightslink® by Copyright Clearance Center Copyright RightsLink Create Account Clearance Home Help Center Title: Analyte-induced spectral LOGIN filtering in femtosecond UMINESCENCE If you're a copyright.com transient absorption user, you can login to RightsLink using your copyright.com credentials. spectroscopy Baxter Abraham,Jesus Nieto-Author: Already a RightsLink user of Pescador,Lars Gundlach want to learn more? Publication: Journal of Luminescence Publisher: Elsevier July 2017 Date: © 2017 Elsevier B.V. All rights reserved.

Please note that, as the author of this Elsevier article, you retain the right to include it in a thesis or dissertation, provided it is not published commercially. Permission is not required, but please ensure that you reference the journal as the original source. For more information on this and on your other retained rights, please visit: https://www.elsevier.com/about/our-business/policies/copyright#Author-rights



Copyright @ 2018 <u>Copyright Clearance Center, Inc.</u> All Rights Reserved. <u>Privacy statement</u>. <u>Terms and Conditions</u>, Comments? We would like to hear from you. E-mail us at <u>customercare@copyright.com</u>

https://s100.copyright.com/AppDispatchServlet

Figure A.6: Copyright permission for material in Chapter 6

1/1