ULTRAFAST ELECTRON TRANSFER IN BIOMIMETIC SOLAR ENERGY
CONVERSION ARCHITECTURES

DISSERTATION

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By

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ABSTRACT

The task of finding a sustainable energy resource is vital for the well being of future generations of human beings. Many researchers are attempting to harness the power of the sun to fuel every day society. This work is an attempt to characterize elementary electron transfer processes that take place in a proposed solar energy conversion architecture.

To follow the electron transfer events, femtosecond time-resolved spectroscopies were used. Using pump and probe pulses with sub 100 fs pulse durations allows for the observation of very fast electronic processes. This allows for the investigation of portions of the solar energy conversion architecture the moment after it is exposed to a light source.

In this work the charge-separated states of the light absorbing photosensitizer RuL_{DQ} and its parent molecule RuL are carefully determined. Although these two molecules are structurally very similar their photophysics are vastly different. Also, a charge relay system involving methyl viologen, ion exchanged into a zeolite framework, is examined. Effects of the zeolite environment on the entrapped methyl viologen are less drastic than reported in previous work. Lastly, an elusive relaxation pathway for photoexcited methyl viologen in water is determined to be the results of a proton-coupled electron transfer reaction with a water molecule.
This work provides insight to the smallest steps of a solar energy conversion architecture in the hope that future investigators can use these results to help advance the field of solar energy conversion, leading to an efficient cost effective solar cell.
DEDICATION

This work is dedicated to my family
for providing me the support and encouragement
to complete this adventure.
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CHAPTER 1

Introduction

1.1 The Importance of Solar Energy

There has been vast research commitment to ensure that a sustainable source of renewable energy is found before the earth’s natural resources are depleted. Roughly 120,000 TW of solar power reaches the Earth’s surface; this is 4 orders of magnitude more energy than is consumed by the Earth’s population.\(^1\) This vast source of energy has led many investigators to attempt to find an efficient way to harness this energy and convert it to a form that is useful to everyday society. Many investigations have focused on solar-to-electrical energy conversion schemes,\(^2\)\(^-\)\(^4\) but others have found that there are possible applications in the solar-to-chemical conversion regime.\(^5\)\(^,\)\(^6\) The most famous and efficient solar-to-chemical energy conversion has been designed and perfected over millennia by Mother Nature; photosynthesis. Using a very complex system of proteins and chlorophyll, photons are absorbed and provide energy for a process to generate electrons. These electrons are in turn used to split water molecules.\(^7\) The fractured portions of water are then combined to form molecular hydrogen and molecular oxygen. The plants use hydrogen for energy and exude the oxygen to the surrounding
environment. This is obviously important for life on earth in many ways that are beyond the scope of this dissertation. The importance of discussing photosynthesis is the recognition of the highly optimized nature of the system. With sunlight, water, and the appropriate conversion architecture there is enough potential energy to power the world.

This research has focused primarily on characterizing the individual components of a solar-to-chemical energy conversion scheme that was developed by Dutta and coworkers (Figure 1.1).\textsuperscript{8,9} Characterization of the photosensitizer and the charge-relay system is important to the incremental development of the efficiency and determining potential losses in the system. Work towards characterizing the basic components of this energy conversion scheme led to an interesting tangent; characterizing a unique decay pathway of the charge relay molecule, methyl viologen, when solvated in neat water. This pathway involves a proton-coupled electron transfer. This conveniently leads back to the discussion of the solar-to-chemical conversion as there has been much interest in studying the proton-coupled electron transfer event that is involved with the water splitting event in photosystem II.\textsuperscript{10}

1.2 Femtosecond Spectroscopy

Femtosecond transient absorption spectroscopy is an extremely powerful tool used to characterize light induced changes in molecules and molecular systems on an incredibly fast time scale.\textsuperscript{11} One of the many processes that can be observed using transient absorption spectroscopy is the transfer of an electron that takes place following the photoexcitation of a molecule. Transfer of an electron can lead to a definitive change to the absorption spectrum of the light absorbing molecule as well as the electron accepting molecule. Femtosecond pump-probe spectroscopy can determine the impact of
the absorption of a photon by a molecule of light as a function of time. First a pump pulse is absorbed by the molecule, exciting it from its ground electronic state to a higher energy state. This higher energy (excited) state will decay via some energy releasing pathway; emission of a photon, internal conversion, charge transfer, or vibration redistribution of energy to the surrounding solvent or other portions of the molecule. Using a second pulse, delayed in time with respect to the pump pulse, it is possible to monitor the change in absorption of the probe pulse as a function of time. This probe pulse can consist of a single color of light providing only dynamical information at that wavelength, or it can consist of an entire spectral region (broadband). When using broadband spectroscopy it is possible to look at both the dynamical and spectral changes that take place following photoexcitation. Broadband spectroscopy is a very powerful technique as the spectral information gained can be compared to model systems to determine the fate of the electron.12

1.3 Ruthenium Photosensitizers

The molecule, tris(bipyridine)ruthenium(II) [Ru(bpy)₃], is the molecular base for many photosensitizers used in the area of solar energy research.¹³,¹⁴ Ru(bpy)₃ has been used as the basis of many photosensitizer designs where one of the bipyridine ligands has been functionalized in an attempt to manipulate the photophysics and charge transfer properties.¹⁵-²¹ These attempts to manipulate the properties of the molecule have focused on absorbing as much of the solar spectrum as possible, creating efficient electron donors,²² transporting the electron a considerable distance from the donor,¹⁵,²¹ and allowing the molecule to be attached to the next step of the solar energy conversion architecture.⁸,²³,²⁴ Efforts have been made to develop ligands that are conjugated. It has
been theorized that an electron can be moved further from the ruthenium center to an electron acceptor if the extended bridging ligand is conjugated. This conjugation should make an “electron highway” effectively moving the electron to the remote ligand. A strong sign for electron transfer from a ruthenium based absorber is quenching of the well known emission that is present in unaltered Ru(bpy)$_3$. The photosensitizer [(bpy)$_2$RuL$_{DQ}$]$^{4+}$ (where bpy = 2,2’-bipyridine, L$_{DQ}$ = 1-[4-(4’-methyl)-2,2’-bipyridyl]-2-[4-(4’-N,N’-tetramethylene-2,2’-bipyridinium]) exhibits an increased absorption that extends towards 700 nm and a nearly complete quenching of the aforementioned emission. These properties make it an excellent candidate to be used as a photosensitizer in a solar energy conversion scheme. Great effort has been spent determining the photophysics of this unique photosensitizer and its unquaternized parent compound [(bpy)$_2$RuL]$^{2+}$ (where L = 1, 2-bis[4-(4’-methyl)-2,2’-bipyridyl]ethane). These molecules, although structurally similar, exhibit vastly different photophysical and charge transfer characteristics. Using broadband transient spectroscopy and target analysis it is possible to characterize the nature and dynamics of a charge-separated state, and to determine the location of the electron in this state.

1.4 Zeolites as a Host for Electron Transfer

In the solar energy scheme developed by Dutta and coworkers, the photosensitizer RuL$_{DQ}$ is anchored into a zeolite membrane. This membrane is constructed from synthetically grown version of a naturally occurring zeolite structure. The zeolite is a aluminosilicate that contains an internal network of pores and tunnels. These pores and tunnels can be filled with molecules that can act in a charge relay system. A possible negative aspect of the zeolite membrane is that it contains a highly charged
microenvironment, with lone pairs of electrons on oxygen and charge balancing cations filling the framework. These charges can potentially wreak havoc on electron motion taking place within. Using methyl viologen as an internal probe molecule allows an investigation into the nature of this environment. Methyl viologen is an extremely potent electron acceptor and exhibits a tenfold increase in electron accepting ability in its excited state.\textsuperscript{31} Understanding the photoinduced processes of methyl viologen entrapped in the zeolite can provide insight into the electron donating properties of the zeolite.

1.5 Excited-State Quenching of Methyl Viologen by Water

It is important to fully understand the photophysics or photochemistry of a probe molecule that is being placed into a unique environment. The excited-state lifetime of methyl viologen (MV) in different solvents has been well established.\textsuperscript{31} The vast difference in lifetime is dependent on the ionization potential of the surrounding solvent. The quenching of the excited-state lifetime in easily oxidized solvents is relatively straightforward; excited-state methyl viologen is quenched by electron transfer from the solvent molecules. Since the molecules are so close to the excited MV this electron transfer process can take place very quickly (<200 fs in methanol). Until recently, the excited-state quenching of MV by water was not fully understood. While a 3.1 ps component was observed it was not initially thought electron transfer from the surrounding water molecules could quench excited-state MV as the IP of water is too high. Monitoring the ground-state recovery it is possible to see that all of the excited population does not recover to the ground state in the experimental window of 3.5 ns. The nature of this quenching is very intriguing. Investigations into this quenching have led to the assignment that a water molecule undergoes a proton-coupled electron transfer
reaction, quenching the excited-state methyl viologen, thereby ejecting a proton to the bulk water network and leaving behind a methyl viologen/hydroxide ion pair that is responsible for the long-lived transient signal.
1.6 References


Figure 1.1. Illustration of the Solar to chemical energy conversion scheme; showing the photosensitizer (RuL$_{DQ}$), the zeolite membrane, and the charge relay molecule (methyl viologen).
Figure 1.2. Structures for the Ruthenium based photosensitizers (a) RuL and (b) RuL_{DQ}. 
Figure 1.3. Structures of (a) electron accepting methyl viologen dication and (b) the molecular host zeolite Y (reprinted from Ref 31 with permission from Elsevier).
CHAPTER 2

Methods and Materials

2.1 Introduction to Femtosecond Lasers

The femtosecond pulses for the pump-probe transient experiments originated from a Titanium-Sapphire (Ti:S) chirped-pulse amplified laser. Two separate femtosecond systems were used: a Clark CPA-1000 (Clark-MXR) provided the pulses (100 fs, 800 nm, 0.5 mJ) for the fluorescence upconversion experiments; and the pulses for the two-color and broad band transient absorption experiments were generated using a Mira seed (Coherent) and a Legend regenerative amplifier (Coherent) (50 fs, 797 nm, 2.4 mJ) (Fig 2.1.). These two systems are based on nearly identical foundations so the description will be limited to the Coherent system. The Coherent system is comprised of a diode-pumped solid-state continuous wave laser (Nd:VO₄, 532 nm) which pumps a mode-locked femtosecond oscillator (Ti:S, 800 nm, 22 fs) providing low-energy femtosecond seed pulses at a high-repetition rate (76 Mhz). These seed pulses are sent into a stretcher where they are stretched in time with a grating, applying positive group delay dispersion to each pulse before being directed into a regenerative amplifier. The regenerative amplifying process uses electrooptics (Pockels Cells) with a waveplate to
select a particular seed pulse to mix with a high energy nanosecond pump pulse (Nd:YLF, 532 nm) in a Ti:S rod. The amplified pulse makes multiple trips through the amplifier cavity allowing it to interact multiple times with the pump pulse, thus building up pulse energy. Once the amplified pulse reaches maximum gain it is ejected from the amplifier cavity using a second Pockels cell plus polarizer combination. The pulse now has very high energy, but only moderate peak intensity due to the long pulse duration. To recover the femtosecond characteristics of the initial seed pulse, a grating setup with reverse geometry with respect to the stretcher is employed. This compressor applies negative group delay dispersion to the pulse bringing the pulse duration back to the femtosecond regime. These high energy, short time duration pulses (2.4 mJ, 50 fs) are used in a variety of optical techniques to generate pump and probe pulses that can be used to determine molecular dynamics on the subpicosecond timescale.

2.2 Harmonic Generation

It is highly desirable to have pump and probe wavelengths throughout the visible and ultraviolet spectrum. The high peak intensity of the femtosecond pulses allows for nonlinear optical processes to take place. These nonlinear processes mix photons together in well known combinations to generate excitation and probe pulses from the deep UV to the mid-IR.

One of the most common nonlinear events is the frequency doubling of the fundamental laser output, using an alpha beta barium borate (α-BBO) crystal (Type II, 30°). This doubling process mixes two 800 nm photons to generate a 400 nm photon with an efficiency near 35%. The 400 nm photon can now be mixed in space and time with an
800 nm photon via a sum frequency mixing process (α-BBO crystal, Type II, 45°) generating a 267 nm photon (Eq. 2.1).

\[
\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3} \quad \text{(Eq. 2.1)}
\]

Where \(\lambda_1\) and \(\lambda_2\) are the wavelengths of light to be mixed (800 nm and 400 nm) and \(\lambda_3\) is the resulting wavelength (267 nm). The 400 nm and 267 nm pulses are primarily used as excitation pulses. Using low energy 800 nm photons, focused into a water cell, sapphire plate, or calcium fluoride window, a continuum of light from \(\sim\)380 nm stretching to the infrared is generated. This continuum of light is used as probe pulses.

A more complex, yet infinitely more flexible, way to generate pump and probe pulses is by using a technique known as Optical Parametric Amplification (OPA). OPAs allow for a wide range of colors to be generated at relatively high pulse energies. Depending on the harmonics packages available, an OPA can be tuned from 240 nm in the UV to the mid IR. For this work wavelengths from 250 nm to 600 nm have been used as both pump and probe pulses. The initial processes are the same for all outputs. First, a small amount of white light continuum is generated to seed the OPA. This white light is mixed with a small amount of 800 nm light in a \(\alpha\)-BBO crystal to generate signal and idler pulses. The signal and idler are then mixed with a higher energy 800 nm pulse in the same \(\alpha\)-BBO crystal to amplify the energies. After the high energy signal and idler are generated they can be frequency doubled or mixed with residual 800 nm pulses in \(\alpha\)-BBO crystals to generate photons in the ultraviolet and visible region of the spectrum.
2.3 Transient Absorption

The femtosecond pump-probe experimental setup\(^1\) used the output of the previously described Coherent laser system (Figure 2.2). The 2.4 mJ output of the amplified system was split with 80% used to pump two OPAs, each with 40 percent of the total laser output. The remaining 20% was used to generate white light probe pulses, and 266 nm pump pulses. The small portion used to generate white light was directed down a motorized delay stage to delay the pulse relative to the pump pulse. After traveling down the delay stage the 800 nm beam was focused in a 1-cm stationary water cell generating the aforementioned white light continuum. A portion of continuum was selected using band pass filters. The same delay stage was also used when the output of the OPA output acted as the probe pulse, with the beam bypassing the white light generation cell. To control the pump intensity at the sample, a \(\lambda/2\)-waveplate was placed in the beam path and rotated to pass a set amount of light through a polarizer placed before the sample. This polarizer was set at 54.7 degrees with respect to the polarization of the probe pulse. An optical chopper (NewFocus) was placed in the pump path and referenced to the laser repetition rate and blocked 2 out of every 3 pulses to limit the pump exposure to the sample. The pump and probe beams were overlapped in the sample cell. The pump pulse spot size is five times larger at the sample than the probe pulse spot size. After the sample, UV probe pulses were passed through a double-grating monochromator and detected with a photomultiplier tube. The visible probe pulses were detected by a joule-meter (Molelectron). Both detectors were linked to a lock-in amplifier (Stanford Research Systems) synced to the input frequency of the optical chopper. The
lock-in amplifier records the difference in the pump on/pump off intensity of the probe and reads the signal out electrically. The instrument response was between 200 and 300 fs depending on pump and probe combinations. Samples are held in a 1-mm path length cell. Two separate cells were used depending on sample conditions: a flowing cell and a spinning cell. The cells are very similar both, comprised of two 1 in. diameter calcium fluoride windows with a 1mm Teflon® or Gylon® (Garlock Sealing Technologies) spacer separating the windows. The spin cell was a small volume cell (~400 µL) and was spun to avoid sample re-excitation. The flow cell was a larger volume cell which moved sample from a ~10 mL reservoir through the sample cell using a magnetically driven pump. This flowing refreshed the sample between each set of pump and probe pulses, avoiding re-excitation of the sample.

Transient absorption can also provide rotational reorientation information. This technique is called anisotropy and uses the same experimental setup as above, only adjusting the polarizations of the pump and probe pulses. This is achieved by exciting the sample with a femtosecond pulse of a known polarization and then using two different polarizations, one parallel and one perpendicular to the pump, to probe the excited sample.

\[
r(t) = \frac{S_{\parallel} - S_{\perp}}{S_{\parallel} - 2S_{\perp}}
\]

(Eq 2.2)

Equation 2.2 gives the anisotropy signal \(r(t)\) by combining the signals of pump and probe with parallel polarizations \(S_{\parallel}\) and pump and probe perpendicular \(S_{\perp}\). Plotting the resultant \(r(t)\) vs. time delay and fitting with an exponential function gives the rotational decay time.
2.4 Fluorescence Upconversion

The fluorescence upconversion experiments (Figure 2.3) were performed using the Clark-MXR CPA-1000 set up (Section 2.1). A 5% portion of the 800 nm fundamental was split off and sent down a motorized delay stage to be used as the gate pulse. The other 95% was used to generate excitation pulses at the third harmonic of the laser fundamental. The pump pulse is set to a polarization of 54.7 degrees with respect to the gate polarization. An optical chopper is placed in the gate beam at 1/3 the laser repetition rate, passing one out of every 2 gate pulses, to provide a reference for gate on/gate off in the lock-in amplifier. The fluorescence was collected on a 1 in. parabolic mirror (f = 50 mm) and then passed through a 295 nm (Andover) long pass filter to block any residual pump light. A second identical parabolic mirror focused the emission on a BBO crystal (Type I, 45°). The gate pulse with a larger spot size was over-lapped with the collected emission. The BBO crystal was tuned to the proper phase matching angle and the resulting upconverted signal was collected with a 2 in. collimating lens (f = 50 mm) and passed through a focusing lens (f = 200 mm) onto the slit of a double grating monochromator and detected with a photomultiplier tube. Samples were held in a home-built cell with CaF₂ windows and a 1-mm in path length. The cell was spun to avoid sample re-excitation.

2.5 Broadband Transient Absorption Measurements.

Broadband transient absorption spectra were recorded using a femtosecond pump-probe spectrometer described previously (Figure 2.4).\(^2\) Pulses were obtained from the Coherent femtosecond amplified system (Section 2.1). A portion of this output was split off and used to pump two Optical Parametric Amplifiers (OPA) (OPerA, Coherent): one
with a UV/VIS harmonics package and one with a Sum Frequency Generation (SFG) package. Between these OPAs, excitation wavelengths of 320nm, 600nm (UV/VIS) and 540nm (SFG) were generated. A second portion was split off for white light generation which was the probe and reference in a broadband transient absorption setup. A motorized linear optical delay stage with a maximum time delay of 3.5 ns was used to delay the probe pulse relative to the pump pulse. An 800 nm pulse was focused onto a 1 mm CaF$_2$ plate in order to generate a white light continuum. The CaF$_2$ plate was rotated 1.5° every three seconds to improve the long-time stability of the continuum. A 50 mm lens collimated the continuum light, which was subsequently passed through an iris to select a uniform region. The continuum was split into probe and reference beams using reflections from the front (probe) and back (reference) surfaces of a 6 mm thick CaF$_2$ plate. The pump and probe beams were overlapped in the sample, while the reference beam passed through the sample approximately 3 mm away. The pump beam was blocked after the sample and the probe and reference beams were focused onto the entrance slit (0.5 mm) of a Triax 550 polychromator (Jobin Yvon) and detected using a thermoelectrically cooled Symphony CCD camera (Jobin Yvon). The pump and probe beams were linearly polarized and the angle between their planes of polarization was set to the magic angle (54.7°) for all experiments performed in this study in order to remove reorientational dynamics. Samples were held in a 1-mm path length flow cell with CaF$_2$ windows.

2.6 Streak Camera Spectroscopy

Samples were excited by the 3$^{rd}$ harmonic (280 nm, 5µJ) of a femtosecond Ti:sapphire laser at 1 kHz (Spectra Physics) similar to those described in Section 2.1. The
excitation polarization was vertical. The resulting emission was collected with a 4 in focal length f/2 fused silica collimating lens and focused with a 9 in. f/4.5 fused silica focusing lens to match the f/4.5 monochrometer (Acton Research). A magic angle polarizer was placed in front of the monochrometer collect data free of rotational reorientation dynamics. Following the monochrometer the emission is imaged by Hamamatsu A1976-01 input optics. The input optics have a spectral transmission range of 200 nm to 1600 nm, and f/5.0. The input light was imaged onto a horizontal photocathode with effective size of 0.15 mm x 5.4 mm. The photoelectrons are accelerated by an electrode and passed through a sweep electrode (sweep from top to bottom, early time swept up, late time swept down). The spectrally and temporally resolved photoelectrons are then amplified by a MCP (micro-channel plate). The amplified electrons are converted back to photons by a phosphor screen and imaged by a CCD (charge-coupled device). The sweep unit used was the Hamamatsu M5676 fast single sweep unit. The temporal range for these experiments was 20 ns, with a spectral range of 100 nm. The instrument response is approximately 20 ps. Samples were held in a 1-cm path length sample cell and stirred with a magnetic stir bar throughout the experiments to avoid sample reexcitation.

2.7 Steady-State Spectroscopy

Steady-state absorption spectroscopy was performed on a Perkin-Elmer Lambda 25 spectrophotometer. To determine sample concentrations and optical densities for flow cell experiments, samples were held in a 1-mm quartz cuvette (Starna). To determine optical densities for spin cell experiments and sample degradation following experiments,
samples were held in a 1-mm path length home built cell with CaF₂. Samples were recorded with an air blank.

Fluorescence spectra were recorded using a Spex Fluorlog-2. Spectra were recorded using a 1-mm excitation slit width and a 0.5 mm emission slit width. Samples for emission spectroscopy were held in a 1-cm quartz cell (Starna) with four polished sides.

Diffuse reflectance spectra were recorded using an integrating sphere attachment with a UV-2501PC spectrophotometer (Shimadzu) using BaSO₄ as the reference.

2.8 Spectroelectrochemistry

Spectroelectrochemical measurements were conducted in an optically transparent thin-layer electrochemical (OTTLE) cell (CH Instruments). The 1-mm path length cell included a head space of ~1 cm³ at the upper portion of the cell to hold excess sample and electrode components. The cell is equipped with a Pt gauze working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. Spectra were recorded with a UV-2501PC spectrophotometer (Shimadzu). Solutions were prepared immediately before addition to the cell and were purged with N₂ for 15 min before use. Absorption spectra of the reduced species were recorded between 250 and 800 nm after drawing new solution into the OTTLE cell, applying the desired potential to the Pt minigrid electrode, and waiting until minimal current was being passed, usually after 1 to 5 min. Samples were prepared with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte.
2.9 Materials

Samples were purchased or synthesized by collaborators. The ruthenium compounds were synthesized by Haoyu Zhang, graduate student of Prof. Dutta, and described thoroughly elsewhere: RuL\textsuperscript{3} and RuL\textsubscript{DQ}\textsuperscript{4}. Synthesis of RuL\textsubscript{DQ} anchored to the zeolite was more complex, and also synthesized by Zhang.\textsuperscript{4} Nanometer-sized zeolite particles were synthesized using a procedure by Dutta and coworkers described previously.\textsuperscript{4} The nanometer-sized zeolites were ion exchanged with methyl viologen by adding zeolites to a highly concentrated solution of methyl viologen (~0.1M). The resulting solution was stirred for 24 hrs and the solution containing excess MV was washed off with water. To determine the methyl viologen loading level, a small portion of the sample was ion exchanged with sodium forcing the MV back into solution. The concentration of MV, determined by UV/VIS absorption, in this solution determined the number of MVs that were present in the zeolite. This procedure was repeated until concentrations of 0.5, 1.0, and 1.5 methyl viologens per zeolite supercage were achieved. Methyl viologen (Sigma-Aldrich) was purchase as a dichloride salt and used as received for water and methanol experiments. Experiments in acetonitrile require that the counter ion to be changed to hexafluorophosphate, to allow the complex to be soluble. The anion exchange was carried out by dissolving methyl viologen dichloride in water and adding an excess of NH\textsubscript{4}PF\textsubscript{6} (Sigma-Aldrich), the MV(PF\textsubscript{6})\textsubscript{2} is insoluble in water and precipitated out. The resulting crystals were separated from the water using a Buchner funnel. The remaining white crystals were dried in an oven at 95 °C for 24 hrs. The resulting crystals were soluble in acetonitrile and the absorption spectrum matched well with previously published results.\textsuperscript{5} Other chemicals; NaOH (Mallinckrodt), HNO\textsubscript{3} (Fisher Scientific), methanol (Burdick and Jackson), D\textsubscript{2}O (Sigma-Aldrich) and acetonitrile.
(Burdick and Jackson) were used as received. All water had a resistance of at least 18 MΩ, generated by a Nanopure water system.

2.10 Data Fitting

Time-resolved data was treated using nonlinear least-squares fitting. Data was fit using different sums of exponentials including: single exponential, double exponential, triple exponential or N exponentials plus an offset. All femtosecond data was also fit with a Gaussian convolution function to determine the instrument response function (IRF) for the given experiment. The IRF was determined by allowing the fitting program to determine the best possible value. The Igor Pro 6.0 program (WaveMetrics Inc.) was used for all fitting procedures.
2.11 References


Figure 2.1. Center for Chemical and Biophysical Dynamics (CCBD) Laser system at Ohio State University. Output parameters of the regenerative amplifier are 2.5 mJ/pulse, 50 fs, 800 nm at 1 kHz repetition.
Figure 2.2. Single wavelength transient absorption setup. Setup currently at Montana State University, based on setup located in the CCBD at the Ohio State University.
Figure 2.3 Schematic of the fluorescence upconversion setup using two 50 mm focal length parabolic mirrors to collect and focus the emission.
Figure 2.4. Broadband transient absorption spectrometer in the CCBD at The Ohio State University.
CHAPTER 3

Ultrafast Electron Transfer Dynamics in Ruthenium Polypyridyl Complexes with a \(\pi\)-conjugated Ligand

3.1. Introduction

A long-standing goal of solar energy research is to use sunlight to form long-lived ion pairs via photoinduced electron transfer. Forward electron transfer should be fast to promote follow on electron-transfer reactions and coupled with a slow charge recombination to allow for a buildup of a population of charge separation. Ru(bpy)\(_3\)\(^{2+}\) has been a model compound for this effort: it has been shown that the long lived \(^3\)MLCT state of Ru(bpy)\(_3\)\(^{2+}\) is accessed within 100 fs following photo-excitation.\(^1\) Several groups have studied complexes with extended ligands to allow the Ru(bpy)\(_3\) core to be further away from the eventual charge acceptor,\(^2-9\) or to anchor the charge acceptor into a membrane architecture.\(^10-12\) This ligand elongation slowed the forward electron transfer to the remote end of the ligand by picoseconds to hundreds of picoseconds. Concurrent with the attempts to create an efficient forward electron transfer it is highly desired to create a long-lived charge-separated (CS) state. Ideally the charge-separated state should be both 1) formed with a high quantum yield and 2) be sufficiently long lived for follow-on
reactions to make use of the stored energy content of the CS state. These follow-on reactions must also compete kinetically with charge recombination. Diad compounds consisting of a ruthenium(II) polypyridyl photosensitizer with covalently attached bipyridinium electron acceptors have shown promise in the past,\textsuperscript{8,13} but efforts to accelerate the rate of forward electron transfer has been coupled with the increased rate of back electron transfer. Many diad compounds have been synthesized to have effective forward electron transfer yet also have a relatively fast back electron transfer (<300ps).\textsuperscript{13-15} The fast back electron transfer quenches the CS state before the electron can be transferred to the eventual charge acceptor. Thus, the challenge lies in developing a system that has both efficient forward electron transfer with slower back electron transfer from the CS state.

A proposed strategy to induce a longer-lived CS state is the use of rigid ligands.\textsuperscript{2,3,16,17} Strouse et al. observed that transition metal photosensitizers containing rigid ligands with delocalized $\pi$-electrons have longer excited-state lifetimes.\textsuperscript{2} They suggested that smaller bond displacements in the excited state are responsible for lowering the rate of nonradiative decay.

This chapter will discuss a study using femtosecond transient absorption spectroscopy to probe the excited-state dynamics of two ruthenium based photosensitizers with conjugated ligands, $[(\text{bpy})_2\text{RuL}_{\text{DQ}}]^{4+}$ and $[(\text{bpy})_2\text{RuL}]^{2+}$ (Figure 3.1) in acetonitrile solution. The ligand L\textsubscript{DQ} (1-[(4-(4'-methyl)-2,2'-bipyridyl)]-2-[4-(4'-N,N'-tetramethylene-2,2'-bipyridinium)] (1, 2-bis[4-(4'-methyl)-2,2'-bipyridyl)]) ethane) is a quaternized version of ligand L (1, 2-bis[4-(4'-methyl)-2,2'-bipyridyl)]) ethane). Henceforth these molecules will be referred to as RuL\textsubscript{DQ} and RuL. These ligands
were selected originally to constrain the conformations that a ruthenium polypyridyl complex can achieve on the surface of a zeolite particle and to elongate the molecule allowing the Ruthenium core to be outside of the zeolite particle. Restricting conformational mobility in ruthenium-viologen diads is one strategy that has been pursued for slowing down charge recombination. It is thought that rigid ligands will be more favorable for long-lived charge-separated states.

A recent study by Zhang et al. explored the charge-transfer reaction between RuL_{DQ} and methyl viologen where the DQ end of the RuL_{DQ} was anchored into a near surface zeolite supercage and methyl viologens in the surrounding supercages provided an architecture for long-lived charge separation. While attempting to determine the excited-state dynamics of RuL_{DQ} in neat acetonitrile it was found that there was no discernable transient absorption spectrum at the earliest detectable time (100 ns) following excitation. Along with the lack of a long lived transient it is also reported that emission was nearly completely quenched in RuL_{DQ}. It was proposed that an ultrafast intramolecular charge transfer quenched the long-lived state that is usually associated with ruthenium(II) photosensitizers.

Using broadband femtosecond transient absorption the CS state of the photosensitizers RuL_{DQ} and RuL were characterized, revealing the location of the electron on the functionalized ligand.

3.2. Data Handling.

Transient decays (ΔA vs. delay time) were analyzed using global nonlinear least-squares fitting. The transient decays were extracted from broadband transient absorption data. Broadband transient absorption difference spectra, ΔA(t, λ_{ref}), depend explicitly on
delay time $t$ between pump and probe pulses and on the probe wavelength $\lambda_{pr}$. Transient spectra were recorded at non-equally spaced delay times in order to sample the entire time window from -100 ps to 2500 ps. The -100 ps point is used to accurately determine the background signal caused by stray light and is subtracted from each spectrum. An excess of data points were acquired near $t = 0$ to accurately perform a group velocity dispersion (GVD) correction which ensures $t = 0$ is identical for each wavelength. In order to reduce the quantity of data for analysis, spectra at each delay time were sampled every 5 nm. Each two-dimensional data set was analyzed by global fitting to a sum of $n$ exponentials using eqn. 1,

$$
\Delta A(t, \lambda_{pr}) = \sum_{i=1}^{n} D_i(\lambda_{pr}) \cdot \exp\left(-t / \tau_i\right) \otimes IRF(t)
$$

(Eq. 3.1)

In equation (3.1), $\tau_i$ are exponential time constants which were globally linked for kinetic signals at all probe wavelengths in a given data set, $D_i(\lambda_{pr})$ are probe-wavelength dependent amplitudes which define the decay-associated difference spectrum (DADS) associated with each decay component, $\tau_i$, and $\otimes IRF(t)$ represents convolution with a Gaussian of FWHM 250 fs that represents the finite instrument response. The DADS were used to estimate spectra of the various transient species as will be described more in more detail in section 3.3.5.
3.3. Results

3.3.1. Steady-State Spectroscopy

UV/Vis absorption spectra of RuL, RuLDQ, Ru(bpy)₃, and ligand LDQ are shown in Figure 3.2. The absorption spectrum of RuL,¹⁹ Ru(bpy)₃,¹ and RuLDQ¹¹ agree well with previously published results. Both RuL and RuLDQ have similar features below 400 nm. Each exhibits a peak at 290 nm, and another peak at ~330 nm, which is more intense for LDQ than for L. Both systems have transitions at ~460 nm; RuLDQ has a second band that appears at ~500 nm. The LDQ ligand has transitions at 290 nm and 336 nm. The absorption spectra in water for RuL and RuLDQ are nearly identical to those in acetonitrile (Figure 3.3). Upon adding 1 M HCl to the sample containing RuL there is a substantial elongation of the absorption band to the red (Figure 3.3). To determine the absorption of the RuLDQ photosensitizer following attachment to the zeolite it was necessary to perform a diffuse reflectance technique, using a solid pellet formed from the sample. This data is displayed in Figure 3.4 in Kubelka-Monk units that correspond well with absorption.²¹ Figure 3.4 shows a slight narrowing of the RuLDQ MCLT band when anchored to the zeolite as well as a shifting of the tail towards the blue side of the spectrum. Also evident is a difference in the ratio between the peak at 290 nm and band at ~470 nm.

An attempt to acquire the emission spectrum of RuLDQ was made, but in agreement with previous studies no emission was observed in the region that the parent molecules RuL emits (600-700 nm).¹¹

Electrochemical studies were preformed on the free ligands to assist in locating the position of the electron following photoexcitation of the ruthenium compounds. The
ligands L and L_{DQ} were electrochemically reduced in an optically transparent thin-layer electrochemical cell. A potential of -1.8 V for ligand L and -0.4 V for ligand L_{DQ} were used (potentials are vs. Fe^{+/0}/Fc). The reduced L ligand exhibits absorption maxima at 510 nm and 700 nm (Figure 3.5b), this agrees reasonably well with results published previously by Strouse et al.\textsuperscript{2} The reduced L_{DQ} exhibits a similar spectrum to that of L with the peaks shifted slightly to the red and located at 525 nm and 720 nm (Figure 3.5a)

### 3.3.2. RuL_{DQ} Femtosecond Pump-Probe Measurements

Broadband transient absorption measurements were preformed on RuL_{DQ} in acetonitrile. Excitation wavelengths were selected to sample the effects of photoexciting different regions of the ground-state absorption band. Probe pulses were from a white light continuum and covered the spectral region from 375 nm to 650 nm. In the initial picoseconds (< 5 ps) after photoexcitation at 320 nm three features are observed: a positive absorption band at 390 nm, a broad absorption band above 520 nm and the slight remainder of a double-welled bleach feature from 440 nm to 500 nm (Figure 3.6). Within 1 ps this state begins to show decay and shifting of the 390 nm band revealing a broader deeper bleach band at 440 nm. At the same time a positive absorption feature grows in, absorbing on top of the region that includes the 500 nm bleach and results in the broad semi-structured band in Figure 3.7b. In the 8 to 80 ps window, the band that is formed above 500 nm evolves by a slight blue-shifting and narrowing which results in a band with two discernable peaks at 505 and 550 nm and the beginning of a band that is just out of the spectral window (>650 nm)

After the spectral shifting is complete the resulting absorption band (475-650 nm) and ground-state bleach band (440 nm) decay at the same rate (k_{eq}^{-1} (ns) = 1.45) (Figure
3.7c). This long-lived state has almost the same absorption as the state formed by 5ps following excitation. Global fitting of the kinetic traces prepared from the broadband data show that these three states have lifetimes of 1.2 ps, 11.7 ps and 1.43 ns (Table 3.1). Excitation at 400 nm has very similar effects to exciting at 320 nm. The 400 nm excitation data is slightly limited due to the saturation of the detector with pump light around 430 nm. The difference in the initial spectrum (comparing Figure 3.7 a & d) is the much smaller spectral growth at 500 nm and longer wavelengths. The 8 - 80 ps windows for 320 nm and 400 nm excitation are remarkably similar, the only slight difference is slightly more structure to the 400 nm excitation spectrum (Figure 3.7 b & e). The final temporal window following 400 nm excitation looks identical to that of 320 nm excitation (Figure 3.7f). The 400 nm data can be effectively fit to three exponentials; 1.03 ps, 16 ps, and 1.46 ns. Following 600 nm excitation, the initial state shows no spectral shift, only small changes to the spectral intensity that are due to laser noise. This noise is more evident when there is a very small absorption cross section at the excitation wavelength (Figure 3.7g). The 8 - 80 ps window shows no dynamics either, just the aforementioned laser noise (Figure 3.7h). The final temporal window (120 ps to 2500 ps) for 600 nm looks very similar to those of 320 nm and 400 nm excitation with the entire spectral region decaying at the same rate (Figure 3.7i). The 600 nm excitation data only requires to exponential lifetimes to effectively fit the data at 0.56 ps and 1.27 ns. The final spectrum closely resembles the final spectra generated when RuL_{DQ} is excited at 400 nm or 322 nm. A common absorption profile is formed in all RuL_{DQ} experiments regardless of excitation wavelength within 21 ps of excitation.
Exciting RuL-DQ in water at 400 nm shows very similar data to that in acetonitrile (Figure 3.8). There are a few slight differences; the larger amplitude of the negative signal at 400 nm, the less pronounced band at 550 nm, and a vastly sped up decay time of the final two lifetimes when compared to acetonitrile. The water results can be fit by 3 exponentials at 1.12 ps lifetime, 4 ps and 334 ps.

3.3.3. RuL Femtosecond Pump-Probe Measurements

The broadband transient absorption spectrum of RuL following excitation at 320 nm (Figure 3.9) shows the fast population of a state that exhibits no change out to 2.5 ns. The slight band shift at 420 nm and growth at 570 nm (Figure 3.9a) can be fit to two exponentials with lifetimes of 0.14 ps and 2.6 ps (Table 3.2). The broad absorption present in the 500 nm to 650 nm region and the strong bleach band at 465 nm persist for the entire temporal range of the experiment out to 2.5 ns (Figure 3.9b). Studies by Dutta and coworkers have shown that signal that appears as a long offset in the transient absorption experiments for RuL has a biexponential emissive decay of 256 ns (18%) 710 ns (82%) in acetonitrile when studied with Time Correlated Single Photon Counting (TCSPC).11

The spectrum generated following 400 nm photoexcitation of RuL in pH 0 (1M HCl) aqueous solution is very noisy (Fig. 3.10). The noise in this sample is due to the very small amount of sample that was available. Even with the low signal-to-noise it is still possible to make some observations. The early time window shows a large bleach signal at 450 nm with a positive absorption band 510 nm, a slight growth of the 510 nm band and decay at 450. In the 10 ps and longer window all regions of the spectra appear
to decay at the same rate. The global fit to this data requires a 3 exponential decay model with lifetimes of 1.4 ps, 20.2 ps and 342 ps.

3.3.4. Single-Wavelength Kinetics.

Figure 3.11 shows a comparison of RuL and RuL\textsubscript{DQ} at multiple probe wavelengths. This display format highlights the differences and similarities that are observed in the broadband data, but when formatted in a $\Delta A$ vs. delay time format it becomes more straight forward to see the rise and decay at a given probe wavelength. In figure 3.11a the decay of the signal at 375 nm is shown. There is a very fast decay component evident for both RuL (black squares) and RuL\textsubscript{DQ} (green circles) the component is $\sim$1 ps for RuL\textsubscript{DQ} and 2.5 ps for RuL, with the RuL\textsubscript{DQ} having larger amplitude of decay. Also, the resulting signal for RuL\textsubscript{DQ} decays in 1.4 ns while the RuL signal persists as an offset for the duration of the experiment. Panel (b) shows the recovery of the bleach signal at 450 nm. There are similarities with both RuL and RuL\textsubscript{DQ} exhibiting fast dynamics with the RuL\textsubscript{DQ} having a larger amplitude and the RuL signal remaining as an offset. Panel (c) illustrates the differences that are observed when looking at the broad band spectra of RuL and RuL\textsubscript{DQ} in Figures 3.6 - 3.10. RuL\textsubscript{DQ} has a very large signal at 500 nm while RuL has some very fast early time dynamics and nearly no signal at delay times longer than 5 ps. At 600 nm (Figure 3.11d) RuL\textsubscript{DQ} exhibits a small amount of fast time dynamics while RuL shows a slower than instrument limited rise to the long offset signal. Lastly in panel (e) the signal for 740 nm probe of RuL\textsubscript{DQ} shows the very fast rise that is observed in a region that is free of the ground-state absorption, followed by the $\sim$1.4 ns decay.
Figure 3.12 shows a normalized comparison of all the solvent conditions for RuL and RuL_{DQ} probed at 525 nm. This comparison highlights the long offset signal observed in RuL in acetonitrile (black) the 1.4 ns decay of RuL_{DQ} in acetonitrile (red, green), the slightly slowed dynamics of RuL_{DQ} in butyronitrile (purple) and the considerable increase in rates of the water samples with RuL_{DQ} in water (blue) and RuLH_{2} in water (cyan).

Figure 3.13 shows preliminary results of transient absorption experiments of RuL_{DQ} anchored to a zeolite particle. The comparison is shown between free RuL_{DQ} in acetonitrile (solid circles) and zeolite anchored RuL_{DQ} in water (open circles) excited at 400 nm. RuL_{DQ} in acetonitrile exhibits the same dynamics as presented in section 3.3.2. The zeolite anchored RuL_{DQ} sample only shows a ~1 ps decay, no longer lived dynamics could be fit due to the poor signal-to-noise at delay times greater than 10 ps. The acetonitrile data is an average of 4 scans, the zeolite data is an average of 27 scans.

### 3.3.5. Kinetic Modeling and Target Analysis

Transient absorption spectroscopy is a form of difference spectroscopy where the signal is given by a sum of difference spectra between each transient species present at delay time \( t \) and the ground-state absorption spectrum. DADS (refer to Section 3.2) for RuL_{DQ} are shown in Figures 3.14a and 3.14c for pump wavelengths of 320 and 400 nm, respectively. DADS do not always correspond to difference spectra of actual transient species. Instead, the spectra of the species responsible for a particular decay constant are calculated from linear combinations of DADS and referred to as species-associated difference spectra (SADS).\textsuperscript{20,22} The linear combinations are determined by solving the differential equations of a proposed kinetic model for the species concentrations as a function of time. Here, Scheme 3.1 shows a sequential kinetic model,
where \( k_1, k_2, \) and \( k_3 \) are the first-order rate constants determined from global fitting (\( k_i = \tau_i^{-1} \) etc.), A, B, and C represent transient excited states, and G stands for the electronic ground state. The appropriateness of this model will be discussed in Section 3.4. SADS were calculated for each transient state using the following equations,

\[
\text{SADS}(A) = \text{DADS}(k_1) + \text{DADS}(k_2) + \text{DADS}(k_3)
\]

(3.2)

\[
\text{SADS}(B) = \frac{k_1 - k_2}{k_1} \text{DADS}(k_2) + \frac{k_1 - k_3}{k_1} \text{DADS}(k_3)
\]

(3.3)

\[
\text{SADS}(C) = \frac{(k_1 - k_3) (k_2 - k_3)}{k_1 k_2} \text{DADS}(k_3)
\]

(3.4)

and results are shown in Figures 3.14b and 3.14d for the two pump wavelengths.

SADS(A) for RuLDQ excited at 320 nm (purple curve in Figure 3.14b) shows positive absorption at 400 nm and >550 nm with a double-welled bleach in between. The bleach minima at 450 nm and 500 nm match the positions of the \(^1\)MLCT transitions in the UV/vis spectrum of RuLDQ (blue curve, Figure 3.2). SADS(B) and SADS(C) are very similar to each other, but the former is broadened and extends to longer wavelengths. Overall, similar SADS are observed at both pump wavelengths.

In order to obtain species associated spectra (SAS), it is necessary to add the ground-state absorption spectrum to each SADS multiplied by a scaling factor, which is generally unknown. Due to the strong ground-state absorption in the spectral window (approx. 375 – 650 nm) of this study, the SAS differ quite strikingly in appearance from their associated SADS. Figure 3.15 shows the SAS for RuLDQ transient species A, B, and
C for excitation at 320 and 400 nm. The cyan curve in Figure 3.15 shows the scaled ground-state absorption spectrum that was added to the SADS in Figure 3.13c and d in order to generate the SAS shown in Figure 3.15. The scaling of the ground-state absorption spectrum was chosen to make the SAS everywhere positive and to give reasonably smoothly varying band shapes. The precise scaling is somewhat arbitrary, but is justified by the good agreement with the spectrum of the reduced ligand (see below). Importantly, the finding that the spectrum of state C is a maximum near 500 nm is insensitive to the precise scaling. Figure 3.18 shows estimated DADS, SADS, and SAS for RuL estimated with the sequential kinetic model in scheme 3.1.

3.4 Discussion

3.4.1. Ground-State Absorption Spectra

The absorption spectra for Ru(bpy)$_3$, RuL and RuL$_{DQ}$ are qualitatively similar. They exhibit $\pi\pi^*$ ligand transitions at 290 nm and broad transitions above 400 nm that are well known metal-to-ligand charge transfer (MLCT) bands.\textsuperscript{1,2} One difference in the spectra is the band at 330 nm; this band is attributed to absorption by the double bond that is located on the L and L$_{DQ}$.\textsuperscript{11} The quaternization of the L$_{DQ}$ ligand helps to enhance the effect of the double bond. The second notable change is the stretching into the red of the RuL and RuL$_{DQ}$ MLCT bands. This elongation of the MLCT absorption band has been described as a delocalization effect due to the conjugated nature of the L ligand.\textsuperscript{2,19} The extended absorption to the red in RuL$_{DQ}$ can be directly tied to the quaternization on the terminal diquat portion of the ligand. As is explained later in Section 3.4.4, diquat is a strong electron acceptor and will lower the energy of the ligand, thus requiring less energy to populate it via a MLCT transition.
The spectra in water highlight the effect of the quaternization of the nitrogens on the terminal end of the ligands. Upon increasing the acidity of the sample solution to 1 M HCl there is a large red shift of the RuL MLCT transition. Zhang et al. showed that the pKa of the first protonation of RuL is 4.9 and the band extends to the red slightly. In that study they increased the HCl concentration to 12 M and recovered a spectrum that is identical to the spectrum shown here at 1 M HCl (Figure 3.5). The protonation should lower the energy of the MLCT band by making the positively charged ligand a more favorable electron acceptor.

3.4.2. Long-Lived Excited States in RuL and RuLDQ in Acetonitrile

The initial goal of this work was to determine the fate of the electron that is transferred following the photoexcitation of the ruthenium photosensitizer RuLDQ. With that in mind it is prudent to begin the discussion of the ultrafast transient absorption results with the determination of the long-lived states of RuL and RuLDQ. From the first look at the structures in Figure 3.1 it is very noticeable that the molecules are very similar in structure with only the addition of the four-carbon bridge linking the nitrogens on the terminal portion of the LDQ ligand. Although the molecules are structurally similar it is evident from the transient spectra that the photophysics are vastly different. The RuL molecule exhibits a broad unstructured very long-lived spectrum, while RuLDQ shows much more structure and a comparably very fast decay that is observable in the 2.5 ns experimental window.
3.4.3. Feasibility of Intramolecular ET Quenching.

MCLT states in ruthenium polypyridyl complexes are formally thought of as intramolecular electron transfer states where the electron is transferred from ruthenium to an attached ligand. With this being the case it is important to identify that the interest here is in a charge-separated state formed when an electron is transferred from a MLCT state to a more distant electron acceptor. It has been shown that bipyridinium compounds, including diquat, efficiently quench the luminescence of photoexcited Ru(bpy)$_3$. Covalently linking these types of compounds to a polypyridyl ligand quenches the long-lived MLCT emission that is observed in many ruthenium photosensitizers by intramolecular ET from the metal to the bipyridinium acceptor. The driving force for this electron transfer, $-\Delta G_{ET}$, can be estimated from the Rehm-Weller equation (Eq. 3.5),

$$-\Delta G_{ET} = e\left[E_{1/2}(A/A^-) - E_{1/2}(D^{*+}/D)\right] + E_{00} - w(r_{DA})$$ (3.5)

In this equation, $E_{1/2}$ values are reduction potentials, $e$ is the fundamental charge, $E_{00}$ is the singlet energy of the excited donor or acceptor, and $w$ is the “work term” or energy change when the distance between donor and acceptor radical ions is decreased from infinity to the distance $r_{DA}$ at which an electron is transferred from donor D to acceptor A. We neglect $w$, which is small in polar solvents like acetonitrile, and approximate the driving force for forward ET as,

$$-\Delta G_{ET} = e\left[E_{1/2}(L/L^{*}) - E_{1/2}(Ru^{3+/2+})\right] + E_{00}$$ (3.6)

Using reduction potentials from Table 3.3, $-\Delta G_{ET} = E_{00} - 2.56$ eV for complex RuL. The value of $E_{00}$ will lie somewhere between the energy of maximum emission at room
temperature for RuL (1.84 eV$^{28}$) and the value of $E_{00}$ for [Ru(bpy)$_3$]$^{2+}$ (2.12 eV$^3$). The $E_{00}$ value is thus too small to yield a positive ET driving force, and ET quenching of the $^3$MLCT state does not take place in photoexcited RuL. This result is consistent with the emissive character and long excited-state lifetime that approaches 1 µs for RuL.$^{28}$

For RuLDQ, the reduction potential data in Table 3.3 predicts $-\Delta G_{ET} = E_{00} - 1.81$ eV. For the nonemissive RuLDQ $E_{00}$ was assumed to have the same value of 1.84 eV as RuL. This value yields a slightly favorable driving force for forward ET. The use of the room temperature emission maximum likely underestimates the true value of $E_{00}$, and the true driving force is likely to be somewhat larger, especially because ET appears to take place faster than relaxation in the initial excited state. Electrochemical considerations suggest that intramolecular ET quenching is feasible for RuLDQ, but not for RuL.

3.4.4. State C for RuLDQ is a CS State.

As shown in Figure 3.7 the transient absorption spectrum of RuLDQ show large positive absorption signals at wavelengths greater than 470 nm. This absorption band shows a maximum at 505 nm with a significant shoulder at 550 nm and the appearance of a second band that is located at wavelengths greater than 650 nm and outside of the experimental spectral window. This absorption band must be due to the L$_{DQ}$ ligand as Ru(bpy)$_3$ only exhibits weak absorption features greater than 500 nm.$^{29}$ Looking at the rightmost column of Figure 3.7, it can readily be seen that the final state of RuLDQ is independent of excitation wavelength. Scaling of these spectra 100 ps after excitation, regardless of excitation wavelength, leads to identical curves. This is evidence of the decay of a single species. Initial conclusions were that the quaternization of the terminal end of the ligand allowed for a charge transfer to take place to this remote end of the
ligand. This view is not well supported by some simple studies done on the spectrum of reduced 4DQ$^{2+}$ (Figure 3.1) that show an absorption maximum at 500 nm, but a molar absorption coefficient ($\epsilon$) of only 2,500 M$^{-1}$ cm$^{-1}$. Even with an ET quantum yield of unity this low $\epsilon$ value would not be able to overcome the ground-state absorption of RuL$_{DQ}$ that is calculated to be 13,300 M$^{-1}$ cm$^{-1}$. Further evidence that 4DQ$^{2+}$ is not the eventual electron acceptor is the large absorption band at 390 nm of reduced 4DQ$^{2+}$. This band at 390 nm is three times larger than the band at 500 nm, and no such band is observed in the spectrum of RuL$_{DQ}$. These observations indicate that the spectrum of the CS state of photo-excited RuL$_{DQ}$ (Figure 3.7) shows little in common with the spectrum of reduced diquats bonded to ruthenium by a non-conjugated bridge.  

Reexamining the L$_{DQ}$ ligand it is quite obvious that the extended $\pi$ conjugation could be expected to perturb the spectrum of the CS compared to the non-conjugated bridges. Treating the entire L$_{DQ}$ ligand as the charge-accepting moiety an entire new set of reference molecules need to be explored. These diazastilbene-like molecules have been extensively studied and provide insight into the CS state of RuL$_{DQ}$. The spectrum of state C in Figure 3.15 shows the very intense absorption at 500 nm. This spectrum is very similar to the spectrum produced from the one electron reduction of trans-1,2-bis(N-methyl-4-pyridinium)ethylene (trans-bpe). This suggests that the electron is delocalized over the entire L$_{DQ}$ ligand, producing a diazastilbene-like radical. The radicals of substituted trans-diazastilbenes show a very strong absorption in the visible. Trans-bpe shows an absorption max at 517 nm with an $\epsilon$ of 57,000 M$^{-1}$ cm$^{-1}$. If the terminal methyl groups are replaced by benzyl groups the result is a “vinylene viologen”,
1,2-bis(N-benzyl-4pyridinium)ethylene, which has an extremely similar spectrum to trans-bpe.\textsuperscript{34}

Further support that the electron is likely delocalized over more of the ligand than just the terminal DQ portion comes from electrochemistry. For Ru(422-DQ) and Ru(424-DQ) (Figure 3.1) there is a very small change in reduction potential of the DQ connected by a saturated bridge when comparing it to the free DQ form (Table 3.4). In contrast, there is a large change when the bridge to the DQ end of the ligand is conjugated as in the case of RuL\textsubscript{DQ}. The first reduction of RuL\textsubscript{DQ} is 0.25 V more positive than Ru(424-DQ) and 0.12 V more positive than 4DQ\textsuperscript{2+}. The difference between the first and second reduction potentials for the diquat ligands are 0.13 V for Ru(424-DQ) and 0.42 V for RuL\textsubscript{DQ}. This data supports that the lowest energy reduction is delocalized across the \(\pi\)-system of the ligand.

3.4.5. State C for RuL is a \(\text{^{3}MLCT}\) State

RuL, unlike RuL\textsubscript{DQ}, has a slightly more enigmatic long-lived state. The long-lived absorption band of RuL (Figure 3.9) is unlike that of Ru(bpy)$_3$\textsuperscript{1} or RuL\textsubscript{DQ} (Figure 3.7). The band has a maximum at \(\sim580\) nm, is very broad and has a lifetime that is much longer lived than the temporal window of the experiment. This spectrum does not match the spectrum generated by the one-electron reduction of the L ligand (Figure 3.5). Time-resolved emission studies by Zhang et al. show that RuL has a biexponential decay with time constants of 256 and 710 ns.\textsuperscript{19} On the surface this biexponential emissive decay is confusing; most systems referenced to this point have a single exponential emissive decay. This biexponential decay suggests two separate emissive states that are not in communication with each other.
Meyer and co-workers have studied a slightly altered version of RuL, one in which dmb ligands replace the bpy ligands.\textsuperscript{2,35} Resonance Raman studies of the dinuclear Ru complex indicated that the lowest $^3\text{MLCT}$ is located over both of the bipyridines of the L ligand.\textsuperscript{2} Suggestions have been made that closely lying $^3\text{MLCT}$ and $^3\pi\pi^*$ ligand localized states can be populated simultaneously.\textsuperscript{36} This suggestion can explain the 10-fold lower emission when compared to Ru(bpy).\textsuperscript{19} The competition between the two states leads to an extensive population of the $^3\pi\pi^*$ state that dominates the transient spectrum instead of the expected $L^-$ like spectrum.

A second explanation for the difference between the long-lived spectrum of RuL and the $L^-$ is that the electron does not completely delocalized across the L ligand in the ruthenium compound. It is possible that the electron remains on the bpy portion of the ligand that is close to the ruthenium. This is supported by the electrochemical data that shows the reduction of RuL is 0.75 V less favorable than that of RuL\textsubscript{DQ}. However, this picture is at odds with the study by Meyer and co-workers in which they state the resonance Raman data suggests that the electron is delocalized across the entire L ligand in a dinuclear ruthenium system.\textsuperscript{2} The major difference from this study and that of Meyer and co-workers is that the L ligand is attached to a ruthenium on both ends of the ligand, potentially promoting the delocalization across the bridge. This being the case, the excited-state spectrum of the dinuclear ruthenium compound containing the L ligand\textsuperscript{2} does not match that of the one-electron reduction of L (Figure 3.5). Schmehl et al. point out that the Raman evidence from Meyer and co-workers does not rule out a localized triplet state on the L ligand as the vibrational bands of the triplet should be similar to the reduced ligand L.\textsuperscript{36}
Considering these results, this study supports the theory that RuL exhibits split triplet state dynamics with some $^3\text{MLCT}$ and some $^3\pi\pi^*$ character.

3.4.6. Short-Time Dynamics and Assignment of States A and B

After discussing the charge-separated states it is interesting to examine the pathway that the electron took to get to the CS state. As evident in Figure 3.11a and b, both RuL and RuLDQ see a fast partial decay at 375 nm and a fast partial recovery at 450 nm. This rapid decay at 375 nm is not seen in Ru(bpy)$_3$ when probing at a similar band 360 nm. This implies that the dynamics at 375 nm are exclusive to the mixed-ligand compounds. This signal is indicative of a population change between two electronic states; either from an excited state to the ground electronic state or to a second, lower lying, excited state. A possible pathway back to the ground state could be an isomerization around the double bond in the L or L$_{DQ}$ ligands. Strouse et al. determined that there was no photoisomerization of the L ligand in their studies. However, Zhang et al. determined there was a small amount of isomerization of RuL, but only in aqueous solutions. If there were isomerization taking place on a large enough scale to generate the types of signals that are observed, a change to the ground-state absorption would be expected. Examining ground-state absorption spectra of both RuL and RuLDQ before and after transient absorption studies showed little change to the spectra, thus ruling out isomerization as the source of these signals. Therefore, the signals must arise from internal conversion to a second excited state.

It has been established that the final state of RuLDQ is a charge-separated state and the state is populated regardless of excitation wavelength. Figure 3.2 shows the effect of different excitation wavelengths: 320 nm primarily excites a ligand localized transition,
400 nm excites a $^1$MLCT state that is primarily from the bpy ligands and 600 nm excites a $^1$MLCT state that is solely from a transition involved with the LDQ ligand.

While examining the spectrum of the SADS (Figure 3.14c and d) and the SAS (Figure 3.15) of the $\tau_2$ state, it is striking how similar the spectrum is to that of the final charge-separated state. The only difference is a slight red shift coupled with a minimal spectral broadening. Looking at the center column of Figure 3.7, the $\tau_2$ component is responsible for a spectral blue shifting of the quickly populated CS state. The lifetime of this component ~12-16 ps compares very well with other reported vibrational cooling times in acetonitrile.$^{40,41}$ For RuLDQ excited at 600 nm, there are only 2 exponentials required to fit the data (Table 3.1). Examining Figure 3.7h there is only laser noise evident in the 8-80 ps time window. There is no longer the blue-shift that is evident for the other two excitation wavelengths. For 600 nm excitation there is only the spectrum of the final CS state evident at very early times and the B state can be left out. It is therefore assigned that the 600 fs rapid dynamics observed following 600 nm excitation is mainly due to vibrational cooling which occurs very rapidly due to the low amount of excess energy.

The very fast dynamics for 320 nm and 400 nm excitation are from different sources as the excitation is not directly to the CS state as it is the case for 600 nm excitation. At these higher pump energies there must be some cascade to the lower energy CS state. As evident from the SADS and SAS in Figures 3.14 and 3.15 the A state looks very different from the B and C states. The difference is assigned to a state associated with a $^1\pi\pi^*$ transition on the LDQ ligand. As a comparison photoexcited trans-
bpe in acetonitrile shows a sharp peak near 515 nm\textsuperscript{42} that matches well with the peak from state A in Figure 3.15.

The assignment for RuL is less straightforward than for RuL_{DQ}. As quenching of the lowest $^3$MLCT by an electron transfer does not take place, it is proposed that the $\tau_1$ and $\tau_2$ dynamics show the rapid decay of the L localized $^1\pi\pi^*$ state or the decay from a higher-energy MLCT state, or both. The spectrum of state A (Figure 3.17 b) is similar to the spectrum of state A in RuL_{DQ} and suggests that it should also be assigned to the ligand $^1\pi\pi^*$ state. The B spectrum from Figure 3.17b is similar to the excited-state absorption for Ru(bpy) from reference 28 and can be assigned to a higher energy $^3$MLCT state on one of the bpy ligands. This assignment would then give a time constant of 2.6 ps for the transfer of population from the bpy-localized MLCT state to the lowest energy MLCT state on the L ligand. This interligand electron transfer (ILET) has been a topic of great debate as to just how long the time constant should or could be. Reports have indicated ILET times from < 1ps to hundreds of ps\textsuperscript{37,43-47}. In a study where a mixture of MLCT states was generated Laird and Vlček reported ILET dynamics of 8.3 ps to a monoquat in acetonitrile\textsuperscript{48}. The result presented here indicates a ~1 ps ILET when exciting multiple ligands at 400 nm.

A second possible explanation for short time dynamics in RuL could be the competitive formation to the two triplet states that was mentioned earlier with the 2.6 ps component resulting from the formation of the $^3\pi\pi^*$ ligand state. Studies of the excited-state absorption of the similar ligand 1,4-bis[2-(4'-methyl-2,2'-bipyrid-4-yl)ethylene]benzene occurs at 445 ± 10 nm and 500 ± 10 nm in acetonitrile\textsuperscript{49}. More
experiments must be done on the free ligand and the RuL compound to definitively assign the early time dynamics.

3.4.7. Solvent Effects

In water, the time constant (1 ps) assigned to forward electron transfer in RuL\textsubscript{DQ} is unchanged. However, the other two time constants are affected. The vibrational cooling time is decreased to 4 ps from the 16 ps in acetonitrile following 400 nm excitation. It is known that vibrational cooling events in water happen roughly 5 times faster than the corresponding cooling time in acetonitrile.\textsuperscript{40} This increase in rate of back electron transfer is likely due to the electrostatics in water.

While the 400 nm excitation results for RuL\textsubscript{DQ} in water are relatively straightforward the results for protonated molecule, RuLH\textsubscript{2} are substantially more confusing. This confusion is compounded by the very low signal to noise and the lack of additional sample to attempt to repeat the experiments. The protonation of RuL leads to a red shift in the ground-state absorption band resembling that of RuL\textsubscript{DQ}. The excited-state lifetime of 342 ps is nearly identical to the 334 ps lifetime that is measured for RuL\textsubscript{DQ} in water. These two results lead to the belief that protonated RuL is acting like RuL\textsubscript{DQ}. This assumption seems to hold water even in light of the most confusing piece of data. Instead of a vibrational cooling component in RuLH\textsubscript{2}, there is a 22 ps component that has greater amplitude than the 342 ps component. In all of the RuL\textsubscript{DQ} data the \( \tau_2 \) component has been assigned to vibrational cooling and the DAS of that component has had amplitude that is on the order of three to five times smaller than the amplitude of the decay of the charge separated state. In RuLH\textsubscript{2} the second component is much too long to be vibrational cooling. At 22 ps, it is even longer than the longest cooling time found in RuL\textsubscript{DQ}.
following 320 nm excitation. In addition to the long lifetime of the component is the large amplitude. The amplitude of the 22 ps component is roughly double that of the 342 ps component.

This is a very perplexing decay profile. To date there has been only one suggestion that could potentially explain the 22 ps decay. This explanation involves an isomerization of the LH$_2$ ligand following photoexcitation of the RuLH$_2$ MLCT band. Figure 3.19 shows the DAS for bands of interest, the dash-dot is the 342 ps band of RuLH$_2$, the solid red is the 22 ps component of RuLH$_2$, and for reference the long lived state of RuL (dotted) and the CS state of RuL$_{DQ}$ (solid black). Both of the DAS of RuLH$_2$ more closely resemble the structure of RuL$_{DQ}$ than that of RuL. Both bands of RuLH$_2$ also resemble each other quite well with only a red-shift of 15 nm to the 22 ps spectrum.

The current model proposes that a portion of the photo excited RuLH$_2$ undergoes a photo-isomerization to the cis form of the ligand, placing the diprotonated end of the ligand much closer to the charge donating ruthenium core, and changing the electrostatics of the ligand driving the electron back to the Ru$^{3+}$. This isomerization model is supported by the result of Zhang et al. that showed the formation of a small amount of cis RuL in aqueous solution when the molecule has been exposed to light.$^{19}$ As stated earlier this is not observed in acetonitrile. Much work has been done on the study of ultrafast isomerization in stilbene-like molecules. If you look at the free L ligand it closely resembles diphenyl-stilbene. The work on the isomerization of these compounds shows that there is a high likelihood that an isomerization of the ligand takes place following photoexcitation, leaving the molecule close to a 60:40 ratio of trans and cis isomers.$^{50}$ As
there was so little sample it was difficult to characterize the spectrum following the pump-probe experiments. More work needs to be done in this area to determine if the photoexcitation of a MLCT band can truly lead to the isomerization of an attached molecule. Zhang et al. have shown that the dimerization of RuL involving an isomerization step is diminished under these high acid conditions. It is possible the dimerization no longer occurs because the excited state that leads to the isomerized molecule is quenched more quickly by Back Electron Transfer (BET) in the protonated compound.

3.4.8 Comparison with ET Rates in Other Dyads

Forward ET to produce the CS state of RuL\textsubscript{DQ} occurs at a strikingly high rate compared to other ruthenium-based dyads. Lomoth et al.\textsuperscript{14} studied the ruthenium polypyridyl complex formed when methyl viologen is connected by a single methylene group to the 4’ position of a ligating 2,2’-bipyridine and reported a time constant of 4.5 ± 0.5 ps for forward ET. Inserting a second methylene group in the bridge slowed the forward ET time constant to 200 ps. The Ru(424-DQ) complex (Figure 3.1) studied by Cooley et al.\textsuperscript{8} in which the ethenyl linker is replaced by a saturated bridge consisting of two methylene units exhibits transient absorption bleach recovery and emission decay times of just over 6 ns. Our results show that replacing the ethyl linker by an ethenyl linker dramatically accelerates the rate of ET quenching. The electron may not have to travel as far in RuL\textsubscript{DQ} because the electron accepting state delocalized “back onto” the bridge. Delocalization may also reduce the reorganization energy allowing the rate of forward ET to proceed at the maximal rate for the available driving force.\textsuperscript{9}
Not only is the CS state of the RuL\textsubscript{DQ} complex formed rapidly, but it also undergoes charge recombination more slowly than is observed in nearly all ruthenium-bipyridinium complexes studied to date. This slower charge recombination allows for a charge hoping event to a separate acceptor to be more competitive with back electron transfer. The rate of back ET was much faster than the rate of forward ET in all Ru-diquat dyads studied by Cooley et al.\textsuperscript{8} Kelly and Rodgers reported faster rates for back ET than for forward ET in Ru-viologen dyads with flexible polymethylene linkers, whenever forward ET took place in nanoseconds.\textsuperscript{6}

3.4.9 Initial Zeolite Studies

Single wavelength transient absorption studies show that there are fast subpicosecond dynamics observed in photoexcited RuL\textsubscript{DQ} that is anchored to a zeolite surface (Figure 3.13). This is potentially at odds with another study that has shown the anchoring of the RuL\textsubscript{DQ} to a zeolite particle brings back a portion of the emission that is observed in Ru(bpy)\textsubscript{3} and RuL.\textsuperscript{11} With only a single decay trace from the ultrafast spectroscopy of RuL\textsubscript{DQ} anchored to the zeolite it is very difficult to draw extensive conclusions. The best explanation is that the extreme electrostatic conditions of the zeolite as well as the confined nature of the zeolite supercage are perturbing the RuL\textsubscript{DQ} CS state. This perturbation may very well exist in two regimes: one where the CS state is inaccessible which leads to the long-lived emission and a second where the CS is accessible and exhibits the very fast dynamics that are evident at 450 nm. Future studies, with a higher concentration of RuL\textsubscript{DQ} on the zeolite or a diffuse reflectance study that would increase the number of RuL\textsubscript{DQ} molecules can shed light on this CT event. Higher concentrations of RuL\textsubscript{DQ} on the zeolite, or a larger number of zeolite particles should give
large enough signals that broadband transient absorption spectroscopy can be utilized. Using the same type of analysis that was used to determine the nature of the photophysics of RuL and RuL\textsubscript{DQ} in neat solution should be able to definitively assign the nature of the charge separated state for RuL\textsubscript{DQ} anchored to the zeolite. The expectation is that there will be a combination of RuL and RuL\textsubscript{DQ} spectra and dynamics. The data should show a decay component of ~1.4 ns with a spectrum resembling RuL\textsubscript{DQ} in acentonitrile and a long-lived offset resembling the spectrum of RuL.

3.5. Conclusions

Excited-state dynamics of two mixed-ligand ruthenium complexes were investigated by broadband femtosecond transient absorption spectroscopy. In RuL, the results provide evidence for subpicosecond ILET which rapidly transfers population to the lowest energy $^3$MLCT state. In RuL\textsubscript{DQ}, intramolecular charge transfer occurs in $\leq$ 1 ps, forming a CS state with the relatively long lifetime of ~1.4 ns. Forward ET in the dyad may occur competitively with the relaxation of upper excited states. Target analysis provides clear evidence of vibrational cooling by the nascent reduced ligand. It was suggested in an earlier report that photoexcitation of RuL\textsubscript{DQ} transfers an electron from the metal to the diquat end of the ligand,$^{28}$ but the results of this study show that the excited electron is delocalized across the $\pi$-system of the LDQ ligand. Low-energy states associated with $\pi$-conjugated bridges could be a general impediment to the robust delivery of an electron to an acceptor in donor-bridge-acceptor compounds. The results in water open the possibility of photoisomerization of the diphenylstilbene-like ligands when attached to a ruthenium core. Finally this study raises, and begins to investigate, the question of the mechanism by which electrons are delivered to further acceptors inside
neighboring zeolite cavities. The initial aim was to determine the CS state of the photosensitizer RuL\textsubscript{DQ}; this aim was thoroughly completed. Over the course of this study many new avenues of examination have been opened which will hopefully be explored by future investigators.
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Table 3.1. Best-fit Lifetimes (ps) for RuL_{DQ}$^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{pump}}$ (nm)</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>320</td>
<td>1.2 (0.08)</td>
<td>11.7 (2.1)</td>
<td>1430 (60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>(0.08)</td>
<td>16 (5)</td>
<td>1460 (70)</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.56 (0.1)</td>
<td>--</td>
<td>1270 (61)</td>
</tr>
</tbody>
</table>

$^a$Uncertainties in parentheses are twice the estimated standard error.
Table 3.2. Best-fit lifetimes (ps, unless otherwise noted) for RuL$^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{pump}}$ (nm)</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>450$^b$</td>
<td>256 ns$^b$</td>
<td>710 ns$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>0.14 (0.04)</td>
<td>2.6 (0.2)</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

$^a$Uncertainties in parentheses are twice the estimated standard error.

$^b$Ref. 19.
Table 3.3. Best-fit lifetimes (ps) for RuLH$_2$ and RuL$_{DQ}$ in water$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\lambda_{\text{pump}}$ (nm)</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuLH$_2$</td>
<td>400</td>
<td>1.38</td>
<td>20.2</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.24)</td>
<td>(3.24)</td>
<td>(114)</td>
</tr>
<tr>
<td>RuL$_{DQ}$</td>
<td>400</td>
<td>1.12</td>
<td>4.1</td>
<td>334</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.05)</td>
<td>(0.5)</td>
<td>(7.0)</td>
</tr>
</tbody>
</table>

$^a$Uncertainties in parentheses are twice the estimated standard error.
## Table 3.4. Reduction Potentials for Ruthenium Complexes and Diquats

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{3+/2+}$ (V)</th>
<th>$E_{1/2}^{2+/+}$ (V)</th>
<th>$E_{1/2}^{+/0}$ (V)</th>
<th>$E_{1/2}^{2+/+}$ (V)</th>
<th>$E_{1/2}^{+/0}$ (V)</th>
<th>$E_{1/2}^{0/-}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuL</td>
<td>0.91</td>
<td>-1.65</td>
<td>-1.86</td>
<td>-2.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuL-DQ</td>
<td>0.91</td>
<td>-0.90</td>
<td>-1.32</td>
<td>-1.77</td>
<td>-1.92</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$<em>3$]$</em>{2+}$</td>
<td>0.89</td>
<td>-1.74</td>
<td>-1.93</td>
<td>-2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(424-DQ)$_c$</td>
<td>0.85</td>
<td>-1.15</td>
<td>-1.28</td>
<td>-1.75</td>
<td>-1.95</td>
<td>-2.21</td>
</tr>
<tr>
<td>4DQ$_{2+}$</td>
<td>-1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(422-DQ)$_c$</td>
<td>0.87</td>
<td>-0.82</td>
<td>-1.27</td>
<td>-1.73</td>
<td>-1.94</td>
<td>-2.19</td>
</tr>
<tr>
<td>2DQ$_{2+}$</td>
<td>-0.73</td>
<td>-1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-dimethyl-2DQ$_{2+}$</td>
<td>-0.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* All values measured in CH$_3$CN and converted to vs. Fe$^{3+}$/Fe using conversion constants in ref. 51. *b* Ref. 28. *c* Ref. 8. *d* Ref. 52.
Figure 3.1. Chemical structure of ruthenium based photosensitizers and charge accepting diquats.
Figure 3.2. Normalized absorption spectra in acetonitrile solution of $[\text{Ru(bpy)}_3]^{2+}$ (black), L$_{\text{DQ}}$ (dashed green), 1:1 molar mixture of $[\text{Ru(bpy)}_3]^{2+}$ and L$_{\text{DQ}}$ (dashed orange), RuL (red), and RuL$_{\text{DQ}}$ (blue). Arrows indicate excitation wavelengths used in transient absorption measurements: 320, 400, and 600 nm.
Figure 3.3. Absorption spectra of ruthenium photosensitizers in water. RuL_{DQ} (solid blue), RuL (solid red), and the diprotonated RuLH_{2} (dashed red). All compounds have 2Cl\(^-\) as a counter ion for solubility in water.
Figure 3.4. Absorption (left axis) spectra of Ru(bpy)$_3$(red), RuL(green), and RuL$_{DQ}$ (blue) in acetonitrile. Diffuse reflectance (right axis) absorption spectra of RuL$_{DQ}$ tethered to zeolite with the DQ portion of the molecule inside of the zeolite supercage closest to the surface(black). Zoom in highlights the MLCT absorption band.
Figure 3.5. Absorption spectra of (a) one electron reduced ligand \( \text{L}_{\text{DQ}} \) and (b) one electron reduced ligand \( \text{L} \), each generated electrochemically.
Figure 3.6. Early time spectrum of RuL\textsubscript{DQ} in acetonitrile photoexcited at 320 nm.
Figure 3.7. Transient spectra of RuL	extsubscript{DQ} in acetonitrile following excitation at 320 nm (panels a-c), 400 nm (panels d-f), and 600 nm (panels g-i) at the delay times given below each column of panels.
Figure 3.8. Broadband transient spectra of RuL<sub>DQ</sub> in water photoexcited at 400 nm with probe delay time listed.
Figure 3.9. Transient spectra of RuL in acetonitrile following excitation at 320 nm at delay times between (a) 5 and 20 ps, and (b) 25 and 2500 ps.
Figure 3.10. Broadband transient spectra of RuL in 1 M HCl excited at 400 nm. The high acid concentration protonates the nitrogens on the terminal end of the L ligand. Delay times associated with each spectrum as listed.
Figure 3.11. Transient absorption vs. time for RuL (black squares) and RuL_{DQ} (green circles) probed at (a) 375 nm, (b) 450 nm, (c) 500 nm, (d) 600 nm, and (e) 740 nm. The pump wavelength was 320 nm for panels a – d and 540 nm for panel e. The time delay axis switches from linear to logarithmic at 20 ps. Fits to the data are shown by solid curves.
Figure 3.12. Kinetic comparison of multiple compounds in multiple solvents. RuL$_{DQ}$ in acetonitrile excitation 320 nm (green) 400 nm (red) in water 400 nm (blue) in butyronitrile 400 nm (purple) RuL in acetonitrile 320 nm (black) and RuLH2 in water 400 nm (cyan).
Figure 3.13. Kinetic traces of RuL_{DQ} in acetonitrile (solid circles) and anchored to a zeolite particle bathed in water (open circles). 400 nm excitation, 450 nm probe.
Figure 3.14. Decay associated difference spectra (DADS) for RuL₇Q in acetonitrile for excitation at (a) 320 nm and (b) 400 nm: τ₁ (purple), τ₂ (green), and τ₃ (black). Species associated difference spectra (SADS) formed from linear combinations of the DADS for excitation at (c) 320 nm and (d) 400 nm: State A (purple), B (green), and C (black), see scheme 1.
Figure 3.15. Species associated spectra for RuL\textsubscript{DQ} excited at (a) 320 nm and (b) 400 nm obtained by adding the scaled ground-state absorption spectrum (cyan curve) to the species associated difference spectra in Figures 6c and d: state A (purple), B (green), and C (black).
Figure 3.16. DAS of RuL_{DQ} in acetonitrile excited at 600 nm. $\tau_1$ (purple) and $\tau_3$ (black).
(Note there are no dynamics with ~10 ps lifetime, thus no $\tau_2$)
Figure 3.17. Target analysis of transient spectra for RuL in acetonitrile pumped at 320 nm: (a) DADS, (b) SADS, and (c) SAS. All curves are colored as in Figures 6 and 7.
Figure 3.18. Comparison of species associated difference spectrum of RuL_{DQ} as function of excitation wavelength vs. the species associated difference spectrum of the long time signal of RuL.
Figure 3.19. Species associated difference spectra of RuL\(_DQ\) in water for \(\tau_3\) (solid), RuLH\(_2\) in water \(\tau_3\) (dash-dot), and long-lived spectra of RuL (dot) Red curve, SADS of \(\tau_2\) for RuLH\(_2\)
4.1. Introduction

Proton-coupled electron transfer (PCET) continues to attract a great deal of research effort due to its importance in biological ET and in biomimetic strategies for solar energy conversion\(^1\)\(^-\)\(^4\). A frequent focus of study is on whether the proton and electron move in a step-wise or concerted fashion. In addition, PCET reactions can be classified by whether the proton and electron travel in the same direction from donor to acceptor, or the proton and electron travel in different directions to separate acceptors.\(^3\) The unidirectional case is illustrated by the oxidation of a quinol derivative by a ruthenium complex\(^5\) and hydrogen atom transfer between phenoxy radical and phenol.\(^6\) The bidirectional case is exemplified by photosystem II (PSII) during the proton transfer event from a tyrosine to a nearby histidine via a hydrogen bond when an electron is transferred to chlorophyll P\(_{680}^+\).\(^3\) Understanding the mechanism in photosynthesis has attracted vast amounts of interest.\(^3\) Characterizing this extremely efficient energy conversion system can possibly help develop an energy conversion technology that can
be economically and sustainably viable. Much work has been done to mimic the PCET process in PSII using so-called photoacids where an electron from a hydroxyl group is transferred toward the core of the molecule; in these model systems this ET triggers proton dissociation into the bulk solvent.\textsuperscript{7-10} This study will explore an avenue that is related to the photoacid studies but involving a methyl viologen-water complex that is not traditionally a photoacid.

Methyl Viologen (MV) is an extensively studied electron acceptor. In common applications MV acts as an electron acceptor, accepting an electron from an electronically excited electron donor. MV is a ferocious excited-state oxidant with the ability to oxidize a nearby solvent molecule if the solvent has a low enough ionization potential (IP).\textsuperscript{11} This electron transfer leads to a long-lived MV radical cation, which is easily identified by its characteristic absorption spectrum: a sharp, intense peak at 390 nm and a broader and somewhat weaker band at 600 nm.\textsuperscript{12} Peon et al. have described the interaction of an electron donating solvent and photoexcited MV.\textsuperscript{11} Following photoexcitation in methanol (IP = 10.84 eV), MV abstracts an electron from the surrounding methanol leading to the MV radical cation. Probing at 600 nm following the 266 nm photoexcitation shows the forward electron transfer event taking place faster than 400 fs. A portion of this population recovers via back electron transfer to the ground state with approximately 12% remaining in the MV radical form. The resulting radical absorption is apparent as a positive offset in the transient signals. In solvents with higher IPs such as acetonitrile (12.2 eV), no radical formation is observed and the excited-state lifetime is found to be 1 ns, as determined by both time-resolved absorption and emission measurements.\textsuperscript{11} In aqueous solution an unexpected result is observed. While water has an even higher IP
(12.62) than acetonitrile, a substantially faster 3.1 ps excited-state lifetime is determined by transient absorption experiments. In D$_2$O solution, the lifetime increases to 5.3 ps.\textsuperscript{11} The Peon study makes a brief but very intriguing note that the signals from a ground-state recovery experiment do not decay to zero, but instead exhibit a long-lived negative offset, indicative of the formation of a long-lived transient species.\textsuperscript{11} However, no offsets are seen at visible probe wavelengths, indicating that the transient cannot be the MV radical cation.

Interestingly, very little sample degradation is observed following prolonged irradiation at 266 nm, indicating that the transient signal is not due to a persistent photoproduct, this agrees with the results gathered by Peon et al.\textsuperscript{11} The nature of this decay is very perplexing. There is no evidence of quenching by radical formation, yet the excited-state lifetime is very short. This study reports that the quenching of optically excited MV in aqueous solution is via a multisite, concerted PCET pathway in which a nearby or attached water molecule acts as both electron and proton donor.

4.2. Results

4.2.1. Steady-State Absorption Spectroscopy

MV has an absorption maximum at 257 nm in water, comparing well with previous results,\textsuperscript{13} and 259 nm in methanol (Figure 4.1). Under high concentration of NaOH (\textgreater 0.5 M), the absorption band is slightly red shifted with the peak maximum shifted by 2 nm to 259 nm (Figure 4.1) and a slight increase is observed in the absorption at wavelengths greater than 280 nm. This change in absorption is more noticeable upon examining the spectrum once the initial MV absorption is subtracted off (red circles; Figure 4.2). The resulting difference spectrum has a maximum positive absorption at 296
nm and a maximum negative feature at 254 nm. The spectrum of MV in high concentrations of nitric acid (~1 M) is unaffected.

4.2.2. Transient Spectroscopy in Methanol

Multiple techniques were used to investigate the excited-state dynamics of MV following 266 nm excitation. Using single-wavelength transient absorption (Figure 4.3, Table 4.1), the excited-state lifetime probing at 600 nm was determined to be 398 fs with a long-lived offset. This matches well with previous results. In addition, ground-state recovery was probed at 250 nm. A fast 324 fs component, a small 7.95 ps component and a long-lived offset were observed. The 250 nm data in Figure 4.3 has been inverted for ease of comparison with the other data. Using a different technique, fluorescence upconversion, signals at 240 nm corresponding to a 343 nm emission were observed. The emissive decay was well fit with a time constant of 280 fs.

4.2.3. Transient Spectroscopy in Water

The excited-state dynamics of MV in water following 266 nm excitation were studied in a similar manner. The excited-state lifetime of MV in neat water probed at 600 nm are well fit with a time constant of 3.16 ps (Figure 4.4, Table 4.2), this corresponds well with previously reported MV lifetimes. The emissive lifetime at 343 nm obtained from fluorescence upconversion was also fit to 3.21 ps (Figure 4.4). The ground-state recovery has a more interesting response, with a bleach signal at 250 nm immediately following photoexcitation. This bleach signal recovers partially with a 3.5 ps lifetime resulting in a small negative offset due to a portion of the population that has not recovered to the original state. The 250 nm data has been inverted for comparison in Figure 4.4. A similar response exists for MV in heavy water; the only change is that the
lifetime of the 3.1 ps component slows to 5.3 ps (Figure 4.5). Figure 4.6 show that probing the red edge of the ground-state absorption band leads to a long-lived signal that exhibits a positive offset.

To determine the spectrum of the long-lived signal present from 240 nm to 320 nm further studies were performed. To generate a difference spectrum, the optical delay was set at 1 ns and the probe wavelength was scanned from 240 nm to 320 nm, taking a point every 2.5 nm (black dots; Figure 4.2). This spectrum shows a maximum positive signal at 296 nm and a maximum negative signal at 258 nm. This long-lived component can be resolved using nanosecond transient absorption probing at 290 nm and is shown to have a lifetime of 1.68 microseconds (Figure 4.7). The nanosecond experiments were performed following 15 minutes of Ar purging as well as under normal laboratory conditions and the exact same 1.68 microsecond lifetime was obtained.

Femtosecond transient absorption experiments were performed on MV in water with an increasing proton concentration to determine the effect of proton concentration on the long-lived state. Protons were introduced to the system in the form of nitric acid. A noticeable change in the signal that appeared as an offset was observed. Once the proton concentration reached 0.07 M [H⁺] (pH = 1.15) a decay was observable in the experimental window (-2 to 2500 ps). The decay at 0.07 M [H⁺] is 3.7 ns and decreases as H⁺ concentration is increased (Figure 4.8, Table 4.3). Making a plot of 1/lifetime vs. proton concentration (Figure 4.9) and fitting the resulting data points to a linear function, a rate of 3.1 M⁻¹s⁻¹ for the quenching of this long-lived state is established.

Femtosecond UV pump-IR probe experiments were employed to detect any potential long-lived signals that are evident in the IR transitions of the molecule. There is
a strong IR transition of ground state MV 1640 cm\(^{-1}\) (Figure 4.10). The depletion and recovery of this IR transition at \(\sim 1645\) cm\(^{-1}\) following photoexcitation at 270 nm is easily observed on the picosecond timescale (Figure 4.11). Kinetic traces are taken from the transient spectra roughly every 10 cm\(^{-1}\) (Figure 4.12) and globally fit to one exponential and an offset with a decay time of 6.64 ps. The spectra of this decay component as well as the small offset are visible in Figure 4.13. The offset is visible at all wavelengths and is likely the result of the BaF\(_2\) windows dissolving, forming BaOD\(_2\) and HF. The OD likely reacts with the MV to form pyridones. Support for this mechanism comes from the observation of the well-known green pyridone emission from the sample at the end of a long experimental run.\(^{14}\) Samples were dissolved in D\(_2\)O, to avoid the water IR band at \(\sim 1650\) cm\(^{-1}\).

4.3. Discussion

4.3.1. Transient Dynamics in Methanol

Much of the initial groundwork for the solvent electron donor to methyl viologen concept was performed by Peon et al.\(^{11}\) It was not thoroughly concluded whether the transient absorption experiments at 600 nm were monitoring the forward electron transfer to MV or back electron transfer to the solvent. The fluorescence upconversion data presented here provides insight to this process. These experiments show that the emissive lifetime is faster than the decay at 600 nm (Figure 4.3). The emissive lifetime is found to be 280 fs, this is faster than the instrument response of the fluorescence upconversion system (\(\sim 400\) fs). This implies that the emissive lifetime could potentially be faster, but we are unable to resolve the absolute lifetime. The upconversion result also shows that the radical formation that is observed in methanol does not contribute to the emissive
signal at 343 nm. This 280 fs emissive lifetime is considerably faster than the 400 fs lifetime evident at 600 nm (IRF 290 fs). The assignment made by Peon et al. that the 600 nm probe monitors the back electron transfer rather than the quenching of the MV excited state is confirmed. It is important to note how fast the forward electron transfer can take place if the electron donor is the solvent itself. This establishes an upper rate for forward ET to MV with a solvent molecule acting as the electron donor. This indicates the donor is in extremely close proximity to the acceptor removing the need for any diffusion, and in the case of methanol, potentially lacking any reorientation of the donor or the acceptor before the forward or backward electron transfer take place. As Peon et al. point out, even though a very high rate of back electron transfer is observed, there is significant MV radical cation formation, determined by the long-lived absorption spectrum which matches the very well characterized spectrum of the radical cation.\textsuperscript{11} The formation of the MV radical indicates that there must be some stabilizing force for this radical to survive for long times. The hydrogen bonding nature of the surrounding solvent could have some ability to stabilize the corresponding methanol radical cation (or methoxy radical). It is possible that the ground-state absorption in methanol is shifted compared to that of water from 257 nm to 259 nm by the formation of a ground state CT band between methanol and MV. This interaction could explain the ultrafast FET forming the well-characterized MV radical.

4.3.2 Transient Dynamics in Water

In water all of the transient techniques show the same ~3 ps decay component (Figure 4.4). Probing at 600 nm, the entire excited-state population decays in 3.1 ps. There is no offset signal that is indicative of the radical cation. This finding is consistent
with the study by Peon et al.\textsuperscript{11} The emissive decay is also 3.1 ps, indicating that the time-resolved emission and absorption are monitoring the same state. As established in the methanol experiments, there is no emission present from the MV radical cation. This implies that the 3.1 ps decay observed state must be the quenching of the MV excited state. It is unlikely that water is acting as a traditional electron donor as the ionization potential of water (12.62 eV) appears to be too high to be oxidized by excited-state MV.\textsuperscript{11} Probing the ground-state recovery at 250 nm provides more insight into this quenching pathway. Again, a ~3 ps decay is detected. The lifetime is slightly longer in the ground-state recovery experiments. This is likely due to some vibrational cooling that slows the arrival time to the lowest vibrational state in the ground electronic state.\textsuperscript{15} Along with the 3.5 ps component a long-lived offset signal is present indicating a population that does not recovery to the original electronic ground state. As previously mentioned, there is no evidence for this long-lived state in either the excited-state absorption or in the emission decays. It was first thought that possibly the MV was undergoing some photoreaction,\textsuperscript{16} but this is unlikely. After irradiating methyl viologen in neat water for an extended period of time with a 254 nm UV source, there is little change to the absorption spectrum or amplitude. This is also the case when measuring the sample absorption before and after time-resolved laser experiments. In addition, the products of a photoreaction should lead to changes in the vibrational structure of the methyl viologen ring that exhibits a strong absorption at 1640 cm\textsuperscript{-1}.\textsuperscript{17} The results of the IR experiments (Figure 4.11) show that there is no long-lived transient change to the vibration at ~1640 cm\textsuperscript{-1}. The lack of a strong positive signal also rules out the formation of a radical as well as the absorption of the radical should be on the order of four times
more intense than the ground-state absorption. The recovery of this IR band can be fit with a 6 ps decay. This is nearly identical to the decay of MV in D$_2$O observed probing at 600 nm and 250 nm. Chloride can be ruled out as an ET partner and photochemistry as the quenching pathway leading to the long-lived offset, as will be discussed in detail in Section 4.3.8. The only possibility that remains is that water is playing a pivotal role in the quenching of excited-state methyl viologen.

### 4.3.3. Proposed Mechanism for the Excited-State Quenching of MV by Water

The proposed a mechanism in which photoexcited methyl viologen can lead to the photo-catalytic splitting of a water molecule (Scheme 4.1) is relatively complex. The initial step following photoexcitation involves a lone pair on the oxygen associating with the photoexcited methyl viologen that is craving electrons. An electron is transferred from the water molecule to the excited MV. As the electron is transferred to MV$^{2+*}$, a proton from the e$^-$-donating water molecule is transferred to the bulk water network. As there is no evidence of signal from a MV radical cation, the back electron transfer to the electron deficient hydroxyl radical must be faster than our instrument response. The dissociated proton can diffuse away leaving behind the MV$^{2+}$ and OH$^-$ that remain in close proximity forming a strongly associated ion pair.

\[
\text{MV}^{2+} + \text{H}_2\text{O} + h\nu \xrightarrow{3.1 \text{ ps}} \text{MV}^{2+*} + \cdot \text{OH} \xrightarrow{\text{H}^+} \text{MV}^{2+} + \cdot \text{OH}^+ + \text{H}^+ \xrightarrow{< 100 \text{ fs}} \text{MV}^{2+} + \text{H}_2\text{O}
\]

### 4.3.4. Species Responsible for the Long-lived Signal in Water

Determining the source of the long-lived transient signal is crucial to confirming the proposed quenching mechanism. Transient absorption spectroscopy shows long-lived
signals are evident in the UV region from 240 nm to 320 nm (Figure 4.2). Comparing the transient spectrum with the spectrum generated under very high hydroxide concentrations in Figure 4.2 shows remarkable similarities. This supports the assignment that MV is in very close proximity to a hydroxide anion, forming an ion pair. The absorption spectra looks qualitatively similar to difference spectra generated after the ion pairing of MV\textsuperscript{2+} with various electron donors.\textsuperscript{19} This spectrum should only form after the dissociated proton from the original water molecule has diffused away. The experiments run in low pH conditions (Figure 4.8, Table 4.3) show a pronounced quenching effect when the proton concentration reaches ~0.07 M. The quenching rate is dependent on proton concentration, indicating a diffusional recombination rate for the proton and ion pair hydroxide. This recombination returns the system to MV\textsuperscript{2+} in neat water (Figure 4.8). This mechanism implies the system has come full circle and explains why there is such minimal evidence for a spectral change to MV following a prolonged exposure to UV light.

4.3.5. Electron Transfer from Water to MV\textsuperscript{2++}

The observed forward ET in water is slow (~3 ps) compared to the ~200 fs forward ET observed in methanol. It is theorized that this is because the process in water is not favorable as MV\textsuperscript{2+*} has been shown to be unable to oxidize potential electron donors with a gas phase IP greater than 10.8 eV.\textsuperscript{11} The gas phase IP of water is 12.62 eV,\textsuperscript{11} requiring some mechanism to assist this event. The coupled proton dissociation can be an avenue to lowering this ionization energy. There are schemes in which water gives up an electron when the initial input energy is much lower than 12.62 eV. Photo ionization of water at 9.1 eV leads to a transient spectrum that can be identified as the
well known solvated electron. Other studies have indicated that the ionization potential of room temperature liquid water is as low as ~6.5 eV. The lowering of the ionization energy is attributed to a proton motion generating a solvated proton as H$_3$O$^+$ and initially a OH:e$^-$ complex leading to the solvated electron. The process taking place at 9.1 eV and the reported value of 6.5 eV is below the threshold solvent IP that is suggested to be oxidized by excited state MV. The proton motion begins to explain why the FET event is slowed and is discussed further in the next section.

4.3.6. Dissociation of the Proton to the Bulk Solvent Network

The 3.1 ps rate for proton transfer to a surrounding water network is slightly slow when comparing to other analogous systems. Steinel et al. report a H-bond breaking time of 800 fs, other reports indicate a < 2ps H-bond lifetime. These reports indicate that a proton can move much faster than 3.1 ps and H-bond breaking alone is not responsible for the 3.1 ps PCET quenching. Fayer et al. have shown that deuteron dissociation in deuterated alcohols takes place in ~2 ps when exciting the OD vibration. The observed 3.1 ps is only slightly slower than these other processes and could reflect a restructuring of the solvent molecules around the highly charged methyl viologen molecule. It is known that the geometry of bipyridine molecules changes upon photoexcitation or one electron reduction. The change manifests itself as a planarization of the two rings bringing the entire system into a higher level of conjugation. The large motion from an angle of nearly 45° to 0° could have an impact on the solvent, forcing it to rearrange and rebuild the hydrogen bonding network. This reorientation of solvent molecules to reach the proper orientation for proton and electron transfer can explain the slow FET. As the FET is completely dependent on the proton transfer the water molecule must be properly
aligned with a proton accepting water molecule. Studies by the Tokmakoff group have shown that non-bonded protons do not exist in this non-bonding state for longer than roughly 150 fs. Coupling this with the idea of the so-called Grotthuss shuttle of the proton away from the ion pair, it is possible that the proton could be 6-8 Å away from the resultant ion pair in less than 2 ps. It has been suggested that a proton separated by 6-8 Å is blind to the OH⁻ left behind.

4.3.7. Photoacids as a Model System

The proposed mechanism for MV excited-state quenching by water involves a step in which the excited MV and the associated water generate a photoacid-like assembly, with a water molecule and MV acting as one unit. Photoacids are molecules that exhibit an extreme jump in pKa following photoexcitation. The excitation leads to an electron transfer from the lone pair on the oxygen to the bulk portion of the excited molecule. This electron transfer is followed by a proton transfer to the surrounding environment, often water. Photoacids show a pH-dependent dissociation. In our experiments, we see no evidence of an effect on the 3 ps dissociation event from pH 0 to pH 13. Ruthenium trisbipyridine/tyrosine systems in which photoexcited Ru(bpy)₃ oxidizes the attached tyrosine, coupled with the acidic proton photo-detaching to the surrounding water solution can be used as a analogue to the system we have studied. A strong electron acceptor (Ru³⁺, MV²⁺*) accepts an electron from a nearby oxygen that is part of an OH group. Concurrent with (or possibly following) this oxidation, an O-H bond is broken with the H⁺ going out into solution. In the Ruthenium tyrosine systems, it is debated whether this is a concerted or step-wise electron proton transfer. As stated earlier, it is likely that MV²⁺* is not strong enough to simply oxidize water leaving behind
a H$_2$O$^+$ that then undergoes a deprotonation. It is likely that the deprotonation occurring in a concerted fashion with the electron transfer to MV lowering the water oxidation to an acceptable level for the water molecule to act as an electron donor. Photoacids show a PCET rate that is dependent on pH, the MV water PCET event does not exhibit a pH dependence from pH 0 to 13. Costentin et al. claim that pH dependence means the reaction must be step-wise.$^{33}$ Recombination in the photoacids should be pH dependent since all of the protons will be equivalent recombination partners.$^{33}$

In some photoacids, the proton transfer does not necessarily quench the excited state, the resulting state can be R$^\ast$O$^-$ that can lead to deactivation by the formation of solvated electrons, or a reaction with water forming a hydroxide anion.$^{34}$ The proposed mechanism for the excited-state quenching of methyl viologen by water exhibits a solvent isotope effect of 1.7. This is possibly due to the differences in rearrangement times of H$_2$O and D$_2$O. There are reports of kinetic isotope effects over a wide range from 2-3 to as large as 50.$^{3,35}$

**4.3.8. Recombination of the Free Proton with the MV$^{2+}$/OH$^-$ Complex**

Eventually the hydrogen ion and the MV$^{2+}$/OH$^-$ complex react bring the system back to the original state. The hydrogen ion reacts with the MV$^{2+}$/OH$^-$ complex on a roughly diffusional rate $\sim3\times10^9$ M$^{-1}$ s$^{-1}$. Literature values for recombination of H$^+$ and OH$^-$ in neat water are $1.1\times10^{11}$ M$^{-1}$ s$^{-1}$. The difference in rates can be explained by the OH$^-$ in the system being bound to a large organic molecule. Another possibility is that the coulumbic repulsion due to the overall positive charge of the MV$^{2+}$/OH$^-$ ion pair is keeping the solvated proton away. It is theorized that once a proton dissociated from a water molecule is within 6-8 Å or 2-3 water molecules that a very fast recombination
reaction with the hydroxide anion can take place. The recombination rates of many
dissociated acids have been studied (Table 4.4). These recombination rates are roughly an
order of magnitude faster than that of the MV$^{2+}$/OH$^-$ complex and water yet are still an
order of magnitude slower than that of H$^+$ and OH$^-$. Currently, it is proposed that the
overall positive charge of the MV$^{2+}$/OH$^-$ complex leads to a coulombic repulsion effect
that slows down the rate of recombination.

4.3.9. Known Methyl Viologen Charge Transfer Pairs

It is important to note that MV in our experiments is a dichloride salt. It is known
that MV$^{2+}$ and Cl$^-$ can form a CT pair. It is prudent to rule out that the signals from the
long-lived transient and ground state ion pair formation are not due to a CT interaction
between MV and Cl$^-$. The Ebbesen results previously discussed indicate that the Cl$^-$ is
not the electron donor, but, for completion, steady-state spectroscopy can definitively rule
this out. It is possible to compare the absorption maximum of the CT difference spectra
for the MV$^{2+}$/OH$^-$ ion pair (296 nm) with that of MV$^{2+}$/Cl$^-$ ion pair (290 nm). This small
change is possibly enough to indicate that the ion pair is from MV$^{2+}$/OH$^-$ but further
evidence comes from a plot (Figure 4.14) of CT absorption max in (eV) vs. 
photoelectron emission threshold energy (eV). The CT absorption maximum for the
MV$^{2+}$/OH$^-$ ion pair fits very well with this trend. This correlation supports that the nature
of the MV in water long-lived signal has been established.

There have been other investigations into photoinduced charge transfer between
MV and associated anions. These experiments were performed under high enough donor
concentrations to exhibit a CT band before photoexcitation and led to the formation MV
radical cation. Ebbesen et al. have shown photo-exciting the MV under high chloride ion
concentration leads to the formation of the MV radical.\textsuperscript{38} This CT formation with a complexed chloride or thiocyanate ion with MV takes place in under 30 ps. Ebbesen’s experiments were limited by not being able to see the true FET event, but comparing the geminate recombination (GR) with that of our ion pair shows a vast difference. Also the recombination time of the MV radical formed by the electron transfer from Cl\textsuperscript{−} has been determined by Ebbesen et al. to be less than 1 ns and could not be further resolved due to signal-to-noise issues.\textsuperscript{39} This study also investigated the ion pair formed with SCN\textsuperscript{−} recombines with a rate of $3 \times 10^{10}$ M\textsuperscript{−1}s\textsuperscript{−1}.\textsuperscript{39} The mechanism that includes GR on a sub-100 fs scale does not compare well with the results presented by Ebbesen. Ebbesen reports a quantum yield of 0.2 for the ion pair in photoexcited MV\textsuperscript{2+/Cl\textsuperscript{−}}.\textsuperscript{19} The quantum yield for the ion pair MV\textsuperscript{2+/OH\textsuperscript{−}} has not yet been accurately determined. Rough, initial calculations indicate that a large amount of the sample must be excited to generate the appropriate pH jump to result in the observed 1.7 $\mu$s recombination time. More nanosecond experiments must be performed to determine the actual yield of the MV\textsuperscript{2+/OH\textsuperscript{−}} ion pair. By determining the initial pH of the solution the number of H\textsuperscript{+} ions in solution before sample excitation is defined. The starting concentration of MV\textsuperscript{2+} will be known, and the recombination time of the H\textsuperscript{+} ion with the MV\textsuperscript{2+/OH\textsuperscript{−}} ion pair will give the concentration of H\textsuperscript{+} following photoexcitation. Determining the H\textsuperscript{+} concentration jump will also give the MV\textsuperscript{2+/OH\textsuperscript{−}} concentration and thus the yield of formation. The quantum yield should be very high as a large number of H\textsuperscript{+} ions must be generated to for the recombination reaction to occur in 1.68 $\mu$s.
4.3.10 Ruling Out Other Proposed Transient Species

Peon proposed a few possible assignments for the long-lived signal generated in his experiments. With the information that was available, many possible conformations were reasonable; however, recent experimental data eliminates some possibilities. Proposed assignments included an isomerization event leading to a prefulvenic-type isomer or the addition of an oxygen atom to the pyridium ring. The prefulvenic-type isomer is known to form in photoexcited N-protonated pyridine. The N-protonated pyridine is essentially one half of methyl viologen. Chachisvilis et al. report that the isomerization takes place in 1.9 ps in water and results from the $^1\pi\pi^*$ excited state. The absorption band of the isomer is at 310 nm and persists for longer than 2 ns. The effect on the molecular structure is a change from a six-member ring to a five-member ring in the pyridine portion of the molecule. This change would lead to a substantial change to the IR spectrum, which is not observed. The second suggestion was the formation of a pyridone. If you examine the absorption bands of the 2- or 3-one, it can be determined that the formation of either of these two molecules would not lead to an increased signal at 290 nm. Also initial studies have shown that the formation of pyridines under extremely high concentrations of hydroxide is irreversible.

Other suggestions not made by Peon were also considered. Possibilities included the known reaction of conjugated ring systems with OH to form a complex referred to as a Meisenheimer Complex. These complexes are transient in nature and lead to a change in the electronic structure. This change could be observed as incomplete recovery in the ground-state bleach experiments. These Meisenheimer complexes have also shown to be quenched by the addition of acid to the system. All of this supports the possible claim
of Meisenheimer complexation. One experiment seems to unequivocally rule out this possibility: transient infrared spectroscopy (Figure 4.11). The formation of the Meisenheimer complex leads to a major change in the ring structure of the parent molecule. This change would be very evident in the femtosecond vibrational experiments. As there is no transient signal beyond 15 ps the Meisenheimer complex can be ruled out. Also, the lifetime of the MV$^{2+}$/OH$^-$ complex is ~1.6 µs: Meisenheimer complexes have lifetimes on the order of tenths of seconds to hours. Another known reaction of methyl viologen in aqueous solution leads to the formation of pyridones, an oxygen doubled bonded to one of the pyridine rings in either the 2 or 3 position.

Pulse radiolysis shows that there are many reactions between hydroxyl radicals, H radicals and MV. It is prudent to rule out these processes as one leading to the long-lived offset. The spectrum produced following the reaction of MV$^{2+}$ with the OH radical forms a N-hydroxycyclohexadienyl type radical with absorption peaks at 315 nm and 470 nm. This radical decays in with a rate of 6.4 x 10$^8$ M$^{-1}$s$^{-1}$ dependent on MV concentration. No long-lived transient signal at 470 nm has been observed, this is also confirmed in the time-resolved spectrum of MV in water produced by Peon et al. The interaction of the MV radical and an H-radical can lead to the formation of a hydrogenated MV. This hydrogenated product results in a radical with the H adding to a ring carbon of MV and has a characteristic absorption at 350 nm. These pulsed radiolysis experiments provide insight into many reactive pathways that result in long lived radical signals with lifetimes >8 µs. The lack of these long-lived spectral features indicates that the mechanism we are observing is drastically different than the mechanisms for reactions between MV$^{2+}$ and OH and H radicals. Although the pulsed
radiolysis experiments are generate MV radical in the presence of OH radical the authors provide no indication of an interaction between these two species. This is most likely due to the diffusional nature of the reactions in these radiolysis experiments as well as detection window that is cut off below 300 nm, the MV$^{2+/OH^-}$ ion pair would just tail into the spectral window.

4.3.11. Impact of Water Quenching Mechanism on Previous Results

As mentioned earlier the photophysics of MV in acetonitrile are quite different from those in water. There is no formation of any radical, and the lifetime is quite long ~1 ns and fairly emissive with a quantum yield of 0.03$^{11}$ This study also reports that the 1 ns signal is quenched upon addition of water to the acetonitrile solution. The nature of this quenching is interesting in light of the new water pathway that has been identified. Small water volumes are enough to quench, but this mechanism seems to indicate that a number of water molecules are required for the quenching to take place. Studies have shown that even though water and acetonitrile are miscible, pockets of water$^{44}$ or hydrogen bonded chains of water$^{45}$ can form in acetonitrile, even at very low water concentrations. This microheterogeneity can explain how efficient quenching of MV in acetonitrile can occur at such low concentrations of water. The water that is quenching the MV excited state is likely H-bonded to a second water molecule allowing for the water PCET mechanism to occur. It would be of interest to study the UV region for the transient species of MV in acetonitrile with varying amounts of water. The recombination rates could provide insight to the extent of the microheterogenous regions.
4.3.12. Comparing the PCET Process in Water and Methanol

After all of this discussion it is interesting to look back at the methanol mechanism. Similar PCET reactions could be taking place in both water and methanol. Using a competitive mechanism for BET and proton transfer in methanol (Scheme 4.2), the lifetime of BET and PT are determined to be 0.49 ps and 3.6 ps respectively. The 3.6 ps compares well with the 3.1 ps PT time in water. The reason we see the excited state for 3.1 ps in water is due to the PT being the rate-limiting step in the concerted PCET. This implies that the PCET in methanol must be step-wise, with the ET in <280 fs followed by the PT in 3.6 ps. In the water mechanism, there is a fast back ET from MV\(^{2+}\) to \('\text{OH}\) leading to the ion pair with the proton off in solution. MV\(^{2+}\) has an electron affinity of 1.24 eV,\(^{46}\) \('\text{OH}\) 1.83 eV and MeO\(^{'}\) 1.57 eV.\(^{47}\) Both the hydroxyl radical has a higher affinity for an electron than MeO\(^{'}\) and MV\(^{2+}\), indicating that back electron transfer should be more favorable for \('\text{OH}\) than for MeO\(^{'}\). It is possible that the MV\(^{2+}\) and MeO\(^{'}\) are close enough and there is a stabilization of the MeO radical that MV radical is favorable under some conditions. Once again the 3.6 ps PT event would indicate a reorientation of the solvent to act as a proton acceptor. It has been stated that solvent-assisted proton transfer in a multisite configuration is difficult to interpret as concerted or stepwise with ET followed by a very rapid PT.\(^{3}\)

\[
\begin{align*}
\text{MV}^{2+} + \text{HOCH}_3 + h\nu & \rightarrow \text{MV}^{2+}\text{OCH}_3 \quad \text{(4.2)} \\
\text{MV}^{2+}\text{OCH}_3 & \rightarrow \text{MV}^{2+} + \text{HOCH}_3
\end{align*}
\]

The differences in the water and methanol models may indicate that there is a way to differentiate between the step-wise and concerted mechanisms.
4.4. Conclusions.

The investigation of a novel water oxidation photo-process using methyl viologen provides evidence for organic oxidation of water as well as a model for solvent active multisite concerted PCET. The quenching of excited-state methyl viologen by water explains the fast 3.1 ps excited-state lifetime. The evidence of electron transfer from water to an organic molecule could be of immense interest to researchers looking into solar to chemical conversion schemes.
4.5. References


(16) Peralta, J. P. *Femtosecond transient absorption studies of charge separation and ion pair dynamics in solution / by Jorge Peon Peralta; Ohio State University: Columbus, Ohio ;, 2001.


<table>
<thead>
<tr>
<th>Wavelength</th>
<th>( \tau_1 ) (fs)</th>
<th>( \tau_2 ) (ps)</th>
<th>IRF (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 nm</td>
<td>398 (0.02)</td>
<td>292 (0.01)</td>
<td></td>
</tr>
<tr>
<td>250 nm</td>
<td>324 (74)</td>
<td>7.95 (2.64)</td>
<td>95 (17)</td>
</tr>
<tr>
<td>343 nm</td>
<td>283 (98)</td>
<td></td>
<td>390 (77)</td>
</tr>
</tbody>
</table>

\(^a\)Uncertainties in parentheses are twice the estimated error. \(^b\)Probe wavelength for transient absorption. \(^c\)Emissive wavelength for fluorescence upconversion study. All samples excited at 266 nm.
Table 4.2. MV in Water Best-fit Lifetimes\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ps)</th>
<th>IRF (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 nm\textsuperscript{b}</td>
<td>3.16 (0.18)</td>
<td>382 (34)</td>
</tr>
<tr>
<td>250 nm\textsuperscript{b}</td>
<td>3.5 (0.12)</td>
<td>117 (10)</td>
</tr>
<tr>
<td>343 nm\textsuperscript{c}</td>
<td>3.21 (0.2)</td>
<td>500 (44)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Uncertainties in parentheses are twice the estimated error. \textsuperscript{b}Probe wavelength for transient absorption. \textsuperscript{c}Emissive wavelength for fluorescence upconversion study. All samples excited at 266 nm.
Table 4.3 Best-fit lifetimes (ns) for MV$^{2+}$ in increasing concentrations of nitric acid

<table>
<thead>
<tr>
<th>Concentration Nitric Acid (M)</th>
<th>$\tau_2$ (ns)</th>
<th>$1/\tau$ (ps$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>0.57</td>
<td>0.001759</td>
</tr>
<tr>
<td>0.285</td>
<td>1.13</td>
<td>0.00088</td>
</tr>
<tr>
<td>0.1425</td>
<td>3.07</td>
<td>0.000326</td>
</tr>
<tr>
<td>0.07125</td>
<td>3.70</td>
<td>0.000271</td>
</tr>
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</table>
Table 4.4 Dissociated Proton Recombination Rates

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$k_{cr}$ (M$^{-1}$ s$^{-1}$) x10$^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-nitrophenol</td>
<td>4.2$^a$</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>3.6$^a$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5.1$^b$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>3.7$^b$</td>
</tr>
<tr>
<td>o-aminobenzoic acid</td>
<td>5.8$^b$</td>
</tr>
<tr>
<td>m-aminobenzoic acid</td>
<td>4.6$^b$</td>
</tr>
<tr>
<td>p-aminobenzoic acid</td>
<td>3.7$^b$</td>
</tr>
<tr>
<td>N-Dimethyl-o-aminobenzoic acid</td>
<td>2.5$^b$</td>
</tr>
<tr>
<td>MV$^{2+}$/H$_2$O</td>
<td>0.31$^c$</td>
</tr>
</tbody>
</table>

(a) Ref. 48  
(b) Ref. 30  
(c) This study
Figure 4.1. Ground-state absorption of MV in water (green) and water with 0.5 M NaOH added (black).
Figure 4.2. Transient spectra recorded 1 ns after photo exciting MV in water (black line with dots). Difference spectra of MV in water with 2.0 M NaOH added (red circles).
Figure 4.3. Decay traces for MV in methanol 266 nm excitation with 600 nm probe (black circles), 250 nm probe (blue triangles) and 343 nm emission (red square); with best fit lines.
Figure 4.4. Decay traces for MV in water 266 nm excitation with 600 nm probe (black circles), 250 nm probe (blue triangles) and 343 nm emission (red squares); with best fit lines.
Figure 4.5. Methyl viologen excited at 266 nm and probed at 250 nm in D$_2$O (black) and H$_2$O (blue) with best fit lines, the x-axis switches from linear to logarithmic at 30 ps.
Figure 4.6. Methyl viologen in water excited at 266 nm and probed at 290 nm (red) and 250 nm (blue) with best fit lines, the x-axis switches from linear to logarithmic at 15 ps.
Figure 4.7. Transient signal of methyl viologen excited at 266 nm and probed at 290 nm acquired with a nanosecond flash photolysis system, with best fit line.
Figure 4.8. Kinetic decays of MV at 250 nm in increasing nitric acid concentration 0.01M (red) 0.1425M (blue) 0.57M (black)
Figure 4.9. Linear fit to graph of 1/lifetime of the acid quenching vs. concentration of nitric acid (slope = $3.7 \times 10^9$ M$^{-1}$s$^{-1}$)
Figure 4.10. IR spectrum of methyl viologen in D$_2$O.
Figure 4.11. Transient fsIR data for 1700 cm\(^{-1}\) to 1580 cm\(^{-1}\) of methyl viologen in D2O. Note the continuing generation of negative signal where there was no original MV IR absorption indicating an artifact effect from the BaF\(_2\) windows.
Figure 4.12. Transient IR decays at the listed wavenumber. This also indicates the negative signal at long time that is evident at all wavenumbers.
Figure 4.13. Decay associated spectra generated from fs time-resolved transient IR of MV in D$_2$O.
Figure 4.14. Absorption max of MV/anion CT band vs. photoelectron emission threshold energy. Absorption max for all ions except for OH⁻ from ¹⁹. Photoelectron emission threshold values from Ref 37.
CHAPTER 5

Spectroscopy of Methyl Viologen Entrapped Within Nanometer Sized Colloidal Zeolite Y Particles.

5.1. Introduction

There is immense interest in the study of the unique internal environment of zeolites. These naturally occurring aluminosilicates contain a 2-D or 3-D internal network of pathways that can include cage-like areas that are ideal for the inclusion of materials. The voids in the internal structure of the zeolite can be used in a wide range of applications, including but not limited to, hosts for chemical reactions,\textsuperscript{1-3} hosts for photochemical and photophysical processes,\textsuperscript{4-7} and as a membrane to achieve long-lived charge separation.\textsuperscript{8,9} For this work the focus will be placed on the photophysics and photochemistry of zeolite Y entrapped molecules as well as the potential to form long-lived charge transfer states with molecules hosted inside of the zeolite framework. A key aspect to the nature of the zeolite is that each time that aluminum replaces a silicon atom in the framework a negative charge is produced and a charge balancing cation is required to keep the structure stable. In zeolite Y there are 8 cations per supercage, this leads to a highly charged environment within a compact space. This charged environment allows for the inclusion of positively charged molecules inside of the zeolite by simple ion exchange reactions.
Many researchers have attempted to use probe molecules to determine the physical and chemical properties of the interior of these zeolites.\textsuperscript{10} A particularly common approach has been to study charge transfer interactions between two molecules that are included together inside of the zeolite.\textsuperscript{4,11,12} There are also reports that zeolites themselves can play a role in charge transfer events, acting as either the electron donor,\textsuperscript{13,14} or in some cases the electron acceptor.\textsuperscript{15} Zeolites potentially acting as a charge transfer partner has drastic implications towards its ability to act as a suitable host for electron or charge transport.

Due to the limited size of the zeolite supercage there are a finite number of solvent molecules that can reside there. The limited solvent environment is of great interest towards the role of the incorporated solvent molecules on the lifetimes and mobility of the guest molecule.\textsuperscript{16} Beyond the interest of solvent molecules inside of the zeolite, there is great interest into the role of limited numbers of solvent molecules in many different types of confined molecular systems.\textsuperscript{17-19}

Commercially available zeolite particles generally have a diameter of a micron or larger making some spectroscopic techniques challenging. It is impossible to use traditional transmissive spectroscopy due to the light scattering from these large particles. Diffuse reflectance techniques must be used to study guest molecules in these larger zeolite particles. As portions of the probe pulse will travel different depths into the sample the time resolution of time-resolved is limited to a few picoseconds, affecting the ability to determine very fast dynamics.\textsuperscript{20} Recently the Douhal group has used fluorescence upconversion to monitor emission of the dye Sudan I, residing inside of the zeolite framework, on the femtosecond time scale.\textsuperscript{21} In these experiments, fluorescence
was collected off the front surface of the sample which leads to some temporal 
broadening caused by the emission from molecules deeper in the zeolite particle. Using 
zeolite Y particles that have a diameter of 250 nm or less we have been able to study sub 
picosecond dynamics of entrapped molecules. These smaller particle zeolites make it 
possible to use traditional transmission based spectroscopy, taking advantage of the sub- 
picosecond time resolution that can be readily achieved as first demonstrated by the Bein 
group.22

Methyl viologen (MV), which has been discussed in much greater detail in 
chapter 4, is a widely studied molecule due to its ability to act as an electron acceptor. 
MV has been shown to be an extremely effective oxidant in its first excited state, and is 
known to oxidize surrounding solvent molecules.23 MV is an attractive probe molecule to 
determine if there are any potential charge transfer interactions taking place inside of the 
zeolite particles. There have been many previous studies of viologens entrapped in 
zeolites and much of this work has been summarized by Clennan.24 Dutta and coworkers 
have proposed using methyl viologen as charge-relay molecules to deliver electrons 
across a zeolite membrane.25 This study delves into the interaction between excited-state 
methyl viologen, the surrounding solvent and the zeolite host. It will also address 
potential solvent dependence and the effect of interactions of limited numbers of solvent 
molecules on the photophysics of methyl viologen.

5.2. Results

5.2.1. Steady-State Spectroscopy

Following ion exchange of methyl viologen into the zeolite Y, a red shift is 
present in the ground-state absorption spectrum (Figures 5.1 and 5.2). The shift is largest
when the zeolite particles are bathed in a solvent. The shift is present for MV in both water and acetonitrile bathed zeolites. MV in neat water has a maximum absorption at 257 nm. When entrapped in zeolite that is completely immersed in water, this shifts to approximately 270 nm (Figure 5.1). The shift when the zeolite is bathed in acetonitrile is from 257 nm to 274 nm (Figure 5.2). A sample that was exposed to the air and packed in a pellet for a diffuse reflectance experiment shows an absorption max shift to 262 nm. The pellet was prepared as an arbitrary combination of MV loaded zeolite mixed thoroughly with barium sulfate. The pellet sample for diffuse reflectance is not immersed in water but still has absorbed water from the laboratory environment.

In water, the emission appears to shift from 349 nm (bulk) to 339 nm (bathed zeolite) in the first sets of data taken (Figure 5.3). In acetonitrile the shift is more drastic and the emission maximum shifts from 349 nm to 310 nm. There is a small shoulder to the red in the acetonitrile spectrum. The spectrum of methyl violagen in zeolite that has been dried at 80 °C overnight and then transferred into dried hexane under a nitrogen environment shows similar emission to that of methyl violagen in acetonitrile (Figure 5.4). Figure 5.5 shows the scattering effect from the zeolite that has not been loaded with methyl violagen (black curve), along with zeolite loaded with MV in both water (blue) and acetonitrile (red) with the curve for MV salt in neat acetonitrile. This experimental result shows a spectral shift in both water and acetonitrile samples.

5.2.2 Time-Resolved Spectroscopy

The dynamics of methyl violagen in solution has been thoroughly discussed in the previous chapter. Briefly, MV exhibits a 3.1 ps excited-state decay in water evident in both time-resolved emission and absorption studies. In acetonitrile both emission and
transient absorption lifetimes are ~1 ns. Ion exchanging MV into zeolite structures leads to additional decay components.

Transient absorption studies in water monitoring the excited-state lifetime of MV inside of zeolite, excited at 266 nm and probing at 600 nm, exhibits a biexponential decay (Figure 5.8, open circles). This decay is well fit with a 4.8 ± 2 ps component and a 38.3 ± 14 ps component (Table 5.1). The errors are large due to the noise resultant from the scattering effect of the zeolite particles. For studies in acetonitrile, the excited-state absorption decay (Figure 5.19) were also fit with two time constants of 39.8 ± 5 ps and 747 ± 290 ps (Table 4.2).

Rotational reorientation studies were done to determine the rotational dynamics of photoexcited MV are shown in Figure 5.10. Studies in acetonitrile are in purple and water are in blue; the open circles indicate samples in zeolite in solution and the solid circles samples free in solution. The rotational decay time of MV in acetonitrile is 20 ps and in water 10 ps. Neither zeolite loaded sample showed any decay out to 100 ps. The water samples are noisier due to the subtraction process to remove the solvated electron signal that is evident at 600 nm.26

Streak camera measurements were used to determine the emissive lifetimes of the MV-loaded zeolites (Figure 5.11). A benefit of the streak camera is the 1-cm path length sample cell; it is possible to get a high enough concentration to determine the emissive lifetime. In water the emissive lifetime was determined to be 37.9 ± 2 ps, with a small 214.5 ± 15 ps tail (Table 5.1). MV, as shown in chapter 4, in water exhibits a 3.2 ps emissive decay, which cannot be observed due to the streak camera 20 ps instrument response. The acetonitrile data can also be fit with two exponentials 120 ± 8 ps and 945 ±
28 ps (Table 5.2) In addition to dynamical information the streak camera can also provide spectral data that can be compared to the steady-state emission data. Emission maximum of MV in zeolite in water and acetonitrile is 347 nm (Figure 5.6). To test the calibration of the streak camera a comparison was made with MV in acetonitrile on a steady-state instrument, excited at 280 nm (1-mm slit) immediately before a study on the streak camera, excited with 5 µJ at 280 nm (Figure 5.7). The steady-state emission is subject to a large scatter signal that is evident from unloaded zeolite samples. This scatter is evident as a tail from the blue edge of the detection window (300 nm) to > 500 nm. The streak camera emission spectra are not subject to the same scatter as the steady-state spectra are due to the collection of emission at delay times not coincidence with the excitation pulse.

5.3. Discussion

5.3.1. Steady-State Shifts

The data shows that incorporation inside of the zeolite framework results in shifts to both the absorption and emission spectra of methyl viologen. What is not completely clear from the data is the absolute magnitude of these shifts as different samples show different results. Slight red shifts to the absorption spectra are observed. In Figures 5.1 and 5.2 the large scatter tails from the zeolite particles can be observed above 320 nm. This scatter gives a slightly larger red shift to the absorption than may actually be present. Figure 5.1 shows the absorption spectrum of MV in zeolite in a packed pellet with BaSO₄, using a diffuse reluctance technique. The zeolites in this sample should still be hydrated as they have been exposed to the humidity of the laboratory environment. The spectral shift has been scaled back from 270 nm to 262 nm. This implies that some of the red shift in the solvated zeolites may be artificial. Attempts were made to model the
scattering curve and to subtract it out (Figure 5.1 and 5.2). A basic background subtraction of the scatter of an unloaded zeolite does not work as not all batches of zeolites exhibit the same scatter curve. Instead a polynomial curve was calculated to best represent an average of a few samples scatter spectra. Subtraction of the model spectra slightly reduces the observed red shift (Figures 5.1 and 5.2).

Authors have reported large shifts to the absorption of MV in zeolites,\textsuperscript{14,27} yet these reports are in conflict with each other. All of the samples in the Alvaro et al. study are dehydrated and show a large shift of the absorption maximum of MV from 257 nm in solvent to \textasciitilde280 nm in zeolite.\textsuperscript{14} Park et al. have a figure that very closely resembles the Alvaro data but they indicate the shifts takes place in hydrated zeolites, and not in dehydrated samples.\textsuperscript{27} If the assumption is made that Park et al. have simply mislabeled their figures, the results are still at odds with the results presented in this study. Comparing what could be slightly different hydration levels between the solvated zeolites and the sample used in diffuse reflectance it is observed more hydrated zeolites lead to more red shifting. Preuss et al. have suggested the effect of coinorporated water or other solvent molecules should shield the effect of the zeolite on the guest molecules.\textsuperscript{28} This suggestion implies that if there was a shift to the MV absorption spectrum following ion exchange into the zeolite framework, it should be more likely in dehydrated zeolites.

The emission data presented here shows some significant disagreement from sample to sample and technique to technique. There are drastically differing results on the emission maxima of MV inside of the zeolite framework. Figure 5.3 highlights these differences. MV, in water and acetonitrile, shows a nice shaped band with a maximum at 350 nm. The MV in zeolite in water band is slightly shifted to the blue at 340 nm and the
MV in zeolite in acetonitrile band, five minutes after sample preparation, is near 345 nm. This data conflicted with earlier data that showed the emission maximum of MV in zeolite in acetonitrile to lie at 310 nm (Figure 5.4). After this discrepancy was noticed a second emission spectrum was taken for the sample that exhibited the 345 nm band. This second spectrum was taken approximately 3 hrs after the sample had been prepared and the emission had shifted to 310 nm (Figure 5.3). It was initially thought that there was a time required for acetonitrile molecules to move out the water molecules that were previously in the zeolite and the sample needed some time to come to equilibrium. This was supported by the data showing the emission maximum of MV in zeolite in dry hexane, where the MV in zeolite had been exhaustively dried and placed into the hexane under a nitrogen environment, showed a peak at 310 nm. It was suggested that this was showing the true interaction between MV and the zeolite with limited solvent molecules interacting, as hexane will not enter the zeolite framework. There is no literature support for this large blue-shifted emission for a molecule that is entrapped in a zeolite framework.

The conclusion that the blue shift was due to an electrostatic zeolite effect has been discounted by very recent streak camera results. The emission spectra at all delay points following photoexcitation resembles the spectra observed in Figure 5.6. This data indicates that there is no difference in the emission spectra between MV in zeolite in acetonitrile or water and MV in neat solution. Just to make sure there was not an equilibration time samples were made and an aliquot of the MV in zeolite in acetonitrile was tested on three separate days and all produce the same unshifted spectrum. This is evidence that there is no shift to the MV absorption and that the shifts observed in the
steady-state experiments are due to scattering effects. The conclusion is that the shift to 310 nm in hexane and acetonitrile is due to an agglomeration effect. The zeolites are in a less stable suspension in these solvents that in water. A sample in water that is well dispersed will stay suspended for days, in acetonitrile for a few minutes and in hexane they can be observed to precipitate out immediately by eye. There is one instance where the shift is observed in water (Figure 5.5). In that experiment the normal sonication process to make a good suspension was cut short in the hope that larger particles would be left in solution. Assuming that this is a viable test for the scattering, the nature of the 310 nm band seems to be explained. Going back to the sample in acetonitrile 5 minutes after sonication it seems there was good initial suspension but over time the particles found each other creating effectively bigger particles.

Time-resolved emission spectroscopy is a reasonable technique to examine the effects on the emission spectrum following entrapment inside of the zeolite. This study shows there is little to no effect of entrapment on the emission spectrum of MV. This is at odds with the previous result from Alvaro et al. that indicates a band at 420 nm along with the band at 350 nm.\textsuperscript{29} The extreme shift seen in Alvaro et al. is suggested to be the result of an impurity in their zeolite or a photoproduct. The results presented here indicate that there are very small to negligible spectral shifts for MV incorporated in solvated zeolites.

5.3.2. Time-Resolved Studies

The transient spectroscopy of methyl viologen in neat solution has been discussed in great detail in chapter 4. Briefly, Peon et al. have shown that the excited-state lifetime of MV exhibits a strong solvent dependence.\textsuperscript{23} MV in acetonitrile shows a 1 ns lifetime
when probed at 600 nm while MV in water is only 3.1 ps. The relaxation in acetonitrile is assigned primarily to the internal conversion to the ground state with a fraction of the population decaying radiatively. In water the assignment is to quenching via a proton coupled electron transfer reaction with a nearby solvent molecule.

Although it is difficult to reach the same concentrations of methyl viologen in an experimental sample cell when trapped in the zeolite framework (~0.2 mM) as in neat solution (0.5 mM.), substantial absorption signal from the methyl viologen can be observed. The MV in zeolite is in much higher microconcentrations inside of the zeolite particles, but the practical limit to amount of zeolite that can be in suspended in solution makes for a lower effective concentration of MV in solution. MV loading levels between 0.5 to 1.5 methyl viologens per supercage have been examined and yield identical results. As the 1.5 MV/supercage (~0.2 mM) samples have the highest signal they were used in all experiments. The signal-to-noise ratio is greater in the zeolite samples than in neat solution due to scattering off of the zeolite particles, but the problem is mostly eliminated through spectral (10 nm bandpass filters) and efficient spatial filtering when probing at wavelengths far from the excitation wavelength.

Ion exchanging MV into the zeolite framework leads to some changes to the dynamics. In transient absorption, a second decay component is observed along with a component that has a very similar lifetime to the bulk solvent. The second component is ~38 ps in both acetonitrile and water. For water the decay is fit to a 4.8 ± 2 ps and 38.3 ± 14 ps components. The 4.8 ps component equal within uncertainty to the 3.1ps decay in neat water. In acetonitrile that data can be fit with 39.8 ± 5 ps and 747 ± 290 ps components. The ~ 38 ps component is observed in both samples indicating that it is
unique to the zeolite environment. There are a few possible assignments for this decay. First, the 38 ps decay could be an indication of a back electron transfer event to the zeolite framework after the zeolite initially donated an electron to excited-state MV. This seems unlikely as 38 ps interaction with the zeolite should quench the 1 ns signal that is observed in the acetonitrile experiments. For this to be the case, two conditions must be satisfied; 1) the back electron transfer must be faster than the forward as there is no evidence for any radical formation and 2) for the water sample, the 3.1 ps water quenching pathway must be inaccessible for the molecules that are quenching in 38 ps. A second, and currently favored, possibility is a PCET event with water inside the zeolite framework. It is reasonable to assume that some water will be trapped inside of the zeolite even in the acetonitrile bathed samples. The explanation for the slowing down of the PCET event from 3.1 ps in neat solution to 38 ps in the zeolite environment is the constrained water environment takes much longer for the water network to reorganize for proton transfer event. Initial results from bleach recovery experiments provide support for this third option as there is a long-lived negative offset in both the acetonitrile and water samples at 280 nm (Figures 5.8 and 5.9). The sign of the offset signal changes from positive in neat solution to negative in the zeolite particles. It is suggested that the CT band formed between MV$^{2+}$ and OH$^-$ is shifted when formed inside of the zeolite framework.

The streak camera data for MV in zeolite in water supports the claim that the 38 ps decay is due to the relaxation of excited-state MV. For samples in zeolite in water a 37.9 ps emissive component is observed and assigned to excited-state MV. The 3.1 ps component is not observed as the instrument response of the streak camera is ~ 20 ps, but
a small (<15%) 215 ps component is observed. The assignment of this long-lived
compontent is still in doubt. One possibility is that it may result from MV that is in a
unique environment in the zeolite, and exists at very small concentrations (< 8%). This
small component could easily be lost in the transient absorption studies due to the
solvated electron subtraction process applied to transient absorption experiments in
water. The streak camera data for MV in zeolite in acetonitrile is not wholly consistent
with that of the transient absorption data. Once again two components are needed to fit
the data. The 945 ps compares very well with the known 1 ns emissive lifetime for MV in
acetonitrile. A faster component is also observed and is fit with a 120 ps time constant.
This lifetime does not match well with the 38 ps component that was observed in
multiple transient absorption experiments. The 120 ps component was also reproducible
in three streak camera studies, albeit on the same sample batch of MV loaded zeolites.
This zeolite sample batch was also used for the water samples that had a great match for
time-resolved emission and absorption decays. Samples for the transient absorption and
streak camera measurements were from different batches and samples were run at very
different times. Figure 5.11 conclusively shows there is no 38 ps decay in the time-
resolved emission in acetonitrile, yet it is unlikely that the bad acetonitrile is the culprit as
free MV in acetonitrile shows a ~1 ns decay on the streak camera. The 120 ps component
remains an enigma and more experiments need to be run to make a conclusive
assignment to the decay.

5.3.3. Comparison with Other Studies

This work shows that there is no indication of radical formation, following
photoexcitation, for MV inside of the zeolite framework. This result is at odds with many
published reports that indicate the formation of MV radical upon photoexcitation of zeolite-encapsulated MV.\textsuperscript{13,14,27} Most of these studies find that the radical is formed in dehydrated zeolites, yet Ranjit et al. show evidence for radical formation in room temperature hydrated zeolites using ESR.\textsuperscript{13} Peon et al. proposed a theory that determined excited-state MV can accept an electron from a donor with an ionization potential (IP) less than roughly 10.8.\textsuperscript{23} A study by Trifunac and coworkers have determined that the IP of the zeolite NaZSM-5 is estimated to be higher than 11.4 eV.\textsuperscript{30} No other reports of a zeolite IP were located, but it is expected that it will vary depending on chemical makeup and solvent conditions. This certainly does not confirm or deny the potential for the zeolite to donate an electron to excited-state MV. It is very possible that changing cations and Si/Al ratios could have a substantial effect on this process, as the number of positively charge counter ions will change. It is possible that flooding the zeolite cavity with solvent allows the viologen to bypass the CT with the zeolite that is inferred from the Alvaro study.\textsuperscript{14} ESR studies have shown that is possible to form MV radicals in hydrated zeolites, although these studies were performed at 77K.\textsuperscript{31} The ESR study shows that the hydrated zeolites have substantially less radical formation than the dehydrated zeolites.

Much of the work done on guest molecules in zeolites has focused on the dimer formation between two closely held guest molecules. These studies have shown results that range from a fast emission quenching, to a longer emission generation from the dimer, to extreme red-shifts in the dimer emission.\textsuperscript{33-36} Methyl viologen has only shown dimer formation in zeolite L,\textsuperscript{32} not zeolite Y which is used in this study. This along with the lack of shift to lower energy emission rules out the potential for dimer formation
being responsible for the 38 ps decay component. A further indication that there is no
dimer formation is the lack of loading level dependence on steady-state or time-resolved
experiments. Dimer equilibrium would be affected by the MV concentration.

5.4. Conclusions

This study has shown that it is possible to use transmissive transient
spectroscopies which retain inherent fast time resolution to look at the photoprocesses
that take place inside the microenvironment of a zeolite framework. The dynamical
processes that are taking place inside of the zeolite framework can be assigned to MV-
solvent interactions that are impacted by the limited solvent environment. These
interactions have not been conclusively assigned and further work needs to be done to
definitively narrow down the exact process of these interactions. The most likely
conclusion, based on the present knowledge, is the small water environment slowing
down of the known proton-coupled electron transfer event that takes place between
photoexcited MV and water. There appears to be little interaction between photoexcited
MV and the zeolite framework. This is a promising result as MV is used as the charge
relay system in the Dutta and coworkers proposed solar energy conversion architecture.25
5.5. References


Table 5.1. MV and MV/Zeolite in Water Best-fit Lifetimes

<table>
<thead>
<tr>
<th></th>
<th>λ (nm)</th>
<th>( \tau_1 ) (ps)</th>
<th>( \tau_2 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV</td>
<td>600(^b)</td>
<td>3.16 (0.18)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>343(^c)</td>
<td>3.21 (0.2)</td>
<td></td>
</tr>
<tr>
<td>MV/Z</td>
<td>600(^b)</td>
<td>4.8 (2.4)</td>
<td>38.3 (14.4)</td>
</tr>
<tr>
<td></td>
<td>350(^c)</td>
<td>37.9 (1.8)</td>
<td>214.5 (15.2)</td>
</tr>
</tbody>
</table>

\(^a\)Uncertainties in parentheses are twice the estimated error. \(^b\)Probe wavelength for transient absorption. \(^c\)Emissive wavelength for fluorescence study. All samples excited at 266 nm, except for MV/Z emission excited at 280 nm.
Table 5.2. MV and MV/Zeolite in Acetonitrile Best-fit Lifetimes

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV</td>
<td>600&lt;sup&gt;b&lt;/sup&gt;</td>
<td>817 (16)</td>
</tr>
<tr>
<td></td>
<td>350&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1000 (40)</td>
</tr>
<tr>
<td>MV/Z</td>
<td>600&lt;sup&gt;b&lt;/sup&gt;</td>
<td>39.8 (5.4)</td>
</tr>
<tr>
<td></td>
<td>350&lt;sup&gt;c&lt;/sup&gt;</td>
<td>120 (8.1)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Uncertainties in parentheses are twice the estimated error. <sup>b</sup>Probe wavelength for transient absorption. <sup>c</sup>Emissive wavelength for fluorescence study. All samples excited at 266 nm, except for MV/Z emission excited at 280 nm. <sup>d</sup>From Ref 20.
Figure 5.1. Comparison of methyl viologen ground-state absorption in water solutions. MV in neat water (solid blue), maximum at 257 nm. MV in zeolite Y in water (blue dashed) maximum 270 nm. MV in zeolite Y with the zeolite scatter subtracted off (black dash). MV in zeolite Y diffuse reflectance absorption (red dash) maximum 262 nm.
**Figure 5.2.** Absorption and emission spectra of methyl viologen in acetonitrile solutions. Absorption; MV in neat acetonitrile (solid purple), MV in zeolite Y in acetonitrile (dashed purple), zeolite scatter subtracted off (dashed black)
**Figure 5.3.** Emission of MV in neat solution and in suspended zeolite Y. MV in water (solid blue), in acetonitrile (solid purple), in zeolite in water (dashed green), in zeolite in acetonitrile immediately after adding zeolite to the solution (dashed burgundy), and in zeolite in acetonitrile after 3 hours (dashed red).
Figure 5.4. Emission spectra of MV. Black curves indicate acetonitrile solvent with dashes and dots indicating zeolite entrapment. Red curve is MV in zeolite in hexane and the blue curve indicates MV in zeolite in water.
Figure 5.5. Emission spectra indicating the scattering of the zeolite samples when compared to samples in neat solution.
**Figure 5.6.** Comparison of emission. MV in neat acetonitrile (black circles), MV in zeolite in acetonitrile (red line), and MV in zeolite in water (green line). The MV in zeolite emission spectra were taken at 5 ps following photoexcitation on a streak camera setup.
Figure 5.7. Comparison of methyl viologen emission spectra; steady state (black circles) and from a streak camera 10 ps following photo excitation (cyan).
Figure 5.8. Transient absorption decays of methyl viologen in water and in zeolite in water. MV in water probe 610 nm (solid blue circles), MV in zeolite in water probe 610 nm (open blue circles), and MV in zeolite in water probe 280 nm (open cyan circles) with best fit lines.
Figure 5.9. Transient absorption decays of methyl viologen in acetonitrile and in zeolite in water. MV in acetonitrile probe 610 nm (solid burgundy circles), MV in zeolite in acetonitrile probe 610 nm (open burgundy circles), and MV in zeolite in acetonitrile probe 280 nm (open red circles) with best fit lines.
Figure 5.10. Transient anisotropy decays of methyl viologen. Solid circles indicate neat solution samples, open circles are MV in zeolite. Blue indicates water samples and purple acetonitrile samples. Lines are best-fit.
Figure 5.11. Streak camera emission decay of methyl viologen in water (green) and acetonitrile (cyan). Emission monitored at 350 nm, with best-fit lines.
6.1. Experimental Conclusions

The work discussed in this dissertation investigates many charge transfer events that take place within the realm of solar energy conversion. These studies provide insight to the electron transfer reactions that take place at the molecular level the solar energy conversion architecture. This research has measured the rate of formation, rate of decay and location of the electron in the charge separated state of the charge-separated state of RuL\textsubscript{DQ}. RuL\textsubscript{DQ} is a photosensitizer molecule that allows the traditional light absorbing Ru(bpy)\textsubscript{3} core to be outside of a zeolite membrane with the charge accepting portion of the photosensitizer locked in the first layer of the zeolite membrane. Quaternization of the terminal ligand of RuL is the basis of formation of RuL\textsubscript{DQ}.\textsuperscript{1} Dutta and coworkers attempted to study the photophysics of RuL\textsubscript{DQ} to compare to the near microsecond lifetime of RuL, but were unable to resolve any kinetics on their nanosecond transient absorption setup.\textsuperscript{1} Using femtosecond broadband transient absorption it was possible to characterize the relatively fast dynamics that are evident in RuL\textsubscript{DQ} in neat acetonitrile. The quaternization of the L ligand leads to efficient formation of a charge-separated state in ~ 1 ps. The 1.4 ns lifetime of the charge-separated state is long enough for subsequent reactions to take place if the next charge accepter is in a proximal location. The electron
in the charge-separated state is delocalized across the double bond of the \( L_{DQ} \) ligand and can take advantage of the portion of the molecule inside of the zeolite membrane allowing for a charge hopping event to an adjacent internal methyl viologen.\(^1\)

The next portion of the solar energy conversion scheme to be studied was the effect of the highly polar zeolite on the internal methyl viologen. It was determined that the zeolite membrane plays a role in the deactivation of excited-state methyl viologen. The initial goal was to determine the effect of the zeolite on the one electron reduced methyl viologen, as this confirmation occurs after a CT event from the Ru\( L_{DQ} \) photosensitizer. Reports from Alvaro et al. indicated that upon photo excitation of zeolite entrapped methyl viologen a significant population of the MV radical would form.\(^2\) This study has refuted those results. What is evident here is that the excited-state decay pathway of methyl viologen is significantly affected by the surrounding zeolite inducing a longer (~30 ps) decay. The nature of this decay is still under investigation but is currently assigned to the quenching pathway that is observed for methyl viologen in water. The reason the decay has been slowed from 3.1 ps in water to ~30 ps in zeolite is due to the unique low water environment inside of the zeolite membrane.

The final portion of the research was the investigation to the aforementioned water quenching of excited-state methyl viologen. A report from Peon et al. in 2001 stated that excited-state methyl viologen was quenched in 3.1 ps in water.\(^3\) This excited-state lifetime did not fit a trend established by an ultrafast (400 fs) decay in an easily ionized (solvent) methanol, and a 1 ns decay in a solvent with a high ionization potential (acetonitrile). While the gas phase ionization potential of water is higher than that of acetonitrile a significantly faster decay was observed. No attempt was made to
characterize the decay pathway in the 2001 report, but a statement of a long-lived signal in the <300 nm range was made.\(^3\) Peon speculated an isomerization or reactive pathway in his 2001 dissertation.\(^4\) These hypotheses centered on reactions that primarily involved proton motions as a 5.1 ps decay was observed in deuterated water, compared to a 3.1 ps decay in water. Recent investigations have shown that many of these reactive pathways are not feasible. All of these would lead to major changes to the vibrational structure of the molecule as additions to or changes in the ring structure would take place. Transient infrared studies have shown that there are no long-lived changes to the vibrations and the ring mode at \(\sim 1640\) cm\(^{-1}\) following photoexcitation. This implies that the signal observed in the UV involved a ground-state methyl viologen. Experimental results conclude that the long-lived state is an ion pair between ground-state methyl viologen and hydroxide, and that the 3.1 ps excited-state quenching is due to a concerted proton-coupled electron transfer event with water as both the electron and proton donor. This low energy ionization of water by an organic molecule is particularly unique. The methyl viologen PCET results provide insight to both concerted and step-wise mechanisms, in water and methanol respectively.

All of these studies provide insight for future investigators as they attempt to expand on solar energy research that will inevitably continue to use ruthenium based photosensitizers and efficient electron acceptors like methyl viologen.

### 6.2. Future Directions

Many research projects seem to lead to more questions than answers. Unfortunately there is not time to investigate every avenue of thought that is opened up
along the way. This section will include a few possible future directions as well as some future experiments that could shed more light on processes discussed.

6.2.1. Ruthenium Photosensitizers

The conjugated bridge to the DQ portion of RuL_DQ is of particular interest. Many groups have attempted to extend the conjugated bridge between ruthenium based donor and acceptor by inserting benzyl rings between double and triple bonds.\textsuperscript{5-7} Although the systems are conjugated it seems that the rings can break the conjugation slightly; this is very evident when comparing RuL_DQ to a very similar molecule studied by Kim et al.\textsuperscript{5} Both molecules have a DQ acceptor but only RuL_DQ shows the extreme shift to the red in the ground-state absorption and the ultrafast CT event. As the charge separated state has been assigned to lie on the bridge to DQ it would be interesting to look at a molecule in which DQ and Ru were separated by multiple double bonds, or triple bonds, but with no phenylene rings on the bridge. It is probably that the bridge energy would be too much to overcome the CT state, but it would be of interest to determine if a true electron highway could be created.

6.2.2. Excited-State Quenching of Methyl Viologen by Water

At this point the decay mechanism of methyl viologen in water is well established. The future research directions would involve more detailed nanosecond studies on the ion pair. The two data points that show that the ion pair has a 1.68 ms lifetime were run in water where the exact pH was unknown. Careful determination of the initial pH should allow for the recombination rate to directly infer the yield of the ion pair. If the initial concentration of protons is known the quenching rate will determine the total proton concentration following photoexcitation. Using these two points the
concentration of protons created by the PCET event will also give the concentration of the ion pair. It would also be of interest to confirm, for completeness, that the recombination of D$^+$ with MV$^{2+/1}$OD$^-$ is slower than that of the proton analogue.

6.2.3. Excited-State Quenching of Methyl Viologen by Water in Zeolite

Potentially the most interesting direction of future research comes from the photoexcited methyl viologen reaction with water inside of the zeolite framework. Although it is quite difficult to do spectroscopy inside of these small zeolite particles it is by no means impossible. It would be interesting to attempt to follow the protons that are generated in the methyl viologen water photo reaction. The zeolite membrane is highly charged and could provide trapping points for the protons. Using the water splitting reaction as a probe it could be possible to accurately determine the nature of the water inside the zeolite as well as the methyl viologen binding to the zeolite. As in the neat water studies the yield of the ion pair inside of the zeolite is of interest.

6.3. Final Remarks

Using ultrafast spectroscopy the transient photophysics of three processes that are involved in one attempt at a solar energy conversion architecture have been studied. The results show that using transient spectroscopy, electron transfer events can be effectively observed. The results presented here lay the foundation for future investigators to go forward with more complex characterizations or to develop new architectures for solar to chemical energy conversion.
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