

shift, effect.^{120, 202-203} There is no consensus on which is correct. Under the conditions described herein, the absorption increases through the visible region and displays no clear peak out to 1100 nm. The lack of a maximum and the high extinction coefficient are inconsistent with assignment as a ligand field ($t_{2g} \rightarrow e_g^*$) transition, like that seen in Ti(III) compounds such as $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, $\lambda_{\text{max}} = 475 \text{ nm}$ and $\epsilon = 5 \text{ M}^{-1} \text{ cm}^{-1}$.²⁰⁶ This implies that the long wavelength TiO₂ absorption has some intervalence $\text{Ti}^{\text{IV/III}}$ character and/or results from electronic transitions that are not easily reconciled on a molecular level. All the unsolvated cations under study are small enough to intercalate into the (101) anatase TiO₂ lattice where they could inductively interact with Ti centers throughout the nanocrystallite.^{196, 199, 202, 207-210} Under more strongly reducing conditions, new absorption features appear that were clearly dependent on the nature of the cation present, Figure A4.4 in the Appendix. The spectra measured in a Li^+ electrolyte were consistent with the known spectrum of the fully intercalated $\text{Li}_{0.5}\text{TiO}_2$ phase.^{202, 211} Strong reduction in the presence of the other cations may also lead to intercalated phases, however this was not studied in as much detail as such conditions were found to irreversibly change the TiO₂ material as evidenced by significant hysteresis in absorption vs. applied potential scans.

Application of a sufficiently positive potential to a $\text{Ru}(\text{dtb})_2(\text{dcb})/\text{TiO}_2$ thin film resulted in absorption changes due to the oxidation of Ru(II) to Ru(III). The electrochemistry itself was non-Nernstian. The equilibrium potential where the concentrations of the two redox states were equal was taken as an estimate of the formal reduction potential. The $E^\circ(\text{Ru}^{\text{III/II}})$ values were about 50 mV more positive with the dicationic Mg^{2+} and Ca^{2+} relative to Na^+ and Li^+ , i.e. $E^\circ(\text{Ru}^{\text{III/II}}) = 1.50 \text{ V}$ vs. $E^\circ(\text{Ru}^{\text{III/II}}) = 1.45$, Figure A4.5 in the Appendix. More significant were the deviations from Nernstian behavior, where a factor of ten change in concentration required 80 mV for Li^+ and 103 mV for Ca^{2+} , Table 4.1. Previous studies of non-Nernstian redox chemistry of molecules anchored to TiO₂ concluded that the non-idealities resulted from surface electric fields.²¹²⁻²¹³ Since cation adsorption does significantly influence the electric field experienced by the sensitizer (see below) the results here are in agreement with this conclusion.

The spectro-electrochemical data were utilized to construct a density of states diagram using a previously described method^{105, 212, 214} for $\text{Ru}(\text{dtb})_2(\text{dcb})/\text{TiO}_2$ in the different electrolytes, Figure 4.7. The density of TiO₂ acceptor states was found to increase exponentially as the Fermi-level was raised toward the vacuum level, behavior that is consistent with many other reports.^{105, 173} The cation dependency is clearly seen at any potential of interest. For example at -0.5 V, a potential that corresponds with the excited state

reduction potential, the density increases in the order $\text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$, a trend that was clear at all potentials where a measureable concentration of $\text{TiO}_2(\text{e}^-)$ s were present. The chemical capacitance distributions for the $\text{Ru}^{\text{III/II}}$ redox chemistry are not Gaussian and reflect the non-Nernstian redox chemistry described above. The magnitudes of the chemical capacitances were proportional to the surface coverage and the different values given in Figure 4.7 were not significant and likely result from the unknown extinction coefficients of the surface anchored compounds. The reduction potential of the thermally equilibrated excited states, $E^0(\text{Ru}^{\text{III/II}*})$, were calculated through a thermochemical cycle and the distribution was assumed to be the same as the ground state.

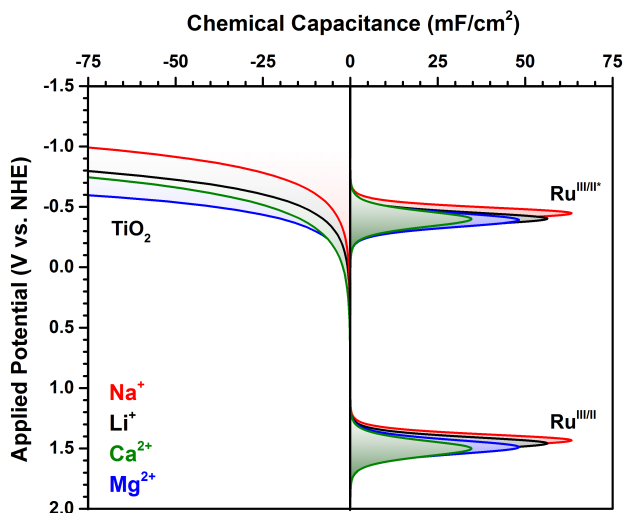


Figure 4.7. Density of acceptor states obtained from spectroelectrochemistry for sensitized TiO₂ compared with the ground- and excited-state $\text{Ru}^{\text{III/II}}$ reduction potentials in 100 mM metal perchlorate acetonitrile electrolytes.

The free energy stored in the thermally equilibrated excited state ΔG_{es} was abstracted from the steady state photoluminescence spectra. It was found that the presence of 100 mM of these cations in the electrolyte that surrounded a $\text{Ru}(\text{dtb})_2(\text{dcb})/\text{TiO}_2$ thin film, resulted in a bathochromic (red) shift of both the absorption and the photoluminescence (PL) spectra of magnitude $\text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$, Figure 4.2. The absorption data is discussed in more detail in the following section. The PL spectral shifts were accompanied by a dramatic quenching of PL intensity. The decrease in intensity is reasonably attributed to quenching by the TiO₂ acceptor states. Indeed, the interfacial density of states shown in Figure 4.6 indicates that excited state injection should be favorable for $\text{Ru}(\text{dtb})_2(\text{dcb})/\text{TiO}_2$ under all conditions. However, PL is an indirect probe of electron transfer and the radiative and non-radiative rate

constants for excited state relaxation may also be influenced by cation adsorption. Indeed, it was recently shown that the PL spectra of Ru(dtb)₂(dcb)/TiO₂ was sensitive to the excitation irradiance and blue shifted as the number of incident photons was increased, behavior attributed to a local electric field.¹⁹³ If the PL quenching were solely due to excited state injection *and* injection did not occur in neat acetonitrile, then the PL data would indicate injection yields of 0.95 for Na⁺ and essentially unity for the other cations. The values measured by comparative actinometry 100 ns after laser excitation were found to be unity for all the cations except Na⁺, indicating that excited state electron transfer to TiO₂ was indeed the main excited state relaxation pathway. The injection yields were consistent with previous studies that showed a correlation between injection yields and the charge-to-size ratio.¹³⁶ This previous work was done at only 2 mM concentrations where the present studies were performed under concentrations where the influence of the cation had reached its maximum value.

4.3.2 – *Electric Fields and Screening.*

Abstraction of the electric field strength from the absorption data was accomplished by an analysis briefly described in the Results Section and in previous publications.^{165, 176, 185, 193} In brief, the magnitude of the absorption shift that accompanied a change in the electric field experienced by the surface anchored Ru compounds, was quantified by both first-derivative and peak-to-peak analyses and found to give the same values within experimental error. The first-derivative spectral features indicated that the field was collinear with the dipole moment change that was assumed to be $\Delta\vec{\mu} = 4.75$ D under all conditions studied.^{167, 193} Previous studies have shown that orientation of the dipole moment vector change that accompanies light excitation parallel or antiparallel to the surface electric field results in absorption shifts that occur in opposite directions.¹⁶⁵ Very recent work has shown that electroabsorption can be used to quantify the distance between the molecular chromophore and the TiO₂ surface.²¹⁵ The data reported herein have enabled characterization of electric field changes that accompany injection in the presence of electrolytes where only the identity of the cation was altered.

The adsorption of ions to semiconductor surfaces is known and expected to generate local electric fields.^{110, 201, 216-220} Previous studies have focused mainly on Li⁺ cations that are most widely utilized in DSSCs. Adsorption isotherms provided an estimate of the room

temperature equilibrium constant, $K = 15 - 80 \text{ M}^{-1}$.¹⁷⁶ Here it was discovered that closely related spectral shifts were observed with Na⁺ and alkaline earth metal cations. The data support the widely held notion that prior to any surface treatments the sol-gel processed TiO₂ nanocrystallites present in the mesoporous TiO₂ thin films are negatively charged.²⁰¹ This negative charge is not attributed to injected electrons as there is no spectroscopic evidence for their presence and the spectral shifts were observed in air saturated solutions, conditions where the injected electrons are known to rapidly react. Instead the charge is attributed to specific functional groups, most likely deprotonated titanol groups, Figure 4.8. Whatever their chemical nature might be, the significant bathochromic (red) shift of the MLCT absorption that accompanied cation exposure reflects both the screening of this charge from the sensitizer *and* the field that is generated by the cation adsorption itself. The magnitude was sensitive to the identity of the cation and followed the trend Na⁺ < Li⁺ < Ca²⁺ < Mg²⁺. A key point though is that there is no *a priori* reason to expect that the surface charge due to cation adsorption is the same for each cation. This is important as the electric fields quantified after excited state injection or electrochemical reduction represent the *change in the electric field* from the initial condition of 100 mM cation concentration as is shown in Figure 4.8.

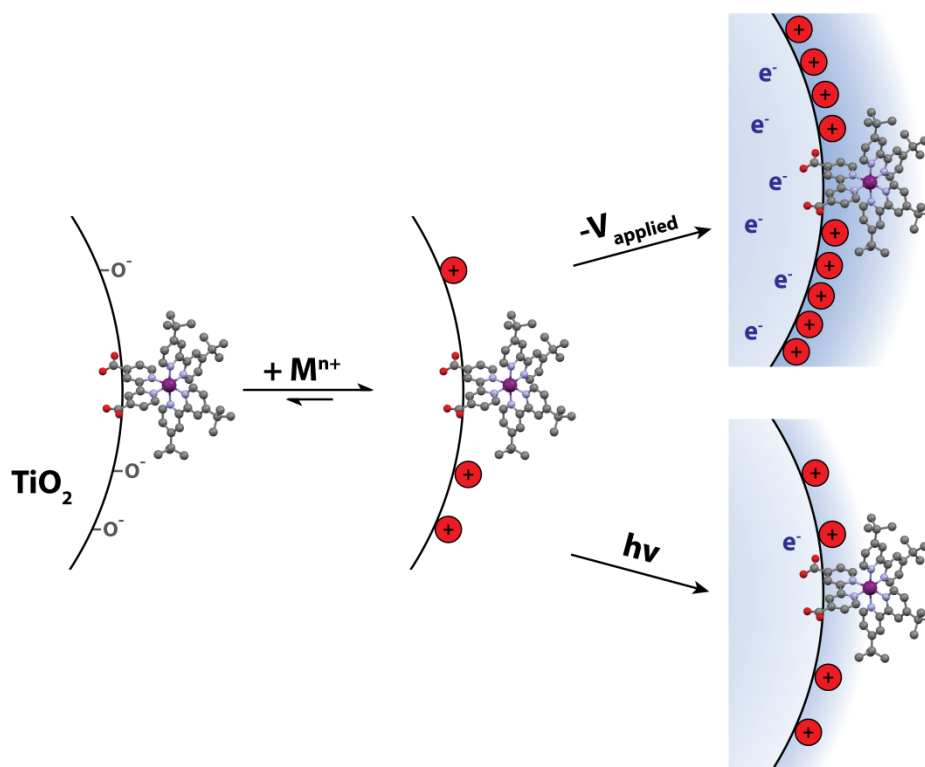


Figure 4.8. Schematic depiction of the light- and potentiostatically-induced generation of injected electrons.

Injection of electrons into a Ru(dtb)₂(dcb)/TiO₂ thin film results in a hypsochromic shift of the MLCT absorption that is opposite in sign to that measured with cation adsorption. Measurements as a function of applied potential revealed a strong cation dependence, Figure 4.3. The potential dependent data was recast as the number of TiO₂(e⁻)s per anatase nanocrystallite. While some experimental uncertainty is introduced by this conversion, the trends reported are unaffected and are important as the number of electrons present, and hence the field strength, at any applied potential were found to be cation dependent. For all four cations studied, the magnitude of the electric field first increased linearly with the number of TiO₂(e⁻)s and then more slowly with the number of TiO₂(e⁻)s, Figure 4.4. The data suggests that the first electrons injected into TiO₂ reside near the interface and subsequent electrons reside further away from the surface where they have a smaller influence on the surface anchored compounds.

About 20 TiO₂(e⁻)s are thought to reside in each nanocrystallite at the power point condition of optimized DSSCs,^{174, 221} so it is of interest to compare the electric fields reported by the sensitizer at this condition. The field strengths varied by about a factor of two and increased in the order: Na⁺ < Li⁺ < Mg²⁺ < Ca²⁺, Table 4.2. Since the number of TiO₂(e⁻)s was the same, the variations in field reflect the ability of the cations to screen the TiO₂(e⁻)s charge from the surface anchored Ru compound. The largest diameter cation, Ca²⁺, was the poorest at screening charge yet Na⁺ was more effective than the smaller Li⁺. Interestingly, Mg²⁺ was found to screen the field more effectively than did Li⁺, but only when the number of TiO₂(e⁻)s per nanoparticle exceeded about 70. Hence the dication Mg²⁺ was more effective at charge screening when the number of TiO₂(e⁻)s was large. As was described in the Introduction, it is not clear whether electric fields and charge screening influence the efficiency of DSSCs; however for recombination to negatively charged acceptors like I₃⁻, screening could be detrimental.^{201, 217}

Pulsed laser excitation enabled charge screening dynamics to be probed after excited state injection. Experimentally, it was found that this was most easily accomplished when iodide was present in the cell. Charge recombination to the oxidized iodide species was much slower than to the oxidized dye and the first derivative absorption signature associated with the Stark effect was much more easily observed spectroscopically after regeneration by iodide, Figure 4.5. The magnitudes of the field measured 2.5 μs after the laser excitation followed the trend Na⁺ < Ca²⁺ < Li⁺ < Mg²⁺, Table 2. However, the amplitudes of the Stark effect were time dependent for each cation making comparisons difficult. After pulsed laser

excitation and regeneration by iodide, there existed a large time window between 500 ns and 1 ms where the number of TiO₂(e⁻)s was constant yet the spectral feature associated with the electric field decreased rapidly. Burdziński and coworkers have suggested that these dynamics reflect electron trapping at grain boundaries.¹⁶⁶ The strong cation dependence reported here indicates that this is not the sole source of the observed dynamics, as there is no *a priori* reason to believe that trapping at grain boundaries would also be cation dependent. It was found that the monovalent cations screened charge much more rapidly than did the dications, $k_{Li^+, Na^+} = 5.0 \times 10^4 \text{ s}^{-1}$ and $k_{Mg^{2+}, Ca^{2+}} = 5.0 \times 10^2 \text{ s}^{-1}$ (see Figure 4.6), presumably because the small number of electrons injected into TiO₂ resulted in spatially isolated Ti(III) sites that were more easily screened by the monovalent cations. These rate constants indicate that charge screening of the field generated by excited state injection was not fully established before recombination to oxidized iodide occurred. Hence the use of an alternative redox mediator that underwent slower charge recombination with TiO₂(e⁻)s would be expected to enable more complete screening by these cations.

As previously discussed, it remains unclear whether the presence of electric fields and charge screening are pertinent to the working mechanism and efficiency of DSSCs. Nevertheless, the direct probe of triiodide species transiently formed right after photoinduced electron injection and subsequent dye regeneration successfully provided critical insights on the role of charge screening affecting the redox mediator mechanism. The presence of surface electric fields may generate electrostatic interaction with any charged specie in the field source vicinity. Although iodide is oxidized after charge transfer to oxidized dyes, it undergoes chemical reactions to produce triiodide (I₃⁻), which is an anionic product. The interaction between two negative charges results in electrostatic repulsion so that electrons and I₃⁻ are thought to repel each other. The last said is one important feature that contributes to the slow kinetics for charge recombination to the electrolyte. The presence of adsorbed cation on the TiO₂ surface was proven to screen the electric field from the photoinjected electrons. Such screening consequently clues to decrease the surface field strength and the electrostatic force with charged species in the electrolyte. Figure 4.9 links the observed cation screening efficiency with the possible electrostatic interaction with the electric field and the I₃⁻ species. *A priori*, the analysis of Figure 4.9 would provide a situation where electron recombination would be slower as the electrostatic repulsion is higher.

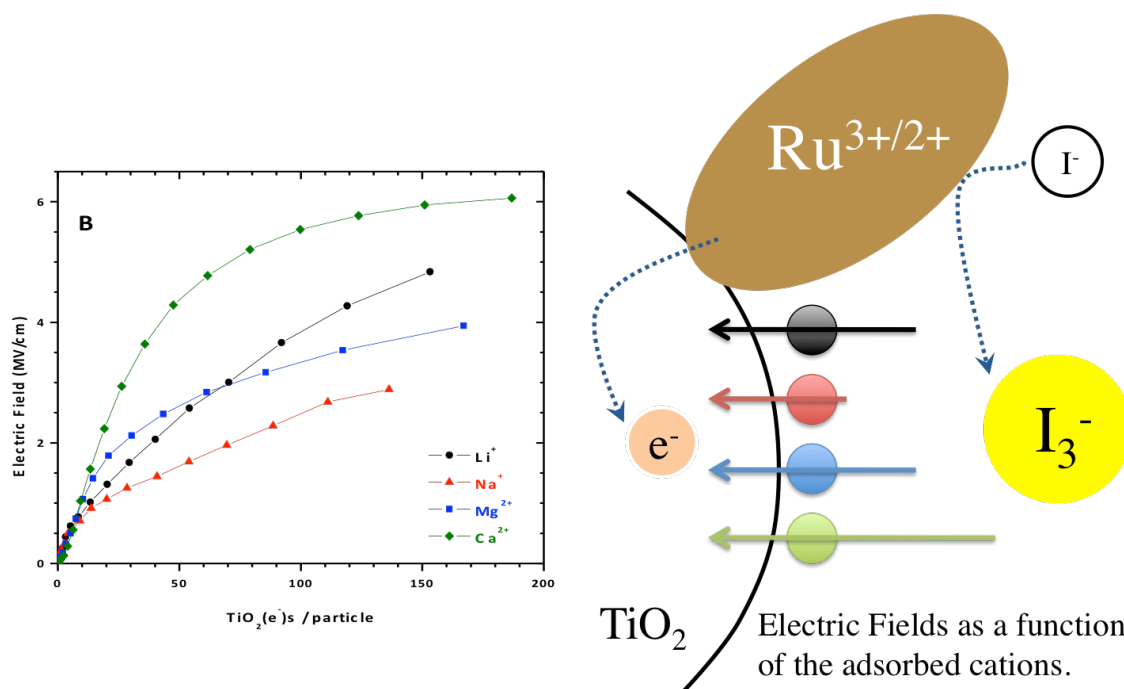


Figure 4.9. Scheme depicting the electrostatic interaction between the electric field of an photoinjected electron in TiO₂ and the anionic triiodide in the electrolyte solution. The colored arrows illustrate the electric field screening by the different cations adsorbed on the TiO₂ surface, following the results found in Figure 4.4B.

Shown in Figure 4.10 are single wavelength absorption changes monitored at 375 nm. This observation wavelength was chosen as the I₃⁻ anion absorbs strongly there and it represents an isosbestic point between I₂⁻ and I₃⁻.³⁵ As a result, the concentration of I₃⁻ can be uniquely probed at this wavelength. The data clearly show a marked electric field dependence for the unwanted TiO₂(e⁻) + I₃⁻ → charge recombination rate constant. This correlation provides compelling evidence that *the larger the electric field – the slower the unwanted charge recombination reaction with I₃⁻*. It is clear that the screening ability of the cations, showed in Figure 4.4B, governs the repeling force at which the I₃⁻ anion is subject to in the recombination process. The rate constants decrease in the presence of the field because the anionic charge of the I₃⁻ is repelled by the field.

The non-exponential kinetics were well described by the previously mentioned KWW function, in which the value of β was fixed to the 0.45 and the time constant allowed to float. An “average” lifetime was calculated as the first moment of the KWW function using Equation II-5, found in the Introduction of PART II. Data is given in Table 4.3. It is worth noting the remarkable discrepancy found between the Na⁺ and Ca²⁺ cases, where the fitting to the KWW function provided recombination time of 5 ms and 100 ms respectively. The

parallel analysis with the single wavelength kinetics for TiO₂(e⁻), Figure 4.10B, also showed the same trend, which was expected since electrons must recombine with triiodide.

Table 4.3. TiO₂(e⁻) + I₃⁻ → Charge Recombination with the Indicated Cations

Cation	Electric Field (MV/cm) ^a	τ_{KWW} (ms) ^b	$\langle\tau\rangle$ (ms)
Na ⁺	1.1	2.2	5.6
Li ⁺	1.3	4.8	12.5
Mg ²⁺	1.8	6.3	16.7
Ca ²⁺	2.2	50	100

^aElectric field change measured after the potentiostatic injection of approximately 20 TiO₂(e⁻) per nanoparticle. ^b β fixed to 0.45.

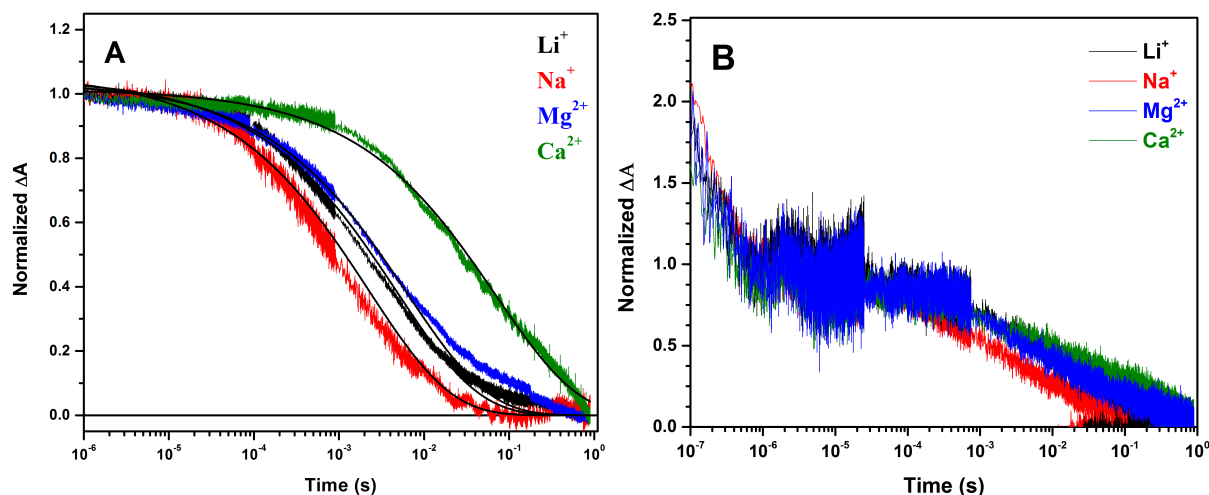


Figure 4.10. Single-wavelength transient absorption kinetic data of Ru(dtb)₂(dcb)/TiO₂ in acetonitrile electrolyte solutions containing 100 mM of the indicated perchlorate salts with 250 mM tetra-*n*-butylammonium iodide observed at: (A) 375 nm, absorption changes that correspond to TiO₂(e⁻) + I₃⁻ → charge recombination; (B) 750 nm, where TiO₂(e⁻) absorbs light. Overlaid on the data are fits to the KWW function with $\beta = 0.45$.

It should also be emphasized that changing the cations in the electrolyte of DSSCs influences many parameters including the transport of the injected electrons,²²²⁻²²⁴ dye regeneration,²⁰¹ and the energy levels of the TiO₂ acceptor states.^{127, 136, 199} Nevertheless, the implications of the results presented herein to DSSCs are clear and significant. Akin to enlarging the space-charge layer thickness in single semiconductor solar cells, increasing the Debye length for charge screening supports more spatially separated and longer-lived anionic I₃⁻ acceptor. Hence screening of the electric field by these alkali and alkaline earth cations in the electrolyte is detrimental to the solar conversion efficiency. Interestingly, complete

screening of the electric field should instead be beneficial for the caionic CO(II/II) redox mediators, i.e. [Co(bpy)₃]^{3+/2+}, employed in champion DSSCs.¹

4.4. CONCLUSION

Local electric fields are generated when electrons are injected into TiO₂ nanocrystallites interconnected in the mesoporous thin films commonly used in dye-sensitized solar cells. The MLCT absorption of Ru(dtb)₂(dcb)²⁺ compounds anchored to the TiO₂ surface were found to be sensitive probes of these electric fields. Exposure of a Ru(dtb)₂(dcb)/TiO₂ thin film immersed in acetonitrile to cations resulted in bathochromic (red) shifts of the MLCT absorption that followed the trend Na⁺ < Li⁺ < Ca²⁺ < Mg²⁺. Injection of electrons into TiO₂, from a potentiostat or an excited state, resulted in hypsochromic (blue) shifts. Pulsed laser excitation enabled the kinetics for charge screening at the interface to be quantified. On average, screening was about 100 times faster for the alkali cations relative to the alkaline earths. This behavior was attributed to excited state injection yielding localized Ti(III) states that were more easily screened by ions with a single positive charge. Finally, it was found that charge screening was undoubtedly relevant on conversion efficiencies with anionic redox mediators like I⁻/I₃⁻, due to electrostatic interaction between I₃⁻ and the surface electric fields from the photoinduced injected electrons.

4.5. APPENDIX

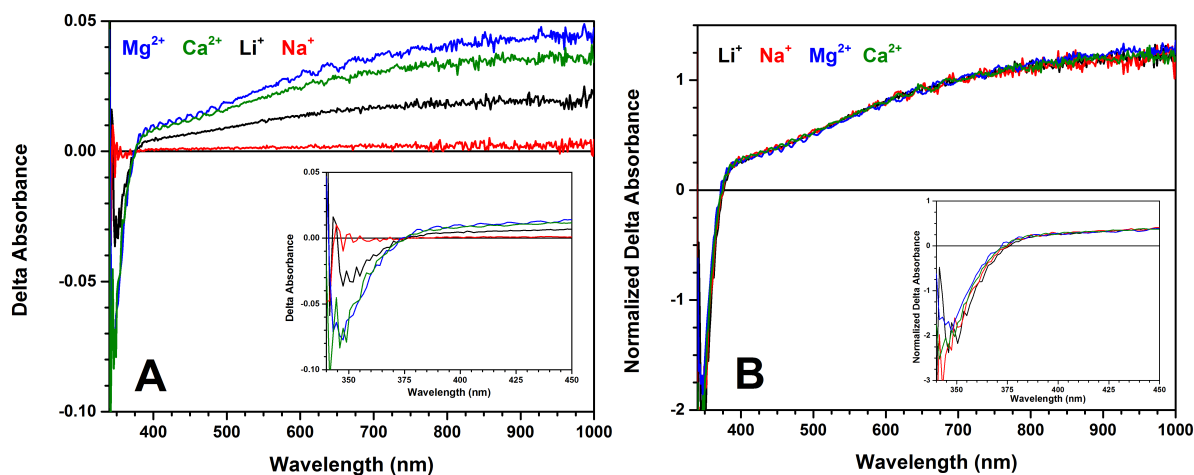


Figure A4.1. Difference spectra of un-sensitized TiO₂ thin films in 100 mM metal perchlorate acetonitrile solutions. (A) Spectra obtained with an applied bias of -400 mV vs. NHE. (B) Normalized spectra obtained at either -500 mV (Li⁺, Mg²⁺, and Ca²⁺) or -800 mV (Na⁺). The insets show close-ups of the 340 – 450 nm regions of the spectra.

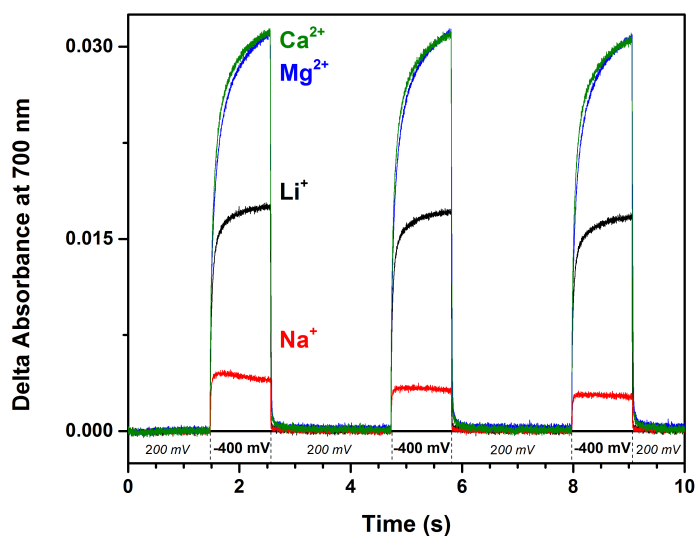


Figure A4.2. Representative spectroelectrochemical charge extraction data for un-sensitized TiO₂ in 100 mM metal perchlorate electrolytes. The change in absorbance at 700 nm was monitored with applied potentials of 200 and -400 mV vs. NHE.

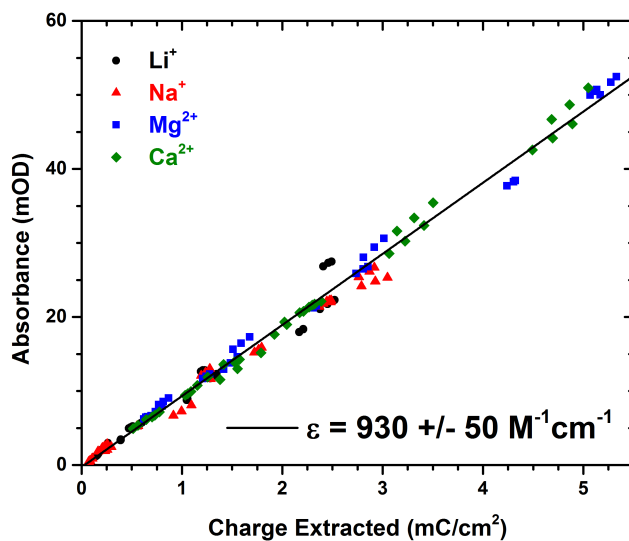


Figure A4.3. Absorbance as a function of the charge extracted from un-sensitized TiO₂ thin films immersed in 100 mM metal perchlorate acetonitrile solutions. The black line indicates the best fit to the data which yields a molar extinction coefficient of $930 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$.

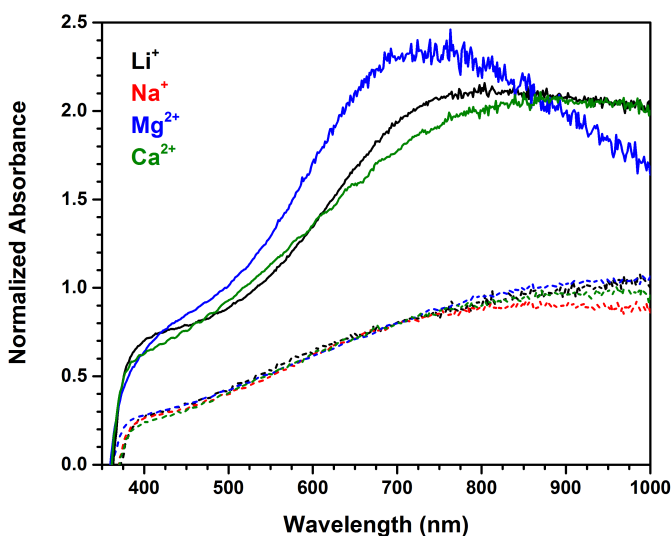


Figure A4.4. Absorbance spectra of un-sensitized TiO₂ thin films immersed in 100 mM metal perchlorate acetonitrile solutions with relatively small negative applied bias, $> -1.2\text{V}$, (dashed lines) and under strongly reducing conditions (solid lines).

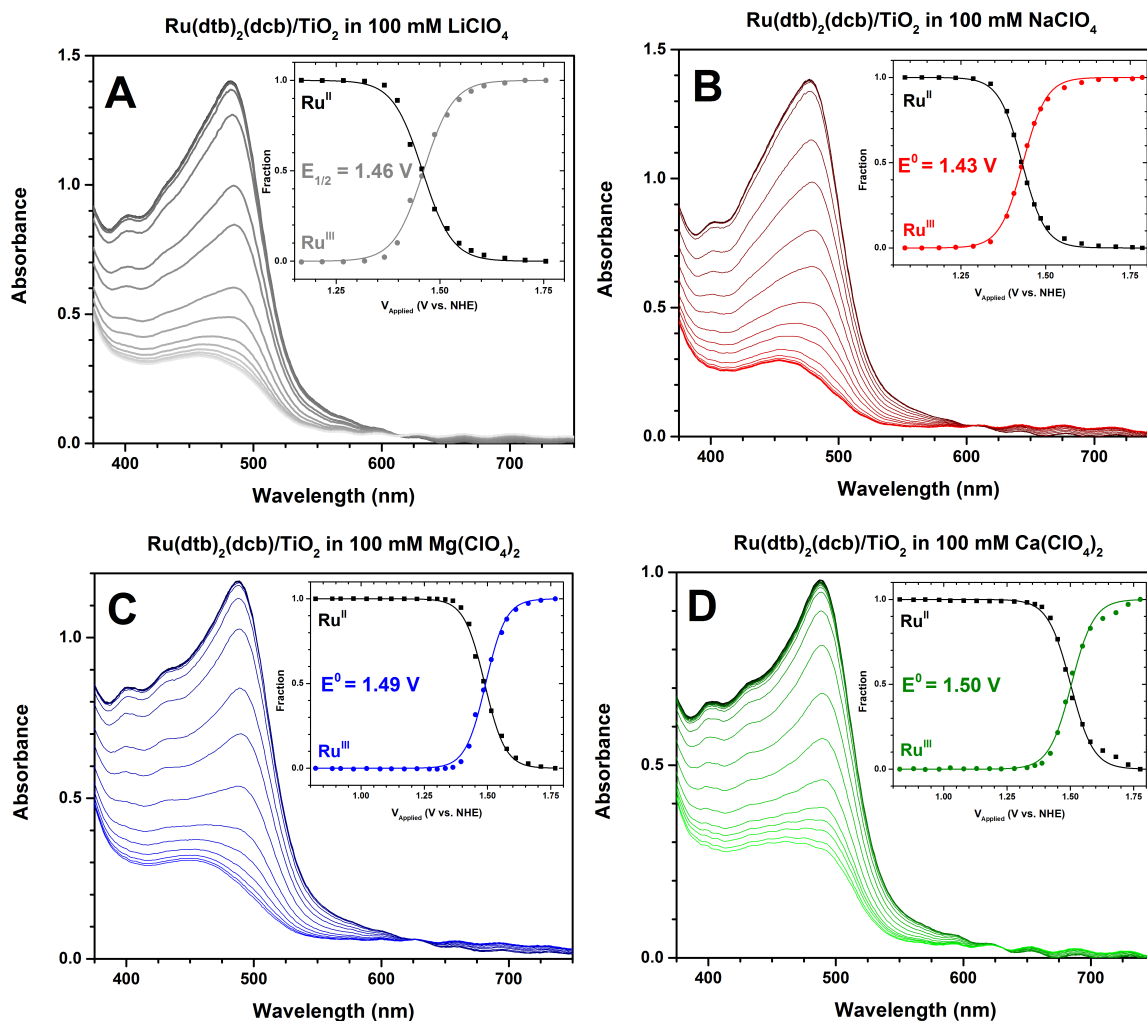


Figure A4.5. Spectroelectrochemical absorbance spectra of Ru(dtb)₂(dcb)/TiO₂ oxidation obtained in 100 mM electrolytes containing (A) Li⁺, (B) Na⁺, (C) Mg²⁺, or (D) Ca²⁺. Insets depict sigmoidal fits to the fraction of Ru^{II} (black squares) or Ru^{III} (colored circles) present where E_{1/2} is given by the equilibrium potential where the fraction of both Ru^{II} and Ru^{III} were equal.

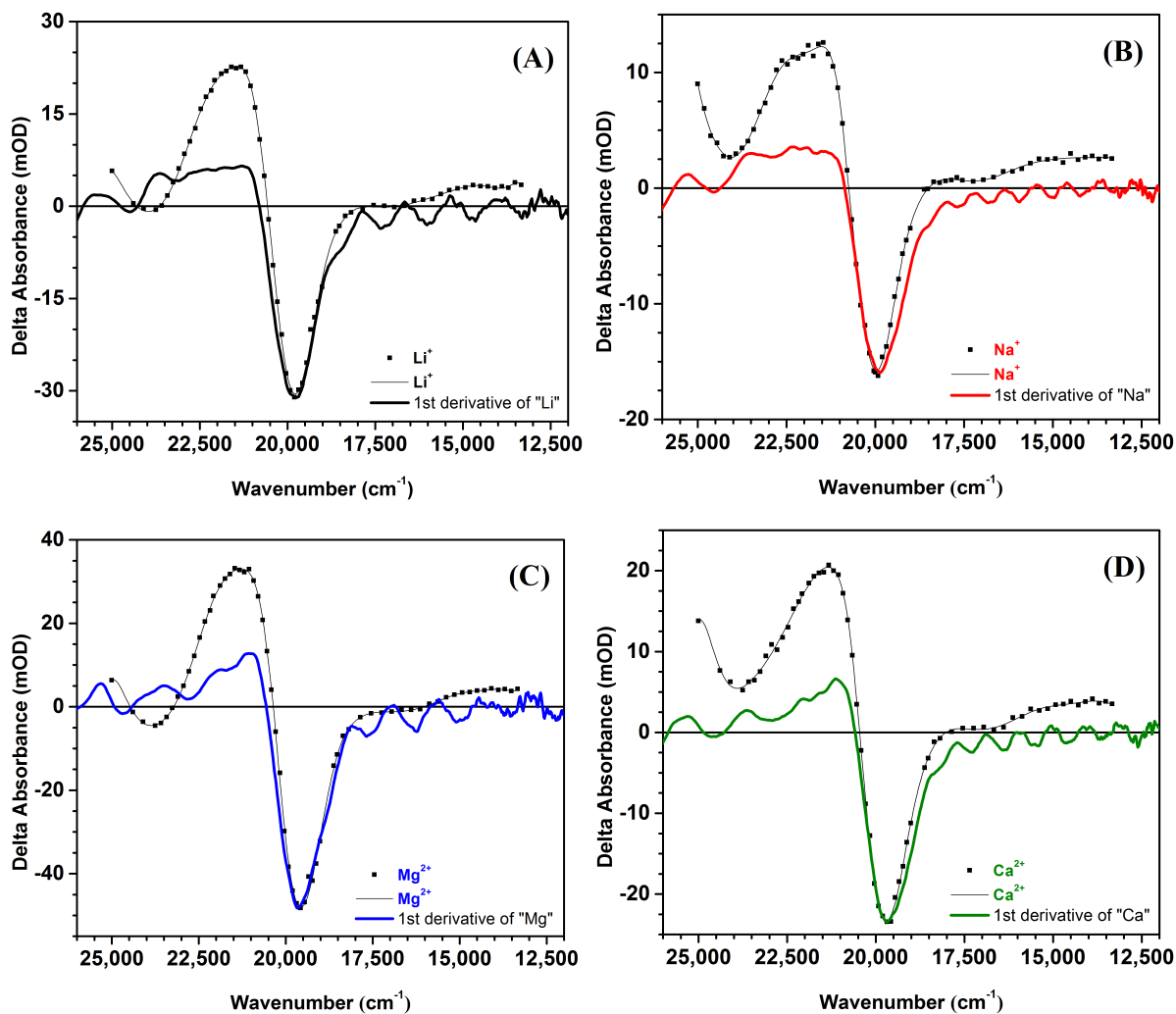


Figure A4.6. Transient absorption spectra of Ru(dtb)₂(dcb)/TiO₂ obtained 2.5 μ s after 532 nm laser excitation immersed in 0.25 M TBAI with 0.1 M of A) LiClO₄, B) NaClO₄, C) Mg(ClO₄)₂, and D) Ca(ClO₄)₂. Overlaid are the corresponding, scaled first-derivatives of the ground-state absorption spectra.

CHAPTER 5 – A Report on the Stark Effect Time Evolution on Ru(NH₃)₅(eina) Anchored to TiO₂ nanoparticles.

5.1. INTRODUCTION

Among the needs of society in a near future, a new source of renewable energy has taken his place on the top. The most direct solution to overcome the world 17 TW²²⁵⁻²²⁶ of energy needs was found by the scientific community to be the abundance of solar photons incident upon the Earth, by the Sun. Since the physicist Edmond Becquerel, perceived that the Sun energy could be harvested by the well know photoelectric effect²²⁷ a lot of effort have been given trying to optimize the light harvesting when the cell's efficiency. Today, silicon is the most commonly used semiconductor material for solar energy harvesting in photovoltaics, reaching efficiencies up to 20%.²²⁸ The inexhaustible researches in solar cells brought, in 1988, what is called to be the third generation solar cells, the dye sensitized solar cell (DSSC).¹⁷⁰ O'Regan and Grätzel introduced a new frontier in sun light harvesting. They developed the clever idea of utilizing mesoporous thin film of nanocrystalline TiO₂ with absorbing light dyes in photoelectrochemical cells.¹⁷⁰ The revolutionary idea turned created whole new fields of science base on energy conversion with nanometer-sized semiconductor materials. The increasing interest of research in this field turned out to be a strong motivation for understanding the mechanistic events of such devices, aiming to optimize the efficiency of such operational solar cells. Intense effort has been dedicated to better understand the properties of the semiconductors.^{116, 229-232} electrons and hole transfer processes^{35, 37, 39, 233} and photoinduced interfacial reactions.^{116, 145, 234} Moreover, the development of new redox mediators and better semiconductors as well as the molecular engineering are emerging as support researches for more efficient DSSC's.

Although a lot has been done for the systematic understand of the DSSC's, there still exists some very lacking information on effects that might arise right after photodriven electron injection into TiO₂. For instance, any charged particle carries an intrinsic electric

field and when placed at the interface, or inside of a TiO₂ nanoparticle, it may affect molecules and ions in the near environment. In the case of dye-sensitized solar cells (DSSCs), it has generally been assumed that any electric field that might be present under illumination would be completely screened from the surface anchored dye molecules by the large dielectric constant of TiO₂, $\epsilon_r \sim 86$,²³⁵⁻²³⁸ and the high permittivity of acetonitrile, $\epsilon_r = 37$.¹⁷⁵ In 2010 two groups have proven that the assumption of effective charge/electric field screening at sensitized TiO₂ interfaces was incorrect, when they reported that electrons injected into TiO₂ had a profound influence on the absorption spectrum of dye molecules anchored to the surface.^{176, 239} The absorption changes i found to be unidirectional due to the fixed orientation of the molecular dipole moment relative to the TiO₂ surface, but very similar to those previously reported in traditional Stark spectroscopy measurements.^{167-168, 177-178}

More recently O'Donnel *et. al.* reported that the presence of cations in the electrolyte solution can screen electric fields emanating from the TiO₂ surface and that this behavior is strongly dependent on the nature of the cation.¹²⁷ Although it remains unclear whether this electric field or charge screening is relevant to power conversion in DSSCs, it may have a deleterious influence on energy conversion efficiencies with anionic redox mediators like I⁻/I₃⁻. The later information can also be found in the end of the discussion of Chapter 4. In the past four years, the Stark effect in DSSCs have revealed critical information and conclusions on the working mechanism of such solar cells. In this work is proposed a new and different analysis of the Stark effect signature and whether it could reveal additional information about screening dynamics, dye molecule orientation, charge recombination, motion of electrons into TiO₂, among others.

This work studies a ruthenium(II) compound with a single monodentate pyridine ligand that when photoexcited injects one electron into TiO₂ which generates the surface electric field. The field then induces change in the ruthenium compound that resembles the 1st derivative of the ground state absorption spectrum. Such changes were monitored via transient absorption experiments that latter could be deconvoluted into two separated contributions: 1) the charge separated state (CSS) and 2) the Stark effect signature. Systematic analysis of both transient species revealed critical information regarding charge carriers motion inside the TiO₂ nanoparticles. It was found that after photoinduced injection, electrons could potentially be located in the semiconductor bulk which would strongly screen the charge electric field from the surface anchored molecules. But after a sequence of multi-trapping and detrapping events it could finally reach surface states in the TiO₂ that are less effective in screening the charges. It was found that the whole dynamics last on average 30 ns, which was abstracted

from the time evolution of the Stark effect signal. The calculated value were found to be in good agreement with transient photoconductive experiments performed by other groups.²³¹

Although the Stark effect has proven to be an important effect to be investigated, more systematically works reporting its time evolution are still very lacking and could provide vital information for the DSSC community.

5.2. EXPERIMENTAL METHODS

5.2.1 – Materials and Preparations

Materials. The following reagents and substrates were used as received from the indicated commercial suppliers: acetonitrile (CH₃CN; Burdick & Jackson, spectrophotometric grade); deionized water; tetra-*n*-butylammonium perchlorate (TBAClO₄; Aldrich, ≥99.0%); argon gas (Airgas, >99.998%); oxygen gas (Airgas, industrial grade); titanium(IV) isopropoxide (Sigma-Aldrich, 97%); fluorine-doped SnO₂-coated glass (FTO; Hartford Glass Co., Inc., 2.3 mm thick, 15Ω/□); and glass microscope slides (Fisher Scientific, 1mm thick). [Ru(NH₃)₅(eina)](PF₆)₂ was available from previous studies.²⁴⁰

Preparations. Transparent TiO₂ nanocrystallites (anatase, ~15 nm in diameter) were prepared by acid hydrolysis of Ti(*i*-OPr)₄ using a sol-gel method previously described in the literature.¹⁴³ The sols were cast as transparent mesoporous thin films by doctor blading onto glass microscope slides for spectroscopic measurements and transparent FTO conductive substrates for electrochemical measurements with the aid of transparent cellophane tape as a mask and spacer (~10 μm thick). The films were sintered at 450 °C for 30 minutes under an atmosphere of O₂ flow and either used immediately or stored in an oven for future use. Sensitization was achieved by immersing the thin films in acetonitrile sensitizer solutions (mM concentrations) for hours to days depending on the desired surface coverage. Unless otherwise noted, the thin films were sensitized to roughly maximum surface coverage, $\Gamma \sim 7 \times 10^{-8}$ mol/cm², which was determined using a modified Beer—Lambert law,¹⁸⁶

$$\text{Abs} = 1000 \times \Gamma \times \epsilon \quad (5.1)$$

where ϵ is the molar decadic extinction (absorption) coefficient (13,185 M⁻¹cm⁻¹ at 515 nm) that was assumed to have the same value when anchored to the surface. Sensitized films were soaked in neat acetonitrile for at least one hour prior to experimentation.

5.2.2 – Spectroscopy and Electrochemistry

UV-Visible Absorption. Steady-state UV-Visible absorption spectra were obtained on a Varian Cary 50 or an Agilent Cary 60 spectrophotometer at room temperature in 1.0 cm path length quartz cuvettes. Sensitized TiO₂ thin films were positioned at a 45° angle in cuvettes filled with the indicated acetonitrile solutions. The solutions were purged with argon gas for a minimum of 30 min prior to transient absorption and spectroelectrochemical studies.

Transient Absorption. Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described in the literature.⁸² Briefly, samples were excited by a Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 5-6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter) tuned to 532 nm with the appropriate nonlinear optics. The excitation fluence was measured by a thermopile power meter (Molelectron) and was typically 1-5 mJ/pulse so that the absorbed fluence was typically <1 mJ/pulse. A 150 W xenon arc lamp served as the probe beam and was aligned orthogonal to the laser excitation light. The lamp was pulsed with 100 V for detection at sub-100 microsecond time scales. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Appropriate glass filters were positioned between the probe lamp/sample and the sample/detection monochromator. Transient data was acquired with a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 350 MHz) with an overall instrument response time of ~10 ns. Typically, 30 laser pulses were averaged at each observation wavelength over the range 400 – 750 nm, at 3 or 5 nm intervals. Full spectra were generated by averaging 2-10 points on either side of the desired time value to reduce noise in the raw data. For single wavelength measurements, 90-180 laser pulses were typically averaged to achieve satisfactory signal-to-noise ratios. Relative excited-state electron injection yields were measured by comparative actinometry on the nanosecond time scale for samples in different metal cation solutions using lithium as the reference.^{187, 241}

Electrochemistry. A potentiostat (Bioanalytical Scientific Instruments, Inc. (BAS) model CV-50W or EC Epsilon electrochemical analyzer) was employed for electrochemical measurements in a standard three-electrode arrangement with a TiO₂ thin film working electrode, a Pt gauze counter electrode (BAS), and a non-aqueous silver reference electrode (BAS). The ferrocenium/ferrocene (Fc⁺⁰) half-wave potential was measured both before and after experiments in a 100 mM TBAClO₄/acetonitrile electrolyte that was used as an external standard to calibrate the reference electrode. All potentials are reported versus the normal hydrogen electrode (NHE) through the use of a conversion constant of -630 mV from NHE to Fc⁺⁰ in acetonitrile at 25 °C.¹⁸⁸

Spectroelectrochemistry was conducted via simultaneous application of an applied potential while monitoring the UV-Vis absorption spectra of TiO₂ thin-film electrodes in the indicated electrolytes. Each applied potential was held for 2-3 min, until the absorbance in the 700-900 nm region became invariant in time. Single-wavelength absorption features plotted as a function of the applied potential were proportional to the cumulative formation/loss of states; for the TiO₂(e⁻) absorption features, this was directly related to the cumulative TiO₂ density of acceptor states.¹⁸⁹

5.3. RESULTS AND DISCUSSION

5.3.1 – UV-Vis and Spectroelectrochemical Measurements.

The coordination compound [Ru(NH₃)₅(eina)](PF₆)₂, where eina is ethyl isonicotinate, was synthesized and attached to optically transparent, mesoporous thin films of nanocrystalline (anatase) TiO₂, abbreviated Ru(NH₃)₅(eina)/TiO₂. A metal-to-ligand charge transfer (MLCT) absorption band was observed for Ru(NH₃)₅(eina)/TiO₂ with a maximum at 515 nm, Figure 5.1. Under the conditions studied (room temperature and 77K photoluminescence experiments), the compound was non-emissive, both in solution and when attached to the TiO₂ surface, with a very fast excited state lifetime due to intense non-radiative pathways for decays from the excited state attributed to vibrational modes of the ruthenium-ammonia bonds. The excited state was considered to be on the sub-nanosecond

time scale because the experimental system to measure it could not resolve processes faster than 10 nanoseconds.

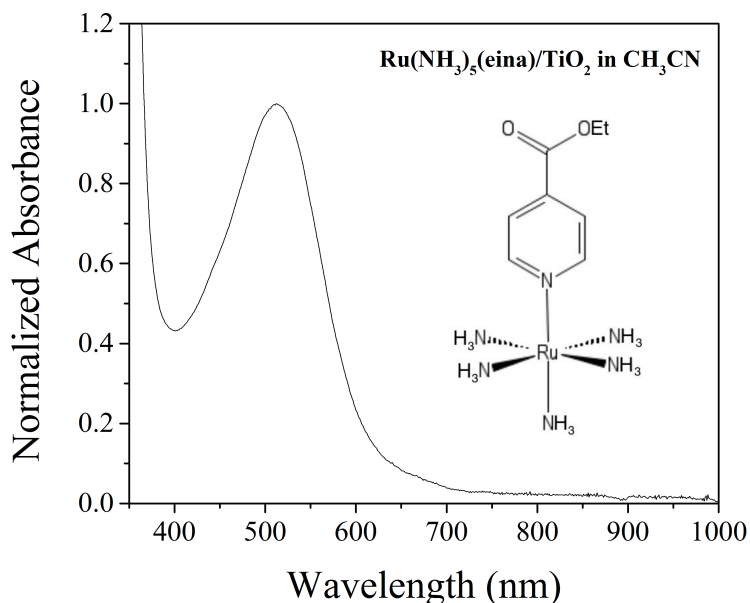


Figure 5.1. Steady-state UV-vis absorbance spectrum of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ in neat acetonitrile.

Spectroelectrochemical studies were performed on $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ with applied reverse (positive) bias which resulted in spectral changes consistent with the formation of Ru^{III} upon oxidation of Ru^{II} , Figure A5.1 in the Appendix. The reduction potential for $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$, $E^0(\text{Ru}^{\text{III/II}})$, was measured to be 570 mV vs. NHE and was obtained at the equilibrium potential ($E_{1/2}$) where the concentration of Ru^{III} and Ru^{II} were equal. The observed redox chemistry was non-Nernstian, where a factor of 10 change in concentration required 370 mV (non-ideality factor, $\alpha = 6.3$). Nonideal redox chemistry behavior of molecules anchored to TiO_2 is consistent with previous literature reports and may result from electric fields present at the TiO_2 interface.^{32, 39, 127}

Application of a forward (negative) bias resulted in reduction of TiO_2 , which was monitored by the characteristic broad absorption features from 400 to 1100 nm attributed to $\text{TiO}_2(\text{e}^-)$ s in the presence of 100 mM tetrabutylammonium perchlorate (TBAClO_4) supporting electrolyte in acetonitrile.^{127, 202} The MLCT absorption band red-shifted simultaneously with the appearance of spectral features related to $\text{TiO}_2(\text{e}^-)$ s, Figure 5.2A. The MLCT absorption peak shifted to lower energy by about 26 nm with an applied bias ranging from 150 to -1303 mV vs NHE. The difference spectra obtained at each applied potential, shown in Figure 5.2B, are consistent with previous studies that relate the 1st derivative spectral shape to the presence

of an external electric field which perturbs the energy levels of molecules anchored to surfaces, the so called Stark effect.^{127, 167, 169}

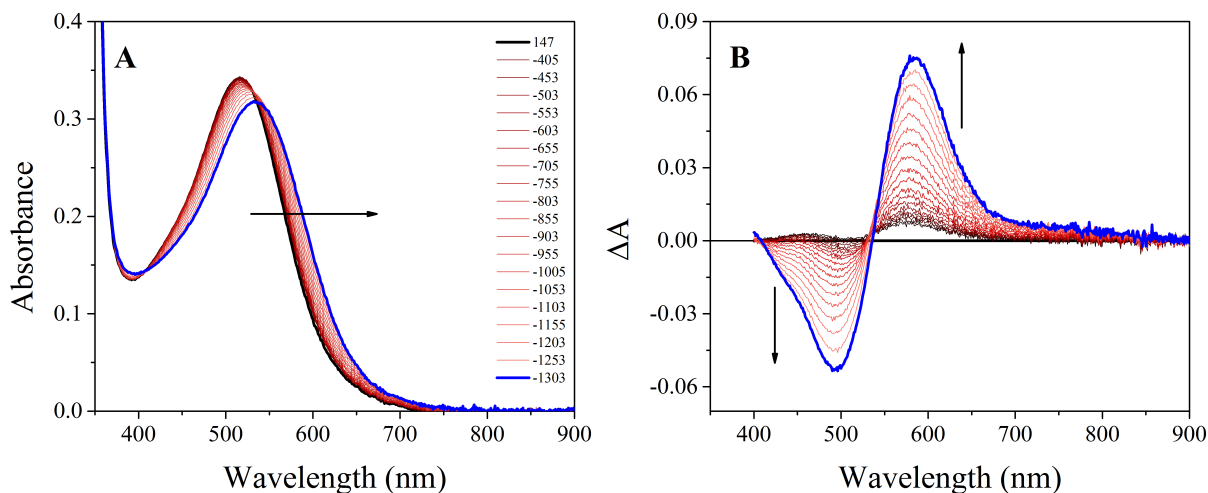


Figure 5.2. (A) Spectra of a potentiostatically controlled Ru(NH₃)₅(eina)/TiO₂ thin film in 100 mM TBAClO₄ acetonitrile solution corrected for the long-wavelength TiO₂(e⁻) absorption features. (B) The difference spectra for the data shown in A. The spectra in black were recorded at +150 mV while the spectra in blue indicate final, most negative potential of -1300 mV with the red spectra obtained at potentials in between the two extremes. The arrows indicate the direction of change with increasingly negative applied potential.

The magnitude of the electric field experienced by the sensitizers anchored to the TiO₂ surface was abstracted using both peak-to-peak and first derivative analysis methods and compared in Figure 5.3.^{127, 169, 176, 185, 239} Both methodologies are well described in previous studies.¹²⁷ Identical values for the electric field strength were obtained within experimental errors, using both methodologies, which is consistent with previous work.¹²⁷ While the first-derivative spectral features only indicate that the electric field was collinear with the dipole moment change of the compound, the direction of the shift indicates that the two quantities must have a parallel configuration. The change in dipole moment was assumed to be $|\Delta\vec{\mu}| = 4.8 D$, the value measured by Oh, Sano, and Boxer using conventional electroabsorption (Stark Spectroscopy) experiments for the structurally related compound Ru(NH₃)₅(pz), where pz is pyrazine.²⁴² The potential dependent electric field strength data was recast in terms of the number of TiO₂(e⁻) per anatase nanocrystallite, Figure 5.3B.

When approximately 10 electrons were present inside each TiO₂ nanoparticle, the calculated electric field was 1.06 mV/cm, which would result in a red-shift of 2.3 nm from the initial absorbance value of 515 nm. At a very negative applied potential (-1300 mV vs NHE)

corresponding to 160 electrons residing in each TiO₂ nanoparticle, the field experienced by the compounds on the surface is 7.70 mV/cm inducing a 17.0 nm red-shift. Although it is possible to estimate the number of TiO₂(e⁻)s, their spatial position and motion dynamics still remain unclear. Many works have been reported on the possible locations and dynamics for electrons into mesoporous TiO₂, mainly concerned about possible trapped states in the semiconductor bulk or near the semiconductor's surface as Ti³⁺ trapped states.^{116, 166, 180, 243}

In a previous study, O'Donnell *et al.* reported a cation dependence on the screening process of the electric field caused by the electrochemical accumulation of electrons into the anatase nanocrystallite.¹²⁷ The work proposed in this Chapter used a perchlorate salt containing TBA⁺ as the counter ion, which is much larger than the cations used by O'Donnell. Such that TBA⁺ is not expected to intercalate into the TiO₂ surface. Also, is believed that TBA⁺ cannot fully interact with the TiO₂ or the ruthenium dyes due its large size-charge ratio and the fact that the positive charge is “buried” underneath the bulky butyl chains. As a consequence, the weak interaction with the positive charge of TBA⁺ could decrease the drift velocity of electrons in the nanocrystallite bulk towards its surface, due the weak electric field played by the TBA⁺.

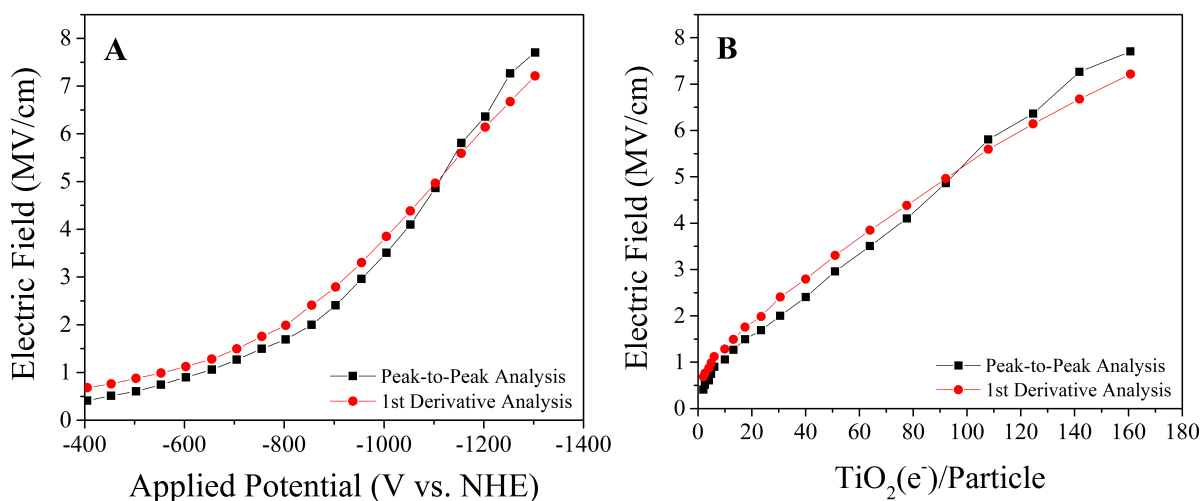


Figure 5.3. Electric field strength experienced by Ru(NH₃)₅(eina)/TiO₂ in 100 mM TBAClO₄ acetonitrile solution, calculated by two different methods: first-derivative (red) and peak-to-peak (black) as a function of (A) applied potential and (B) the number of TiO₂(e⁻)s on a per particle basis.

The spectroelectrochemical data for Ru(NH₃)₅(eina)/TiO₂ was utilized to construct a density of states diagram using a previously described method^{32, 105, 244}, Figure 5.4. The density of TiO₂ acceptor states was found to increase exponentially as the Fermi-level was raised toward the vacuum level.^{105, 245} Calculation of the excited state reduction potential,

$E^0(\text{Ru}^{\text{III/II}*})$, could not be accomplished because the compound was non-emissive, under the experimental conditions used (room temperature and 77K).

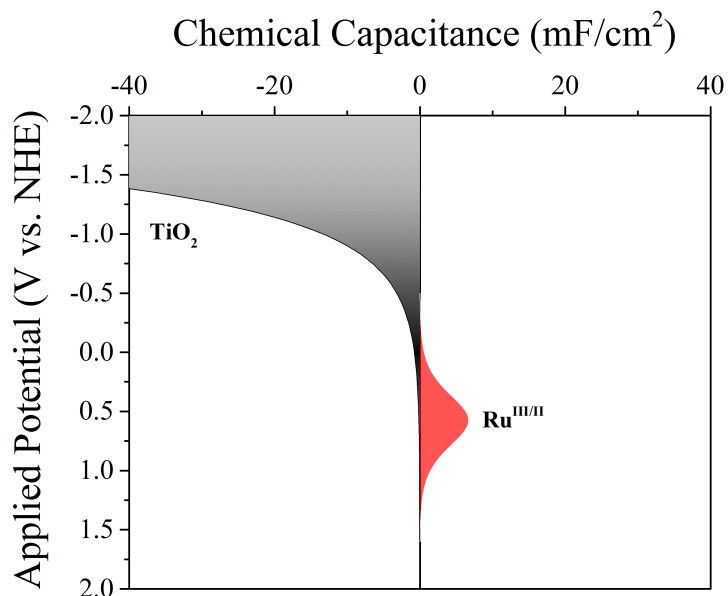


Figure 5.4. Density of states obtained from spectroelectrochemical measurements of Ru(NH₃)₅(eina)/TiO₂ sensitized thin films in 100 mM TBAClO₄ acetonitrile solution. The horizontal lines indicate values measured using cyclic voltammetry where the surface pH of the TiO₂ was adjusted prior to sensitization.²⁴⁰

5.3.2 – Transient Absorption and the DAS deconvolution.

Pulsed 532 nm laser excitation into the MLCT absorption band of Ru(NH₃)₅(eina)/TiO₂ thin films immersed in neat acetonitrile were obtained over a time range from 30 ns to 80 μ s after laser excitation. The initial transient absorption spectra, ~30 – 100 ns, were consistent with interfacial charge separated states comprised of spectral features from oxidized ruthenium compounds and electrons injected into TiO₂, Figure 5.5A. However, as time progresses, a second strongly pronounced spectral feature started to appear which was reminiscent of the first-derivative spectral shape observed for the Stark effect and was similar to the features observed in Figure 5.2. The transient absorption data shows the presence of two independent processes: 1) the photogenerated charge separated state and 2) the induced Stark effect generated by a photoinduced injected electron into the TiO₂.

When depicted as normalized spectra (normalized at the bleach), the transient absorption spectra exhibit a much more pronounced growth at 590 nm. This behavior could be easily understood by assuming the TA spectra was a sum of the two processes: 1) the

transient data resulted from the charge separated state, the bleach, which is faster, and 2) the Stark effect signature which has slower disappearance. If the bleach (faster kinetics) is chosen for normalization, any region where the kinetics is slower, it will become more pronounced, in this case, the growth region at around 590 nm, Figure 5.5B.

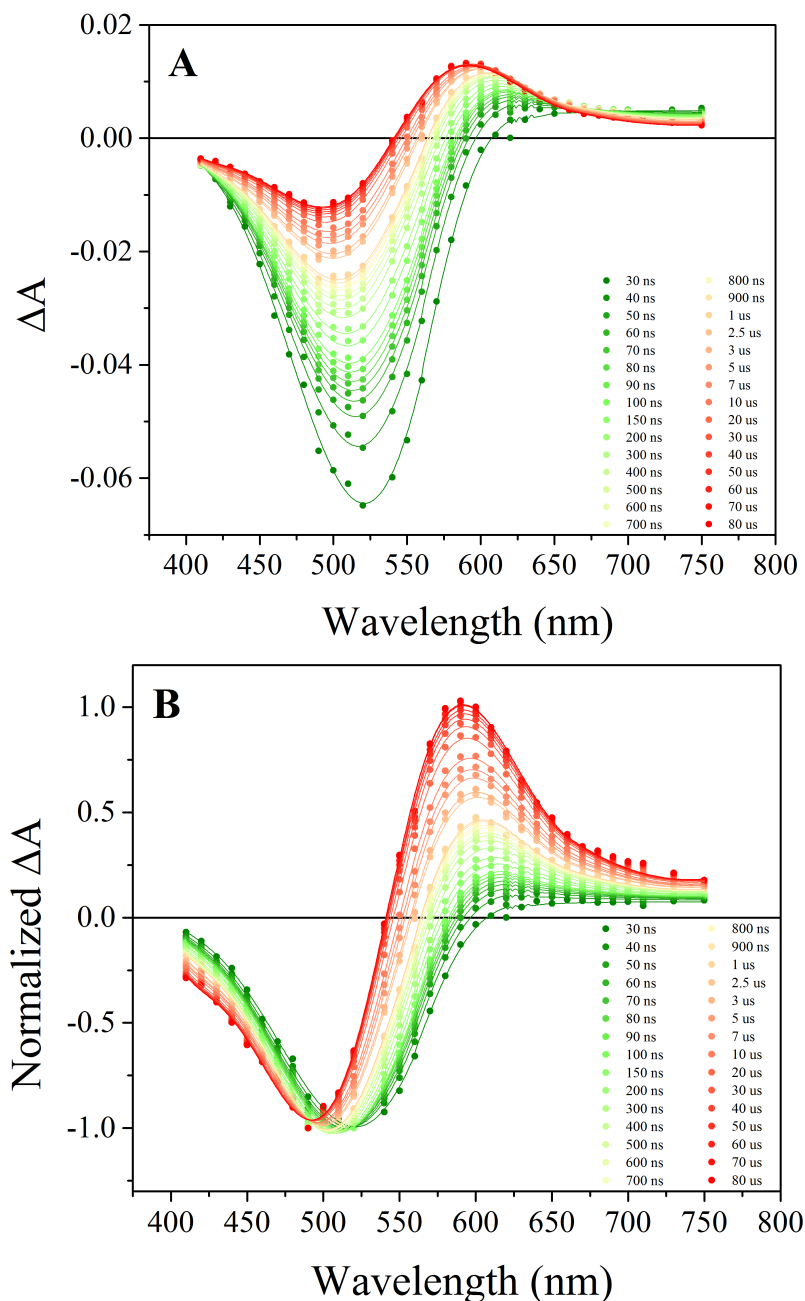


Figure 5.5. Transient absorption spectra obtained over a 30 ns – 80 μs time window after pulsed 532 nm excitation of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ in neat acetonitrile (A) and the normalized spectra (B). Figures (A) and (B) can also be found as function of the number of injected electrons in the Appendix, Figure A5.2 in the Appendix.

In order to better understand the obtained transient absorption data, the Decay Associated Spectra (DAS) analysis method was used to separate both processes into their individual and independent contributions.²⁴⁶⁻²⁴⁹ In brief, this method uses the concept that a specific time delayed transient absorption can be written as a sum of kinetics (the number of which depends on the number of processes involved) for each wavelength of the spectrum weighted by specific amplitudes. In other words, the DAS is the spectrum of the amplitudes associated with a specific kinetic component. Data are then analyzed assuming a sum of exponential components, and the decay associated spectra are the spectra of the pre-exponential factors. The series of decays are fit simultaneously where the lifetimes are held independent of wavelength, but the amplitudes are unrestricted, resulting in a set of lifetimes τ_i and amplitudes $A_i(\lambda)$, where i is the number of exponentials (which is equal to the number of transient species/processes):

$$f(\lambda, t) = \sum_i A_i(\lambda) f_i(\lambda, t) \quad (5.2)$$

where $f(\lambda, t)$ is the *homogeneous* transient population total intensity, $A_i(\lambda)$ are the pre-exponential factors corresponding to the initial amplitudes, and $f_i(\lambda, t)$ are the temporal exponential functions of each species “ i ”. In this work, all kinetics were well modeled to the Kohlrausch-Williams-Watts (KWW) stretched exponential function:

$$A_i f_i(t) \rightarrow I_i(t) = I_{0i} \exp [(-t/\tau_i)^{\beta_i}] \quad (5.3)$$

where I_{0i} is the initial amplitude, τ_i is a characteristic lifetime constant, and β_i is inversely proportional to the width of an underlying Lévy distribution of rate constants, $0 < \beta_i < 1$.^{176, 195} The final DAS spectra is then constructed plotting the corresponding calculated amplitudes for each data wavelength :

$$DAS = \sum_i A_i(\lambda) \quad (5.4)$$

First, it is important to identify a spectral range in the transient spectra where a single process dominates. The region around 590 nm is predominantly due to the Stark effect and DAS analysis in this range allowed for determination of the KWW parameters for the Stark

effect. The single wavelength absorption kinetics at 590 nm, Figure 5.6 (dark red trace), shows a very interesting kinetic behavior. Immediately after pulse excitation and up to $\sim 80 \mu\text{s}$ a growth is observed, followed by a decrease in amplitude until the signal returns to baseline around 1 s. The kinetic range from $\sim 80 - 100 \mu\text{s}$ to 1 s was taken to be that where the Stark effect dynamics was predominant and KWW modeling over this range provided the τ_i and β_i parameters ascribed as the Stark effect kinetic parameters, τ_S and β_S .

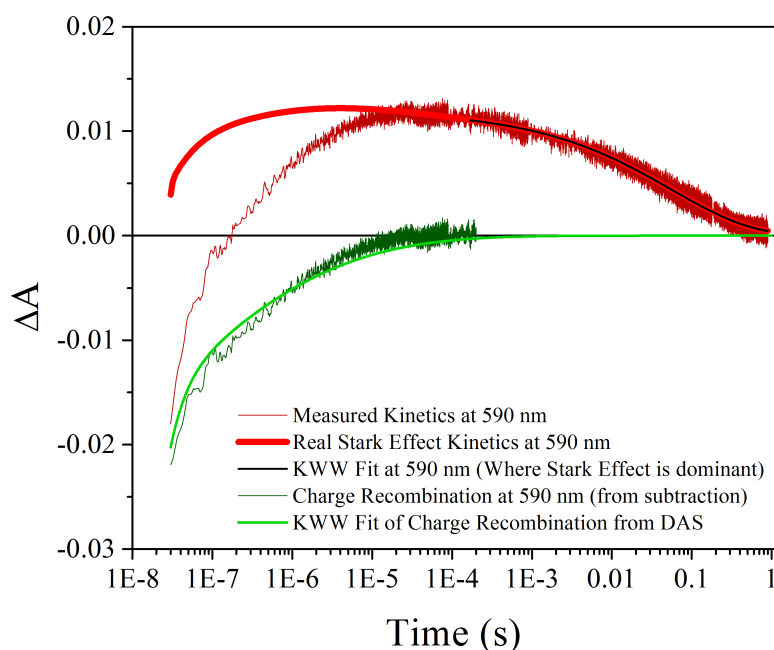


Figure 5.6. Single-wavelength transient absorption kinetic data of Ru(NH₃)₅(eina)/TiO₂ in neat acetonitrile, observed at 590 nm (in dark red). Overlaid in black is the fit to the KWW function after 100 μs , where the Stark effect is dominant; and in light red is the representation of the real kinetics associated to the Stark effect process. In dark green, is the extracted kinetic data associated with the charge separate state and in light green is the obtained KWW fit from the DAS analysis.

Once the KWW kinetic parameters were determined, another wavelength was analyzed (the minimum position of the bleach, at 490 nm) and fitted with a sum of two KWW functions, where one was fixed to the previously obtained τ_S and β_S , and the remaining KWW parameters were floated to obtain a best fit, yielding the parameters associated with the charge separated state kinetic, τ_{CSS} and β_{CSS} . With the KWW kinetic parameters of the charge separated state and the Stark effect determined, each wavelength was fit to the sum of two KWW functions with the pre-exponential amplitudes allowed to float while τ and β were fixed to the previously determined values. Finally, the acquired pre-exponential amplitudes, $A_S(\lambda)$ and $A_{CSS}(\lambda)$, were plotted versus wavelength to yield the DAS spectra shown in Figure

5.7. All the resulting parameters are shown in Table 5.1. (It was done for 02 other wavelengths, 440 nm and 560 nm, and were found similar results as for the chosen 490 nm).

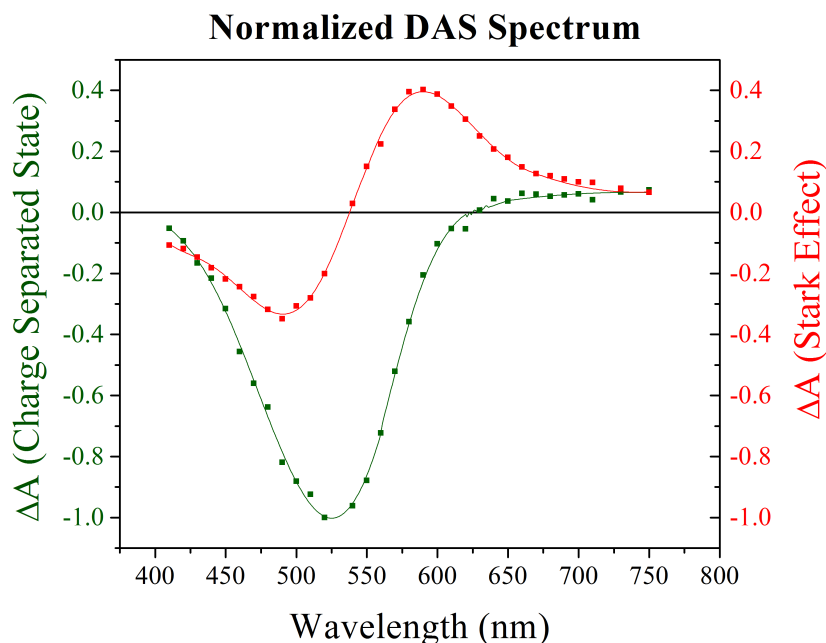


Figure 5.7. Normalized Decay Associated Spectra (DAS) of the transient absorption spectra of Ru(NH₃)₅(eina)/TiO₂ in neat acetonitrile with the spectral component characteristic of the charge separated state shown in green, left axis, and that attributed to the Stark effect shown in red, right axis.

Table 5.1. KWW function parameters of Ru(NH₃)₅(eina)/TiO₂ in neat acetonitrile.

Wavelength	τ_S (s)	β_S	τ_{CSS} (s)	β_{CSS}
590 nm ^a	0.056 ^a	0.43 ^a	---	---
490 nm ^b	0.056	0.43	2.53×10^{-6}	0.33

^aValues determined from the single wavelength transient data used to fit the range from ~80 – 100 μ s to 1 s, where the Stark effect is dominant, black line in Figure 5.7. ^bKinetic trace from the transient absorption data shown in Figure 5.5.

The obtained Stark parameters could also be used to extract the Stark effect process from the full kinetics probed at 590 nm, Figure 5.6 (red line). Subtraction of the latter from the experimentally measured kinetic, at 590 nm, provided the data associated with the charge separated state, dark green trace. The light green line shows the kinetic fit of the charge separated state, obtained from the DSA fittings. The traces from subtraction (dark green) and the kinetic fit (light green) have close similarities.

Separation of the two existing processes from the transient absorption data using the DAS spectrum was used to model the transient spectrum at all time delay in Figure 5.5A by

taking the linear combination of the processes, Figure 5.8. The method reproduced all spectral shapes satisfactorily, but the key point here was to show the transient absorption spectra, at each time delay, as the isolated charge separated state and the Stark effect.

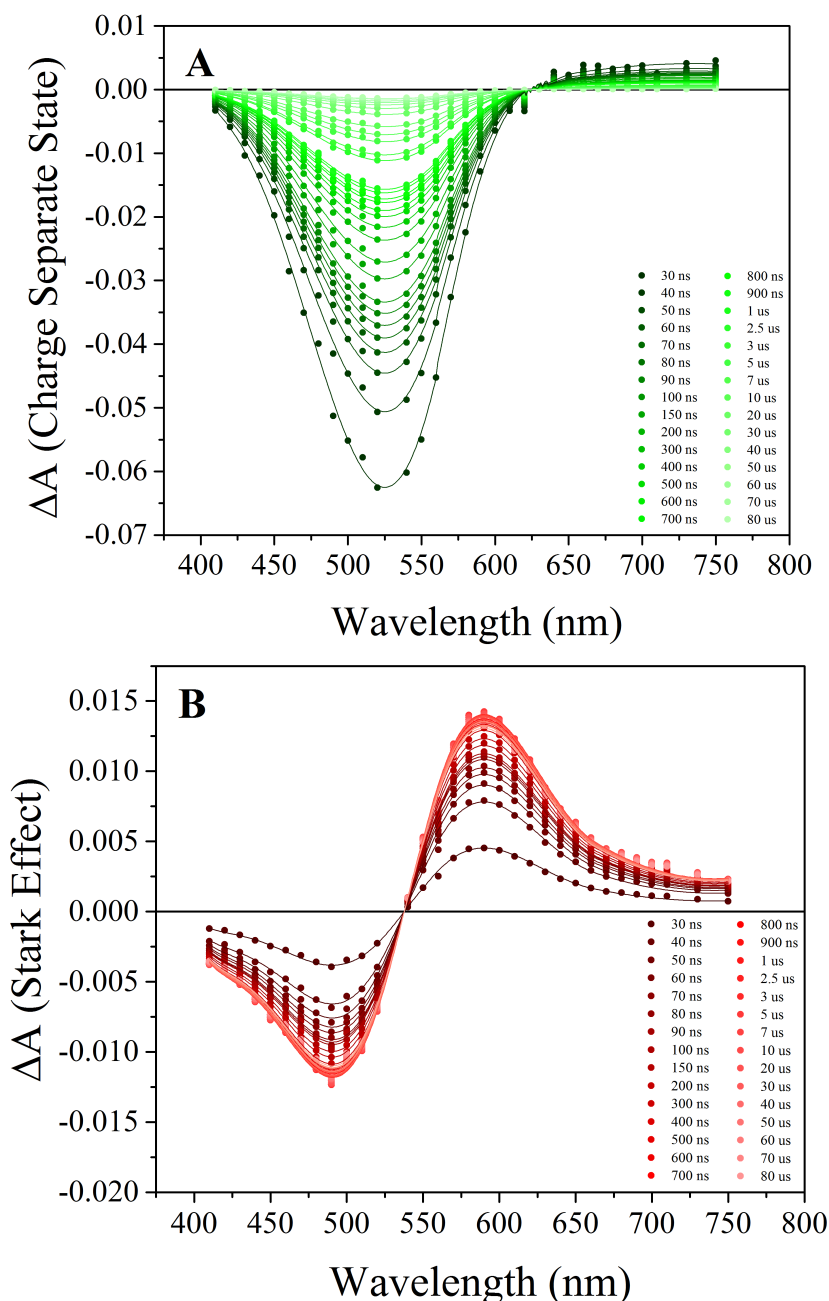


Figure 5.8. Transient absorption spectra of Ru(NH₃)₅(eina)/TiO₂ in neat acetonitrile, deconvoluted into its individual components: (A) the charge separated state and (B) the 1st derivative like Stark signature. Figure 5.8B can also be found in Appendix (Figure A5.4) with a three colors separation for better visualization of the trends. Also Figures (A) and (B) were plotted as a function of the number of injected electrons, Figure A5.3.

The deconvolution procedure can also be accomplished in other ways, such as through the use of the spectroelectrochemical data in Figure A5.1 in the Appendix, and Figure 5.2B, which are the charge separated state and Stark effect signatures respectively. It is also important to note that in Figure 5.5 the minimum position of the bleach *apparently* blue-shifts. This move could be wrongly assigned as the shift of the ground state bleach (charge separated state), which is clearly associated with the shift of the ground state MLCT absorption band. If the ground state absorption was to move back to its original position (after electron injection and consequently the appearance of the Stark effect), showing a blue shift, mandatorily the Stark signature should decrease in intensity, behavior not observed before the first 30 μ s. As discussed before, the Stark effect exhibits much slower kinetics than the charge separated state, and it does not considerably decrease over the monitored 80 μ s, Figure 5.5 and latter confirmed in Figure 5.8B. For this reason, the analysis carried out by the DAS could be more trustful in this case, since it directly used its own transient kinetics to individually extract all the involved processes, and it did not rely on spectra measured in other experiments. Nevertheless, general methods for extraction/interpretation of the useful information encoded by a time-varying Stark effect within transient absorption spectra are lacking, but this analysis shows that extraction of the Stark effect process can be accomplished using a DAS analysis providing greater information than the raw data alone.

The charge separated state and the Stark effect, Figure 5.8A and Figure 5.8B respectively, were both in good agreement with the spectral shapes observed by spectroelectrochemistry, in Figures A5.1 in the Appendix and Figure 5.2B. Additionally, Figure 5.8 clearly shows that the Stark effect had a much slower decay rate compared to disappearance of the charge separated state and, even more intriguing, that it increased in intensity during the first 500 ns after the laser pulse.

Time evolution of the Stark effect can have two origins. The first possibility results from the change in the number of dyes perturbed by the photoinduced electric field. This would arise if the concentration of photogenerated charges were changing due to injection or recombination. A second possible contribution is the change in the electric field strength at the semiconductor interface followed by the movement of the existing charges toward or away from the interface. Comparing Figures 5.8A and 5.8B, it is apparent that the Stark effect increases while the number of injected electrons decreases, evidenced by decreasing amplitude associated with the charge separated state as injected electrons recombine with oxidized molecules. The fact that the electric field strength was enhanced while the number of

charges decreased got us to focus on the second possible contribution to the time evolution of the Stark effect.

Previously researchers believed, and it was generally assumed in the community, that any electric fields emanating from the semiconductor would be completely screened from the surface anchored dye by the large dielectric constant of the TiO₂, and the high permittivity of the solvent acetonitrile.^{109, 127} This assumption was proven to be incorrect in 2010, when two groups reported that electrons injected into TiO₂ had a profound influence on the absorption spectrum of dye molecules anchored to the surface.^{165, 176} In fact, when the electron resides in the bulk of the anatase nanocrystallite, its intrinsic electric field can be strongly screened. However, as the electron approaches to the TiO₂ surface the anchored sensitizers start to feel the suppressed field and their molecular orbitals are perturbed. A simple classical electromagnetic calculation of the electric field from a point charge (an electron) in a medium, accounting for its boundary conditions at the interface, is proposed here in order to elucidate what would be the electric field strength at a distance of 0.5 nm outside of the TiO₂ nanoparticle, as a function of the electron position inside the anatase nanocrystallite (simulating its injection distance), Figure 5.9. The distance of 0.5 nm was chosen to be that of half of the diameter ($d = 1.08$ nm) of the well known ruthenium tris-bipyridine compound, Ru(bpy)₃.⁹²

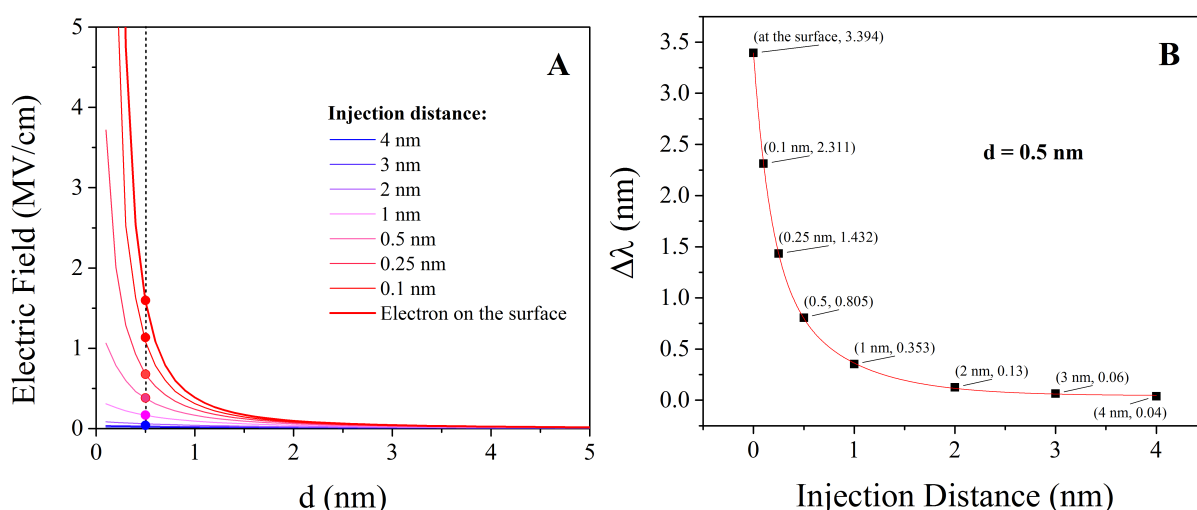


Figure 5.9. (A) Calculated electric field and its respective wavelength shift, from 515 nm, due to one electron at a distance “ d ” from the outer surface of the TiO₂ nanoparticle as a function of the injection distance (inside the TiO₂). The dotted black line depicts the electric fields and $\Delta\lambda$ values at 0.5 nm away from the TiO₂ surface. (B) Calculated electric field at 0.5 nm outside of the TiO₂ nanoparticle and its respective wavelength shift, from 515 nm, due to one electron as a function of the injected distance inside the TiO₂ nanoparticle.

The electric fields were calculated using Equation 5.6:

$$E = \frac{1}{4\pi\epsilon} \frac{Q}{d^2} \quad (5.6)$$

where E is the electric field, Q is the elementary charge, 1.602×10^{-19} C; d is the distance from the TiO₂ outer surface where the field is measured, and ϵ is the permittivity of the medium; also written as $\epsilon = \epsilon_r \epsilon_0$, where ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m) and ϵ_r is the relative permittivity (also called dielectric constant) of the medium (TiO₂ = $86^{235-238}$ and CH₃CN = 37.5). At the interface, the boundary condition for an electric field was used from Equation 5.7:

$$E_{TiO_2} \times \epsilon_{TiO_2} = E_{CH_3CN} \times \epsilon_{CH_3CN} \quad (5.7)$$

where E_{TiO_2} , ϵ_{TiO_2} and E_{CH_3CN} , ϵ_{CH_3CN} are the electric field and dielectric constants of the TiO₂ anatase nanoparticle and acetonitrile, respectively.

Figure 5.9B clearly shows how the electric field was effectively screened from an anchored molecule, measured at 0.5 nm from the TiO₂ outer surface, when the electron resides in the semiconductor bulk, injection distance >3 nm. If, after injection, an electron occupied a position 2 – 4 nm inside the TiO₂, the remaining field at 0.5 nm outside the TiO₂ was so weak that it would generate extremely small shifts in energy (corresponding to $\sim 10^{-2}$ nm). However, as the electron approached the TiO₂ inner surface, the field was less screened and the sensitizer started to respond to the increased field strength, showing changes in its photophysical/absorption spectrum properties. When the electron moves to the semiconductor surface, the calculated electric field is sufficient (~ 1.55 mV/cm) to cause a 3.4 nm red-shift (relative to 515 nm) of the UV-vis absorption band of an anchored molecule. The literature provides an estimative to the electron mean free path of 1 – 2 nm in nanostructured TiO₂.^{231, 250-251}

The Terahertz Spectroscopy community strongly believes that the slow charge recombination of mobile electrons resultant from injection, in TiO₂, is also associated with the screening of the electrostatic interaction in TiO₂ due to its high dielectric permittivity. While for ZnO the low dielectric permittivity (ZnO = 8) enables a strongly electrostatic interaction

between the injected electrons and the oxidized molecules on the surface, making charge recombination much faster.²³⁸

Transient photoconductivity dynamics of dye-sensitized TiO₂ have shown that electron transport through the nanoparticle network predominantly occurs in the conduction band. At early time scale, sub-nanosecond to first couple of nanoseconds, multiple trapping – detrapping events at energetically distributed intra-band-gap states results in the decrease of the average charge mobility.^{116, 231-232} Comparison of nanosecond photoconductivity dynamics with transient absorption studies (which probe the charge density), have allowed the general idea that the observed decay in THz conductivity at early-time decay is predominantly due to trapping of mobile electrons, rather than recombination of electrons and holes.^{231, 252-253}

After the brief analysis given above, the growth of the Stark effect at very early time delays was assigned to an enhancement of the local electric field experienced by the anchored molecules as a response to the charge motion inside the TiO₂ nanoparticle; an important aspect of the electric field screening dynamics. The non-exponential growth fitting of these kinetics could be associated with an average time for electron motion from regions of the bulk semiconductor to its surface. The proposed idea indicated that electrons would exhibit an average time for the diffusion from the bulk to the surface of ~30 ns, Figure 5.10. Tiwana *et al* have found, through photoconductivity experiments, trapping times for electrons in the conduction band in the order of tens of nanoseconds and independent of the excitation wavelength.²³¹ So that the obtained time of 30 ns for the Stark effect growth clearly corroborates with the idea that injected electrons can either be screened when located in the bulk or when immobilized by trapping sites (probably Ti³⁺ sites) in the bulk or at the TiO₂ surface.

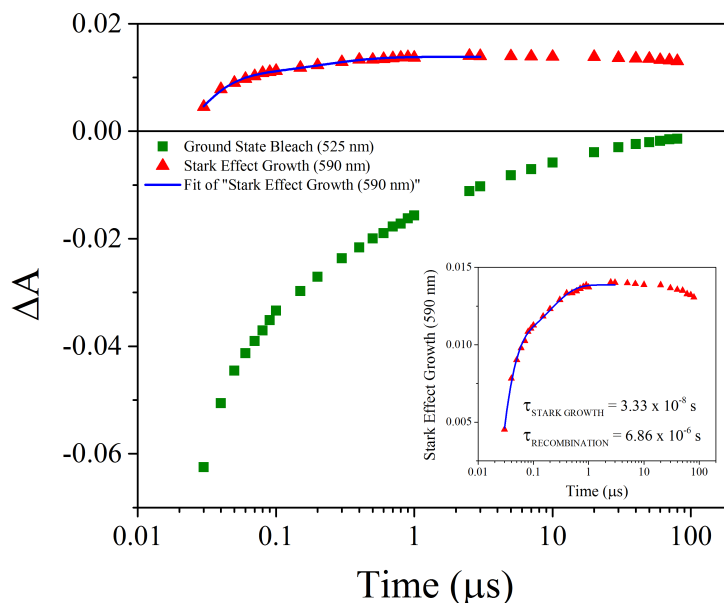


Figure 5.10. Kinetic trace, in the logarithm scale, assembled using the maximum amplitudes of the two observed processes: (in green) the charge separated state and (in red) the Stark signature. Overlaid in blue is the bi-exponential growth fit in the range where the Stark effect shows a growing signal. The inset indicates the rescaled Stark effect growth for clarity.

In a very interesting work, Meister *et al.* proposed a study of the time evolution of the Stark effect using ultra-fast transient absorption experiments to observe charge dynamics.²⁵⁴ However, their system consisted of a complete DSSC such that electrons rapidly diffused through the TiO₂ and were collected by the working electrode, while the generated holes were collected by a solid-state hole conductor material. Since hole diffusion was much slower than that of the electrons, the Stark effect was generated from the point of view of the positive charges of the holes inside the solid state mediator. Although their work looks a little different, the idea and processes are quite similar, and ultra-fast transient absorption, as well as TD-DFT calculations, indicated an increasing intensity of the Stark effect up to 3 ns. The authors were convinced that the Stark effect growth was due to charge diffusion dynamics. And again, studies on the time evolution of the Stark effect are still lacking.

The obtained success on reporting the time evolution of the Stark effect, were only possible after considering some very important experimental facts. First, any molecule having a photoluminescence lifetime longer than a few nanoseconds would completely hide any existing short timescale Stark growth signal due to excited state species, i.e. due the overlapping photoluminescence (which is much more intense) and Stark absorbance. Second, any presence of adsorbed cations on the TiO₂ surface could perturb the motion of electrons in the TiO₂, either by screening charges from the surface or acting on the motion dynamics of

electrons to the surface by drift forces. And third, iodide regeneration takes hundreds of nanoseconds for completion. In this work, all of the aforementioned disadvantages are absent: 1) the molecule does not exhibit time resolved emission, > 10 ns, nor steady state emission at 77K^{240, 255}; 2) these experiments were performed in the absence of adsorbed cations on the nanocrystallite surface; and 3) there was no addition of iodide.

Figures 5.8 and 5.10 show a trend where the amplitude of the Stark effect signal is much higher than the charge separated state (CSS), at longer time delays, > 2.5 μ s. Moreover, at sufficient longer time delays, > 40 μ s, the CSS signal approaches to values close to the zero line, while the Stark effect remains pronounced. In a first moment, these results might be contradictory since the Stark effect is directly related to the number of injected electrons, which is equal to the number of oxidized molecules. To better understand it a more systematic investigation was done. Using the Beer-Lambert law and the transient absorption data related to the CSS, the number of oxidized molecules (and consequently the number of injected electrons) was calculated as a function of the transient ΔA of the CSS spectra, as shown in Table A5.1, in the Appendix.

In a measurement where the observed transient signal for charge separation, ΔA , reaches values below 5×10^{-3} , there are still $\sim 10^{13}$ injected electrons in the TiO₂ nanoparticles, which would give an average of 1 – 0.5 electrons per single TiO₂ as the ΔA decreases to 2×10^{-3} . Below this value, the transient absorption apparatus used could not provide enough resolution for accurate measurements. But using the Beer-Lambert law we can estimate the number of injected electrons per TiO₂ further away in time.

Observing Figure 5.6, 5.8 and 5.10, the Stark effect only starts to decrease after 30 – 50 μ s, when at least 1.5 electrons remain per each TiO₂ nanocrystallite. When this ratio achieves values on the order of 10^{-1} and 10^{-2} , the rate at which the Stark effect decreases is much faster, Figure 5.8 after 1 ms. But, the main reason why the Stark signal is still observable while the CSS has disappeared, is that the generation of the CSS ΔA occurs in a one-to-one ratio, while the Stark effect occurs in a much larger ratio. In other words, a single electron can perturb many anchored molecules at once, making the ΔA signal attributed to the Stark effect much higher in intensity than that observed for the CSS.

Finally, a first derivative analysis can also be done in the Stark transient data to abstract the electric field strength, Figure 5.11. Interestingly, if it is assumed that all the electrons reside at or near the semiconductor surface under conditions of 1 electron per TiO₂ nanoparticle, then the calculated electric field is very close, within experimental error, to that

obtained through the classical electromagnetism calculation shown in Figure 5.9B, for a point 0.5 nm distant from the surface.

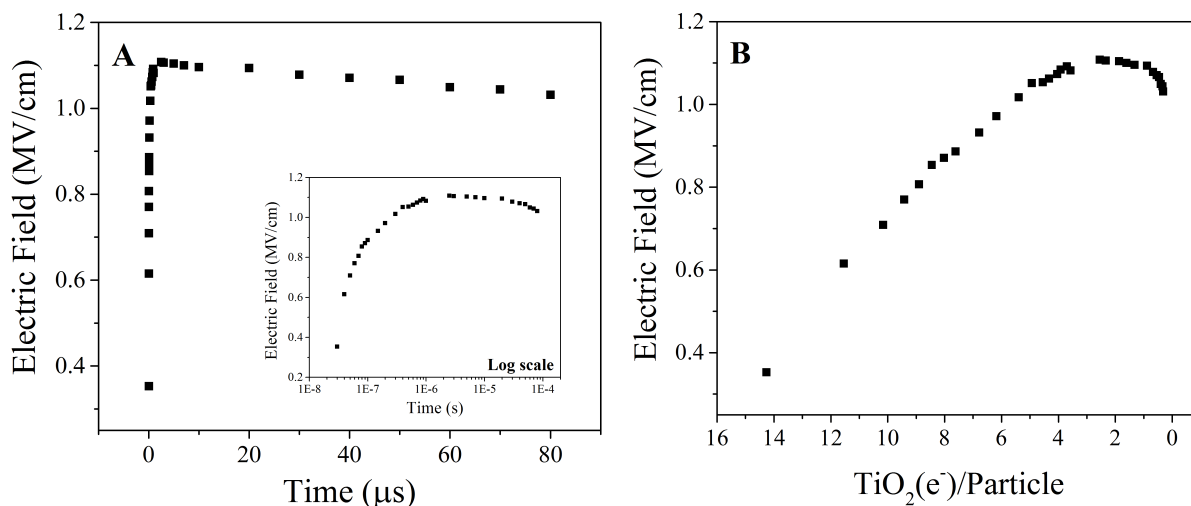


Figure 5.11. Calculated electric fields from the deconvoluted Stark signature using the 1st derivative analysis (A) in a kinetic frame and (B) as a function of the number of injected electrons into the TiO₂ nanoparticle after pulse 532 nm excitation.

The number of injected electrons was estimated by using Equation I-2, in the Introduction of Part I in which the Transient Absorption method is discussed. In brief, first it must be pointed out that the number of injected electrons is equal to the number of oxidized molecules left on the TiO₂ surface right after photoinduced electron injection. Through spectroelectrochemical experiments it is possible to simulate the existence of oxidized molecules anchored to the TiO₂ surface, Figure A5.8 in the Appendix, and their extinction coefficient can be extracted. Once the changes in absorbance, ΔA , for the charge separated state is known, Figure 5.8A, the concentration of oxidized molecules is easily obtained.

Figure 5.11B, might be very controversial, since *a priori* the electric field should increase as the number of electrons increase, but the opposite trend is seen. But one of the main key points in this work is to raise the curiosity of where electrons might be located into the TiO₂, and how important is their motion dynamics to the generation a substantial Stark effect at the interface TiO₂ – dye molecules.

The results found in Figure 5.9 critically relate the position of an electron inside the TiO₂ with its electric field outside of the nanoparticle, screened by the TiO₂ high permittivity. A model sustained by this finding can then be used to better understand the trend found for the Stark effect growth with the increasing number of TiO₂(e⁻), Figure 5.12. There are mainly

two aspects to be considered in the model: 1) the overall concentration of $\text{TiO}_2(e^-)$ and 2) the *surface* $\text{TiO}_2(e^-)$ concentration. What really matter to the Stark effect are electrons at the semiconductor's surface, where they aren't efficiently screened. So, although the overall concentration of electron is high, possibly the surface concentrations is low, and consequently the interfacial electric field is not substantial. As the electrons have to recombined back with the oxidized molecules, their motion dynamics controls both concentration, the total and at the surface. As the surface concentration of electrons increase, the interfacial electric field also increases and the Stark effect responds through an enhancement. In the event time-line there must be a moment where the electron surface concentration only decreases, so that the Stark effect also starts to vanish.

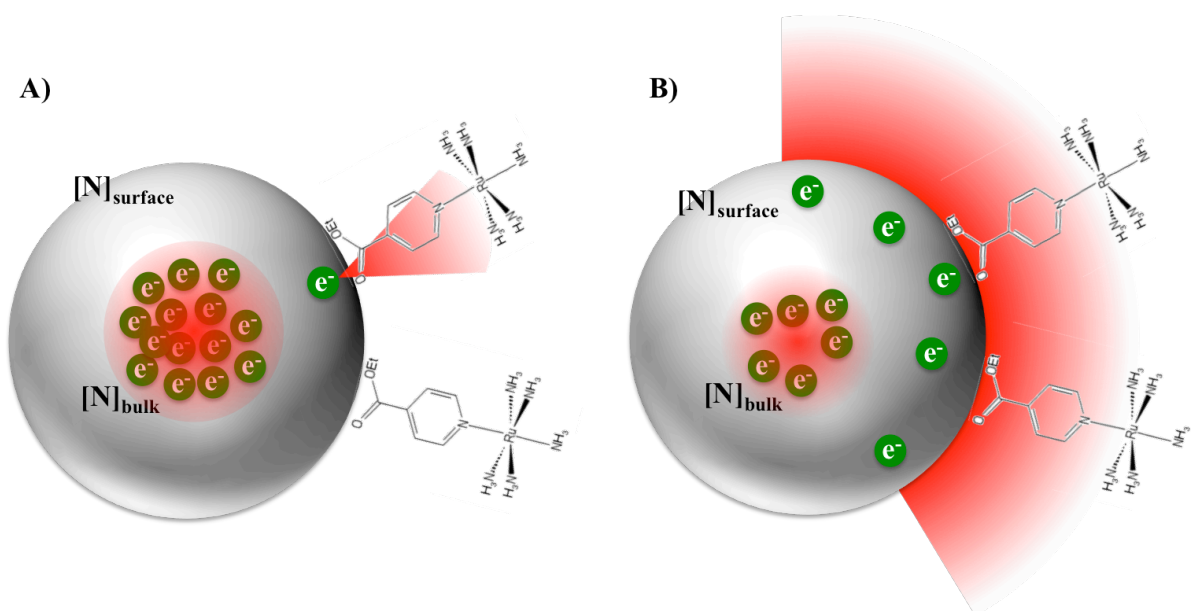


Figure 5.12. Scheme depicting the proposed model for the Stark “rise time”, based on the concentrations of electrons $[N]$, where: A) the concentration of electrons in the bulk, $[N]_{\text{bulk}}$, is higher than in the surface, $[N]_{\text{surface}}$; and B) $[N]_{\text{surface}}$ is increased as electrons move towards the surface .

From Figure 5.12, it is possible to better understand the unexpected trend in Figure 5.11B. At a initial moment, right after electron injection, the concentration of electrons in the bulk, $[N]_{\text{bulk}}$ is larger than at the surface, $[N]_{\text{surface}}$. As electrons recombine back with the oxidized dye molecules, $[N]_{\text{bulk}}$ tends to decrease while $[N]_{\text{surface}}$, at a first moment, might increase before its definitive vanish. Although at early times the overall concentration of electrons is high, what really matter to the Stark effect, is $[N]_{\text{surface}}$, which is low. As time evolves, the total concentration of $\text{TiO}_2(e^-)$ decreases, but $[N]_{\text{surface}}$ increases. The proposed model can satisfactorily fulfill the understanding of Figure 5.11.

In contrast to spectroelectrochemical experiments, which has about 10 electrons per TiO₂, the electric field strength of ~ 1 MV/cm found in transient absorption experiments is associated with ~ 1 electron per TiO₂ nanoparticle. The discrepancy is clearly remarkable, but the experiment conditions are different. While the steady-state experiment is absent of oxidized dyes and then charge recombination is absent, transient absorption generates photoinjected electrons that must undergo recombination with the existing oxidized dyes. In the first case, mobile electrons in the conduction band can be present in the bulk as well as at the surface, susceptible to multiple trapping events, yet there is no preferential direction for the electron to move. When the photoinjected electron is generated, electrons have a preferential direction to move through the surface, increasing charge motion towards the surface. So, although there exist 10 electrons in the spectroelectrochemical experiment, most of them might be restricted to the bulk region of the nanocrystallite where it is completely screened by the high TiO₂ permittivity, and it can also remain longer times confined in trapped sites.

In addition, the abstracted electric field strength of ~ 1.0 MV/cm associated with the 30 ns trapping/diffusion time and the electron mean free path of 1 – 2 nm, it was possible to estimate the electron drift mobility (μ) value of $\sim 10^{-6}$ cm²/(Vs). The obtained value has the same order of magnitude reported in other works.²⁵⁶⁻²⁵⁹

5.4. CONCLUSIONS

Injection of electrons into TiO₂, from a potentiostat resulted in bathochromic (red) shifts, due to generated local electric field at the interface. The observed difference spectrum resembles the 1st derivative of the ground state absorption spectrum, behavior well described by the Stark effect literature. Pulsed laser excitation enabled the kinetics for the Stark effect to be monitored and quantified. The deconvolution method utilized to interpret the observed transient absorption data, provided critical quantitative and qualitative information regarding charge dynamics into TiO₂, from extraction of the time evolution of the Stark effect and the charge separated state. It was shown that the position of the injected electrons is determinant on the interfacial electric field strength, since the high permittivity of TiO₂ can effectively screen charges located in the semiconductor bulk. Based on such time evolution dynamics, it

was proposed an average time of ~30 ns for electrons to move towards the TiO₂ surface after multi-trapping and detrapping events. Also, the presence of adsorbed cations on the TiO₂ and also the presence of oxidized molecules could drift electrons more rapidly to the TiO₂ surface.

5.5. APPENDIX

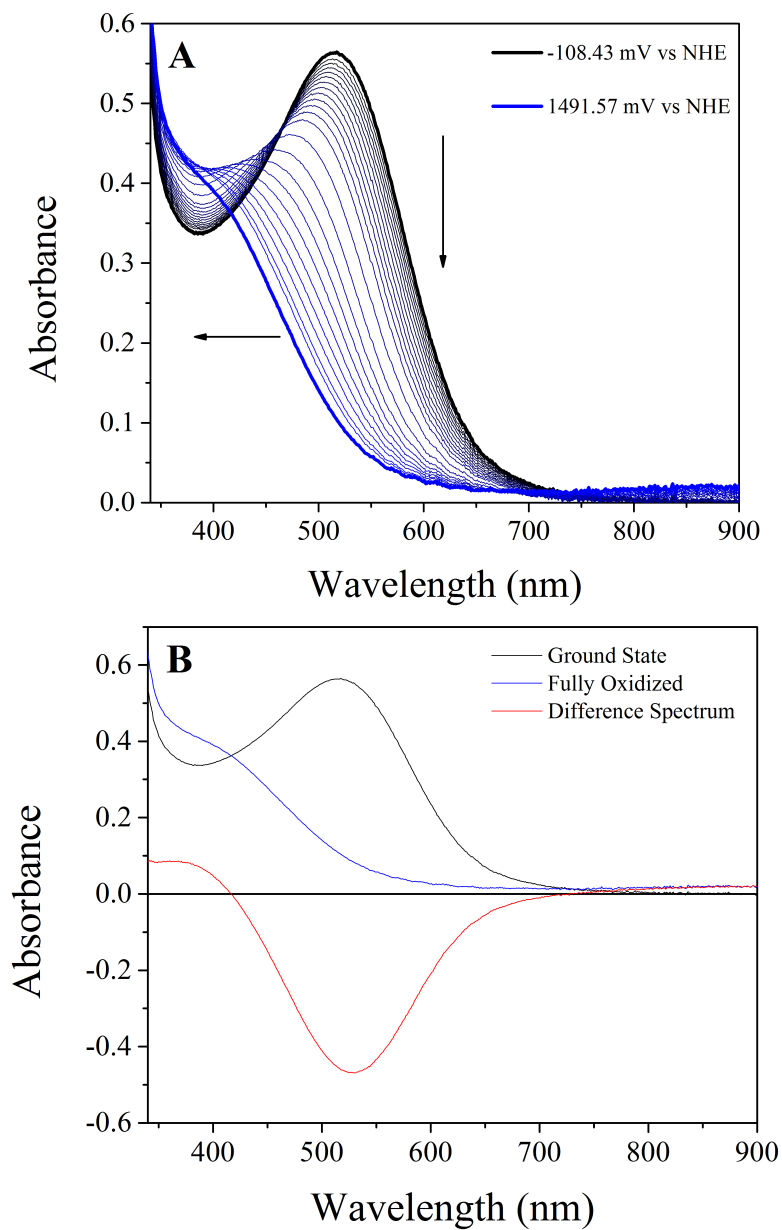


Figure A5.1. Spectroelectrochemical absorbance of Ru(NH₃)₅(eina)/TiO₂ oxidation in 100 mM TBA(ClO₄) acetonitrile solution: (A) shows the changes in absorbance as the potential was varied from 108.43 mV to 1491.57 mV vs NHE; (B) shows the ground state absorbance spectrum of Ru^{II}(NH₃)₅(eina)/TiO₂ in black and the absorbance spectrum of the fully oxidized Ru^{III}(NH₃)₅(eina)/TiO₂ in blue, and the difference spectrum in red.

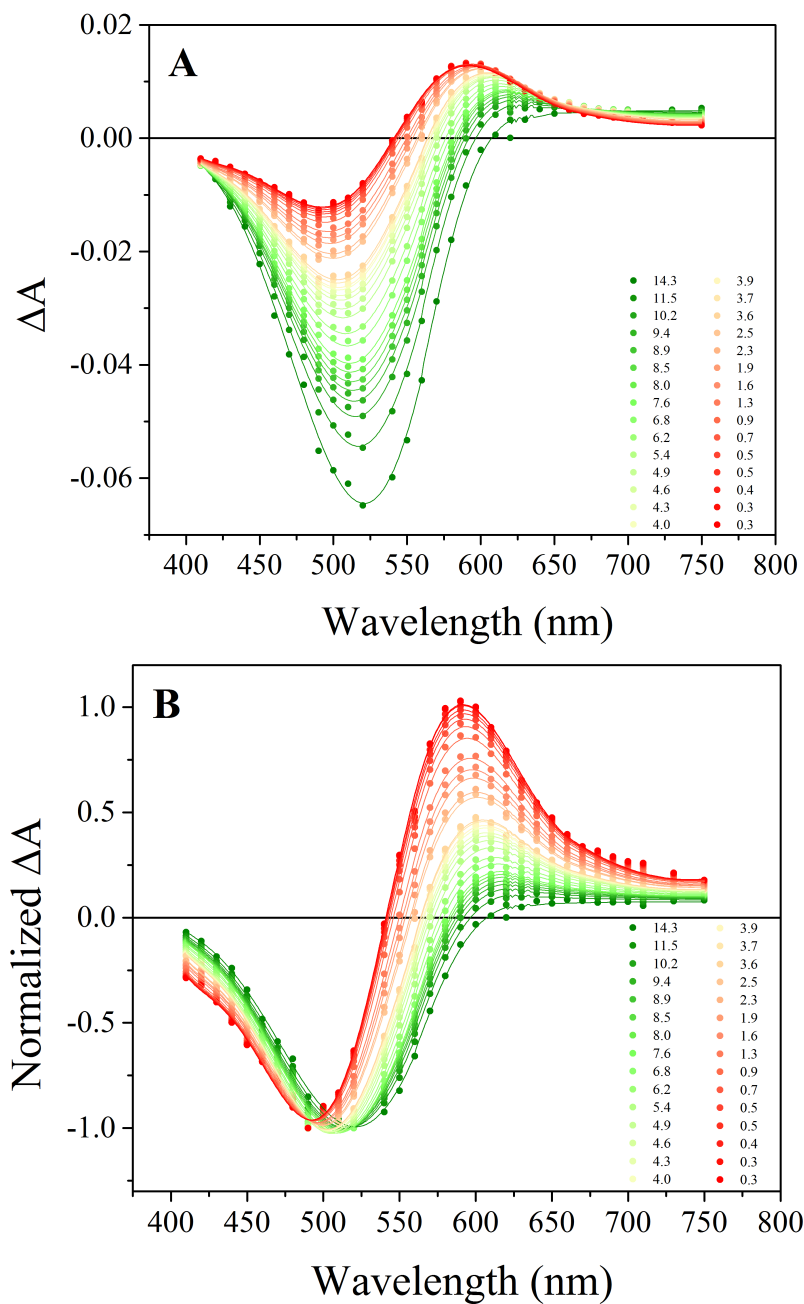


Figure A5.2. Transient absorption spectra obtained at a 30 ns – 80 μs time window after pulsed 532 nm excitation of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ in neat acetonitrile (A) and its normalized spectra (B). Shown as a function of the number of $\text{TiO}_2(e^-)$ per nanoparticle.

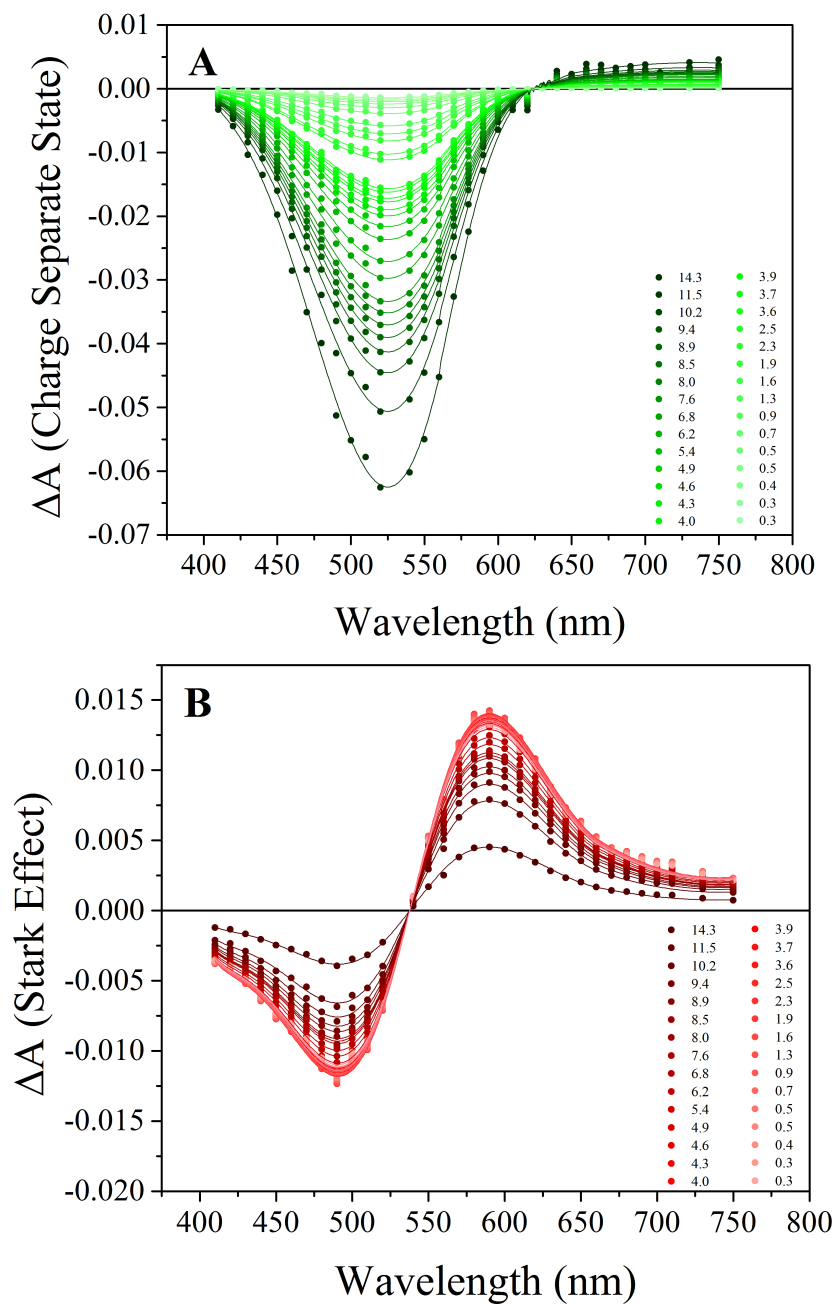


Figure A5.3. Deconvoluted transient absorption spectra of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ in neat acetonitrile, in its individual contributions: (A) the charge separated state and (B) the 1st derivative like Stark signature. Shown as a function of the number of $\text{TiO}_2(\text{e}^-)$ per nanoparticle.

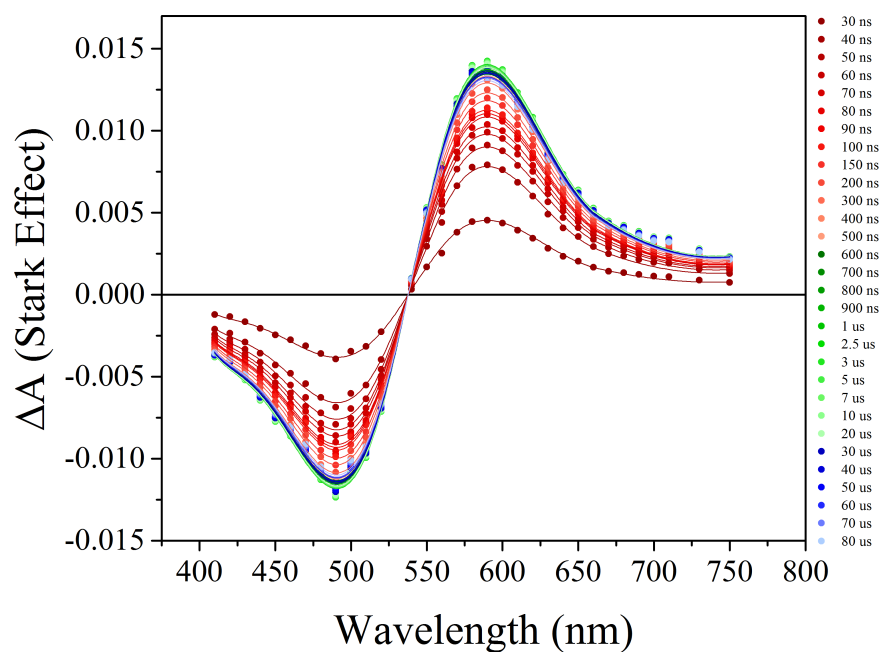


Figure A5.4. Deconvoluted Stark effect transient absorption spectra of Ru(NH₃)₅(eina)/TiO₂ in neat acetonitrile. The spectra were separated in three spectral ranges: (red) Stark effect growth, (green) a nearly constant Stark effect, and (blue) when the Stark effect started to decrease in intensity.

Table A5.1. Calculated number of oxidized molecules and electrons relative to the charge separated state transient absorption data.

Absorbance ^a	Number of Oxidized Molecules ^b	Number of TiO ₂ (e ⁻) /particle ^c	1 electron at each "n" TiO ₂ particles
100 mOD	1.27E+15	22.8285	0.04
90 mOD	1.14E+15	20.5457	0.05
80 mOD	1.01E+15	18.2628	0.05
70 mOD	8.88E+14	15.9800	0.06
60 mOD	7.61E+14	13.6971	0.07
50 mOD	6.34E+14	11.4143	0.09
40 mOD	5.07E+14	9.1314	0.11
30 mOD	3.80E+14	6.8486	0.15
20 mOD	2.54E+14	4.5657	0.22
10 mOD	1.27E+14	2.2829	0.44
9 mOD	1.14E+14	2.0546	0.49
8 mOD	1.01E+14	1.8263	0.55
7 mOD	8.88E+13	1.5980	0.63
6 mOD	7.61E+13	1.3697	0.73
5 mOD	6.34E+13	1.1414	0.88
4 mOD	5.07E+13	0.9131	1.10
3 mOD	3.80E+13	0.6849	1.46
2 mOD	2.54E+13	0.4566	2.19
1 mOD	1.27E+13	0.2283	4.38
0.9 mOD	1.14E+13	0.2055	4.87
0.8 mOD	1.01E+13	0.1826	5.48
0.7 mOD	8.88E+12	0.1598	6.26
0.6 mOD	7.61E+12	0.1370	7.30
0.5 mOD	6.34E+12	0.1141	8.76
0.4 mOD	5.07E+12	0.0913	10.95
0.3 mOD	3.80E+12	0.0685	14.60
0.2 mOD	2.54E+12	0.0457	21.90
0.1 mOD	1.27E+12	0.0228	43.80
90 uOD	1.14E+12	0.0205	48.67
80 uOD	1.01E+12	0.0183	54.76
70 uOD	8.88E+11	0.0160	62.58
60 uOD	7.61E+11	0.0137	73.01
50 uOD	6.34E+11	0.0114	87.61
40 uOD	5.07E+11	0.0091	109.51
30 uOD	3.80E+11	0.0068	146.02
20 uOD	2.54E+11	0.0046	219.02
10 uOD	1.27E+11	0.0023	438.05

^aAbsorbance of the bleach minimum of the CSS transient data. ^bCalculated using Beer-Lambert law $\Delta A = \Delta \epsilon \times N \times L$. ^cCalculated using method described in reference 31.¹²⁷ The region filled with a red color represents values for the ΔA that the signal-to-noise ratio is detrimental to ensure the liability of the measured data.

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Areas of Expertise

Major Area: Exact and Earth Sciences/ *Area:* Physics/ *Subarea:* Condensed Matter Physics/
Speciality: Optical and Spectroscopic Properties of Condensed Matter; Other Interactions of Matter with Radiation and Particles; Photophysics and Photochemistry of Molecules.

Research Areas

- Photophysics and Photochemistry of Organic and Inorganic Molecules. Using steady state techniques such as UV-Vis absorption and fluorescence spectroscopy, as well as Laser-Flash Photolysis (transient absorption) to analyze molecular systems, particularly porphyrin and ruthenium compounds.
- Nonlinear optics. In particular studying excited states absorption dynamics of molecules.
- Investigation of excited states, photodriven electron and energy transfer in organic and inorganic compounds,
- Photophysics of inorganic coordination compounds and their mechanism of interfacial charge transfer into mesoporous TiO₂ surfaces.
- Investigation of electric fields generated after photo-induced electron injection into TiO₂ surfaces and the role it plays on interfacial dynamics of dye sensitized solar cells.

Articles Published in Scientific Journals

S. F. Sousa, R. N. Sampaio, N. M. Barbosa Neto, A. E. H. Machado and A. O. T. Patrocínio. *On the photophysics of fac-[Re(CO)₃(NN)(bpa)]⁺ complexes: a theoretical/experimental study.* Photochemical & Photobiological Sciences, 13, 1213-1224, **2014**

O'Donnell, Ryan M.; Sampaio, Renato N.; Barr, Timothy J.; Meyer, Gerald John. *Electric Fields and Charge Screening in Dye Sensitized Mesoporous Nanocrystalline TiO Thin Films.* Journal of Physical Chemistry. C, 118, 16976-16986, **2014**. (Michael Grätzel special issue)

Sampaio, R. N.; Machado, A. E. H.; Piovesan, E.; Gonçalves, P. J.; De Paula, R.; Cavaleiro, J. A. S.; Barbosa Neto, N. M. *Influence of the solvent-porphyrin interaction on the UV-Vis absorption of free base imidazol cationic porphyrin*. Dyes and Pigments, 100, 73-78, **2014**.

Sampaio, R. N.; Gomes, W. R.; Araujo, D. M. S.; Machado, A. E. H.; Silva, R. A.; Marletta, A.; Borissevitch, I. E.; Ito, A. S.; Dinelli, L. R.; Batista, A. A.; Zílio, S. C.; Gonçalves, P. J.; Barbosa Neto, N. M. *Investigation of Ground- and Excited-State Photophysical Properties of 5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphyrin with Ruthenium Outlying Complexes*. The Journal of Physical Chemistry A. 116, 18-26, **2012**.

Franzen, P.; Zílio, S.; Machado, A.; Madurro, J.; Brito Madurro, A.; Ueno, L.; Sampaio, R. N.; Barbosa Neto, N. M. *Experimental and theoretical investigation of first hyperpolarizability in aminophenols*. Journal of Molecular Structure, 892, 254-260, **2008**.

Articles Submitted in Scientific Journals

Sampaio, Renato N.; O'Donnell, Ryan M.; Barr, Timothy J.; Meyer, Gerald John. *Electric Fields Control $\text{TiO}_2(e^-) + \text{I}_3^- \rightarrow \text{Charge Recombination in Dye Sensitized Solar Cells}$* .

Articles In Preparation to Submit in Scientific Journals

Sampaio, R. N.; Silva, M. M.; Machado, A. E. H.; Borissevitch, I. E.; Batista, A. A.; Meyer, G. J.; Barbosa Neto, N. M. *Photophysical and Photochemical Properties Comparison of a Free Base Tetrapyrrolyl Porphyrin With External Ruthenium Groups*.

Sampaio, R. N.; Barbosa, M. I. F.; Borissevitch, I. E.; Batista, A. A.; Meyer, G. J.; Barbosa Neto, N. M. *Sensitization of Mesoporous TiO_2 Thin Films With a Ruthenium Meso-Substituted Free Base Tetrapyrrolyl Porphyrin Without Functional Binding Groups*.

Sampaio, Renato N.; O'Donnell, Ryan M.; Barr, Timothy J.; Meyer, Gerald John. *A Report on the Stark Effect Time Evolution on $\text{Ru}(\text{NH}_3)_5(\text{eina})$ Anchored to TiO_2 Nanoparticles*.