

DISSERTATION

ACCESSING MOLECULAR STRUCTURE AND DYNAMICS OF
PHOTOELECTROCHEMICAL SYSTEMS WITH NONLINEAR OPTICAL
SPECTROSCOPY

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ABSTRACT

ACCESSING MOLECULAR STRUCTURE AND DYNAMICS OF PHOTOELECTROCHEMICAL SYSTEMS WITH NONLINEAR OPTICAL SPECTROSCOPY

Photoelectrochemical cells (PEC) are a class of solar energy device that have a variety of applications and can be used to directly generate electricity or convert the sun's energy in the form of chemical bonds through photosynthetic processes. The first PEC dates to Becquerel's discovery of the photovoltaic effect in 1839; and, after nearly 200 years of its first creation, the PEC is constantly evolving with the discovery of new fabrication techniques and materials. Sunlight harvesting materials are used in PECs to capture the sun's radiation and drive electron transfer and photocatalytic reactions. Understanding the photophysical properties of the materials used within PEC chemical systems informs on the development of high-performance, low-cost, and sustainable solar energy devices needed to address current global climate challenges and meet societal energy demands.

Chemical systems in PEC architectures are nontrivial and often rely on several components working harmoniously in tandem with one another to stimulate photovoltaic or photocatalytic processes. Dye-sensitized solar cells (DSSCs) are a type of photovoltaic PEC that use molecular chromophores to absorb light, transfer electrons to a semiconductor, and accept electrons from an electrolyte. Local environmental structure of the chromophore can either promote or hinder these electron transfer events within a device. To this end, investigating the molecular structure of the chromophore, including the parameters that influence the structure, is

necessary for fabricating DSSCs with optimal efficiency. The work presented in this dissertation utilizes the nonlinear optical spectroscopic technique of heterodyne-detected vibrational sum frequency generation (HD-VSFG) to investigate the interfacial structure of N3-dye, a popular chromophore used within DSSC devices. It is discovered that the interfacial structure of N3 is influenced by the substrate, pH conditions upon deposition to the substrate, and by the presence of an electrolyte.

Additionally, the work presented herein investigates exciton dynamics of monolayer MoS₂ photoanodes within an operational PEC. Monolayer transition metal dichalcogenides (TMDs), such as MoS₂, are two-dimensional semiconducting materials with fascinating photophysical properties. Only recently have monolayer TMDs been investigated for their integration within optoelectronic devices, such as PECs. By utilizing ultrafast transient absorption (TA) spectroscopy, unique exciton properties of the MoS₂ photoanode are identified within operational conditions. Photocurrent generation via ultrafast hot carrier extraction is discovered, challenging the preconceived notions of the Shockley-Queisser limit; further, we explore the dynamic control of the exciton energy by tuning an external voltage bias to the PEC.

PEC chemical environments are ubiquitous and the photophysical properties are dependent on many underlying parameters. Set forth in this dissertation is the foundation for applying the nonlinear optical techniques of HD-VSFG and TA across a variety of chemical systems pertaining to PECs and assessing data within an established theoretical framework to elucidate molecular structure and dynamics.

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CHAPTER 1 – INTRODUCTION TO PHOTOELECTROCHEMICAL CELLS AND NONLINEAR SPECTROSCOPY

The first chapter of this dissertation contains a brief introduction to the development of a solar energy device known as the photoelectrochemical cell, including a specific type of photoelectrochemical cell commonly known as a dye-sensitized solar cell. Additionally, this chapter introduces the field of spectroscopy and its use for investigating molecular properties within these photoelectrochemical systems.

1.1 Motivation for Solar Energy Devices

The development of renewable energy sources is necessary to meet modern society's growing energy demand and address global climate challenges. Solar energy devices hold great promise as a renewable energy technology due to the immense amount of solar power the sun provides earth, which is approximately 124,000 terawatts.¹ To put that into perspective, currently, humanity uses 18 terawatts, with a projected consumption of 20 terawatts by the year 2030.² The total power consumption of civilization is a fraction of the seemingly endless and substantial power provided by the sun every day. Ending our energy dependence on fossil fuels is a very tractable reality if we could only harness the power of the sun. However, harvesting solar energy is not a trivial problem, and the development of solar energy devices remains an important field of research.

First generation solar energy devices were modernized and viable for consumer markets starting as early as the 1950's with the development of the silicon-based photovoltaic device, that is, a device that creates electricity using sunlight.³ The basic premise a solar device can be broken down into a series of sequential steps. First, a material or molecule must absorb incident light from

the sun and promote a photo-response, most commonly a photoexcitation of an electron. Second, the transfer of the electron is necessary to drive an electrical current through the system to produce electricity. Lastly, the material or molecule that initially lost an electron due to photoexcitation must be replenished with an electron such that the process can happen continuously to sustain the flow of electrons and production of electricity. With these processes in mind, new solar energy devices are being designed with the goal of optimizing each of these steps.

The development of next generation light-driven energy devices is an ongoing field of research for scientists and engineers. Indeed, the quest for a “perfect” solar energy device remains elusive due to the variety of photoactive molecules and the criteria for an ideal device. An ideal solar energy device is one that is optimized to be efficient and made with materials that are inexpensive, non-toxic, and sustainably sourced.^{3,4} Advances within the field have given rise to new types of light driven devices that branch away from the traditional silicon based photovoltaic devices in pursuit of creating the ideal solar energy device. These new devices include multi-junction photovoltaics,⁵ perovskite-based photovoltaics,⁶ devices that utilize quantum dots,⁷ and organic solar cells.⁸ Additionally, another device that has been extensively studied, and will be the focus of this dissertation, is the photoelectrochemical cell.⁹

Photoelectrochemical cells (PECs) differ from conventional silicon based solar panels on the market today in that they have electrolyte solution in direct contact with a semiconductor. This solid-liquid interface replaces the typical solid-state semiconductor positive-negative (p-n) junction used within silicon-based solar panels. Depending on the semiconductor and electrolyte used within the photoelectrochemical device, the device can be made to either produce electricity or solar fuels. A well-known electricity generating PEC is the dye-sensitized solar cell, which is

discussed further in the next section. The discussion on PEC for solar fuel generation is discussed later within this chapter.

1.2 The Dye-Sensitized Solar Cell

Within the broad scope that classifies a device as a PEC, there exists a specific type of PEC called the dye-sensitized solar cell (DSSC). DSSCs have been investigated as a solar energy device since their modernization in the late 1980's with the pioneering work from O'Regan and Grätzel.¹⁰ A DSSC device operates using the same premise for a photovoltaic described in the previous section, that is: absorb sunlight and excite an electron, transfer the electron, replenish the lost electron, and repeat to create an electrical current. This process is described in more detail in Chapter 4.

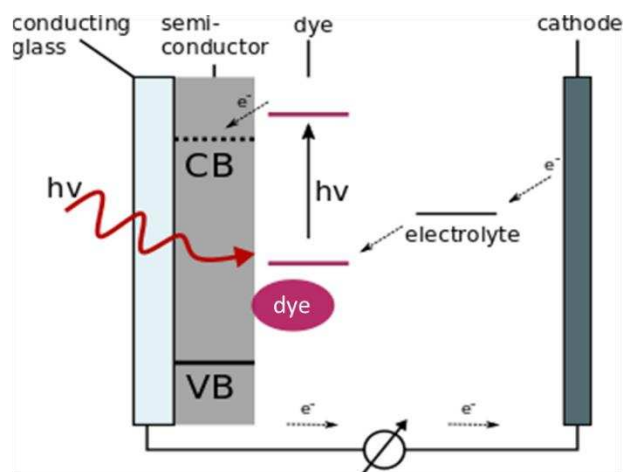


Figure 1.1 Simplified diagram for the working principle of a DSSC device. The energy of the incident photon is labeled as $h\nu$. Electricity is generated by the motion of the electrons within the system, shown by the dashed arrows.

Briefly,¹¹ DSSCs utilize a light-absorbing dye molecule to absorb the incident radiation from the sun. The absorption of a photon promotes the dye to an excited electronic state, and in this excited state, the dye molecule transfers an electron to a semiconductor's conduction band. The electron travels through the semiconductor to a conductive substrate where it then passes

through an external load, eventually arriving at a counter electrode (the cathode in Figure 1.1). An electrolyte between the two electrodes shuttles electrons to the dye and replenishes the dye with the electron that it had lost. This process, shown in Figure 1.1, happens continuously and generates an electrical current.

The efficiency of DSSCs cannot currently compete with the efficiency of solar energy devices on the market today. Currently, DSSCs can reach efficiencies of approximately 12%.^{11,12} To put the efficiency of a DSSC into context, typical silicon based photovoltaics have efficiencies near 20%.³ However, DSSCs can be made using inexpensive material, which lowers the cost of production, and be made to be flexible – both desirable traits to have in a solar device. Therefore, the research and development of DSSCs is necessary to make these devices viable in today's energy economy.

One aspect of the device that would make DSSCs viable for consumer production would be to increase the efficiency. There are many parameters that influence the efficiency of DSSCs.^{12–14} The choice of dye, semiconductor, and electrolyte can all directly impact the efficiency of the device. Though, a crucial aspect of the DSSC that needs to be fundamentally understood to truly optimize performance is the electrolyte /dye/semiconductor interfacial chemistry. It is at this interface that absorption of light, transfer of the photoexcited electron, and replenishment of the electron all take place. This interfacial region, spanning less than 10 nanometers across, facilitates the core operation of the DSSC device. Investigating this interfacial region is important for developing DSSCs with higher efficiencies and is the motivation for the work presented in chapters 3, 4, and 5 of this dissertation.

1.3 Photoelectrochemical Cells for Solar Fuels

Besides directly converting solar radiation into electricity, photoelectrochemical cells can be fabricated to create solar fuels.⁹ The solar fuel generating PECs are also sometimes referred to as photosynthetic cells because they create solar fuels during operation. The working principal of a PEC generating solar fuels is to store the energy harnessed from sunlight into new chemical bonds formed within the syndissertation of these solar fuels. The syndissertation of hydrogen gas from the oxidation of water¹⁵, or syndissertation of methanol, methane, ethanol, and ethane from reduction of carbon dioxide¹⁶ are typical solar fuels synthesized from PEC devices. These fuels can be stored and combusted for energy production, which is an advantage because the energy can be stored and used later when there is no sunlight.

The generation of solar fuels can be done solely through electrolysis, for example, the electrolytic splitting of water into hydrogen and oxygen gas. This, of course, needs energy to drive the reaction and defeats the purpose of making the solar fuel since it is taking energy to make the product. By using a semiconductor that absorbs sunlight in the electrochemical cell, the energy needed to split water into oxygen and hydrogen can be reduced.¹⁷ The integration of the semiconductor, or photocatalyst, within the electrochemical cell is what makes a *photoelectrochemical* cell. Consequently, PECs typically need an external power source (an applied electrical voltage) to drive the production of solar fuels; however, the use of different semiconductor materials can enhance the production and significantly lower the energy needed to produce solar fuels.¹⁸

There are a significant number of semiconductors that have been used and studied for their application within PECs. Metal oxide semiconductors, such as TiO_2 , ZnO , RuO_2 ,^{18–20} semiconducting nanoparticles,²¹ and perovskite semiconductors²² have all been studied for their

viability within PEC architectures. Particularly studied within these materials are the photophysical properties. Radiation of sunlight is what drives the photochemical reaction of these materials, so it follows that a fundamental knowledge of the photophysics is necessary for the design of efficient PECs. Studying the photophysical properties of a new class of semiconductor, monolayer transition metal dichalcogenides,²³ and their integration within PEC architectures is primarily focused on within chapters 6 and 7 of this dissertation.

1.4 Introduction to Spectroscopy

Spectroscopy is used to study the PEC systems introduced in the previous sections of this chapter. Spectroscopy, simply defined, is the study of the interaction of light and matter.²⁴ When the oscillating electromagnetic field of light interacts with matter, the electromagnetic field exerts an external force on the electric field of the atom or molecule. The atom/molecule responds to the light typically through either absorption, emission, or scattering events. Studying these light-matter interactions is the core principle for the field of spectroscopy. Spectroscopy is useful for studying chemical systems because the molecular response to the incident light informs on the physical properties and chemical conditions of the system.

Different spectroscopic methods utilize specific wavelengths of light to investigate different molecular responses. For example, Fourier transform infrared (FTIR) spectroscopy uses wavelengths of light within the infrared region to probe resonant molecular vibrations. Another example is the use of ultraviolet-visible (UV-vis) absorption spectroscopy to study the electronic transitions of an atom/molecule when an electron is excited from orbitals in the ground state to orbitals with higher energy, also known as an excited state. These different physical responses give specific information regarding the chemical environment and molecular properties.

The local chemical environment that a molecule experiences can manifest itself within the detected spectroscopic data, or spectrum. For example, the molecular vibrations of water are different in bulk solution compared to water molecules situated at an interface, and these differences to the local environment and structure of the water molecules are reflected in the measured vibrational spectra.²⁵ Changes to the measured spectrum of a chemical system can include alterations to absorption intensity, line shape profile, and resonant energy. Analyzing spectra and establishing experimental conditions is what makes spectroscopy a powerful technique for studying chemical systems.

1.5 Introduction to Nonlinear Optical Spectroscopy

The previous section describes the basic principle of spectroscopy, which is the study of matter's interaction with light for investigating chemical and physical properties of a system. To this end, this can be accomplished by directing light from a light bulb to a chemical system and measuring the light that comes out – a photon input to the system, and a photon output by the system. The incident light from the lightbulb is weak compared to the electric fields of the electron cloud, and as a result, the light weakly interacts with the system. This weak interaction of light and matter is a linear interaction and encompasses common spectroscopic techniques like FTIR and UV-vis mentioned in the previous section.

However, what were to happen if the intensity of the electromagnetic field of the light was increased; for example, what if instead of a lightbulb, the intense light was from a laser source? At larger intensities, the light's electromagnetic field has a strong, nonlinear interaction with the molecular system.²⁶ Multiple intense light sources can exchange energy, destructively and constructively interfere, and couple with each other within the chemical system. From linear spectroscopy, a wealth of knowledge can be gained; now imagine the immense amount of chemical

information that can be achieved from not just one, but *multiple* interactions of light and matter, this motivation drives the field of nonlinear optical spectroscopy.

With high intensity, pulsed laser sources as our “lightbulb”, we can get change timing between laser pulses, combine different colors of light to make new colors, and retrieve molecular information that is unachievable with linear spectroscopic methods. Discussed in more detail in Chapter 2, second-order nonlinear optical spectroscopy experiments can be designed to selectively probe the interfacial structure of molecules at a surface,²⁷ while other time-dependent nonlinear experimental designs can be performed to observe excited state dynamics.^{28,29} It is these two crucial pieces of molecular information, the structure and dynamics of a system, that drives the work presented within this dissertation; to seek fundamental understanding of chemical and physical properties of PEC architectures.

1.6 Outline of Dissertation

The work presented here focuses on two photoelectrochemical cell systems, the dye-sensitized solar cell and a photosynthetic PEC. Within the DSSC system, the interfacial structure of a popular dye molecule (N3-dye) is studied and the parameters that influence the interfacial structure of this molecule are investigated. Interfacial structure of the dye is probed using vibrational sum frequency generation spectroscopy, which is a second-order nonlinear optical technique. The photosynthetic PEC integrates a monolayer transition metal dichalcogenide (MoS_2) photoanode within an operational device. Excited state dynamics are investigated during operational conditions using ultrafast visible transient absorption spectroscopy, which is a third-order nonlinear optical technique.

Discussed in the next chapter are the motivation for studying the specific chemical systems, as well as the methods of sample preparation. Additionally, chapter 2 gives a more detailed explanation to the theory of nonlinear optical spectroscopy, and provides the methods for conducting the spectroscopic experiments, data collection, signal processing, modelling, and data analysis.

Chapters 3-7 are a combination of a published paper, a submitted paper, manuscripts preparing for publication, and other work with significant results. Finally, chapter 8 is a brief summary and conclusion.

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CHAPTER 2 – MOTIVATION AND METHODOLOGY

The goal of this work is to study photoelectrochemical (PEC) systems using nonlinear optical spectroscopy. This chapter explores the chemical systems and experimental methods for the nonlinear spectroscopic laser table used to study the interfacial structure of N3-dye for dye-sensitized solar cell (DSSC) applications and exciton dynamics of monolayer MoS₂ photoanode within an operational PEC. A brief theoretical background of nonlinear optics is discussed to setup the theoretical framework for the two spectroscopic techniques used here, which are heterodyne detected vibrational sum frequency generation and transient absorption. Data acquisition, signal processing, modelling, and fitting procedures are also described. First, the motivation for studying the chemical systems presented herein is discussed.

2.1 Light Harvesting Chemical Systems for Photoelectrochemical Cells

One of the important components of a solar energy device is to have chemical and material components that can harvest the light from the sun. Described within this section are two chemical systems that are excellent absorbers of light and have the potential to be used in next generation light-driven devices. Presented first is the molecular chromophore known as N3-dye, followed by the photoactive semiconductor, monolayer MoS₂. Investigating the chemical and photophysical properties of these two systems will inform on their integration into solar energy devices and pave the way for the development of new light-driven technologies.

2.1.1 The N3-dye Chromophore

Transition-metal chromophores are a particular class of photocatalysts that have received attention due to their remarkable efficiency in photo-driven systems.¹⁻⁴ Upon absorption of sunlight, transition metal chromophores are promoted to an excited state. This excited state is

typically associated with a metal to ligand charge transfer. As studies have shown, selection of the ligands allows one to tailor the optical properties of the metal complex.^{3,5,6} Additionally, transition metal complexes are typically accompanied by spin orbit coupling contributions and electron spin flipping relaxation processes, which can extend the excited state lifetime of the chromophore.^{7,8} These considerations of tunability and prolonged photo-induced excited state lifetimes make transition metal complex desirable for fabricating photocatalytic and photovoltaic systems.

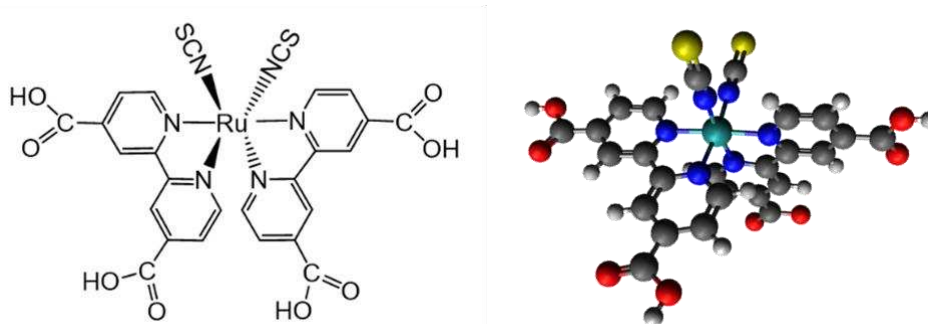


Figure 2.1 Chemical structure of the N3-dye (left). The geometry optimization structure of N3-dye from density functional theory using the B3LYP functional and LANL2DZ basis set (right).

N3-dye $\{[cis\text{-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II))}]$, shown in Figure 2.1, is a chromophore within the well-known family of ruthenium-based polypyridyl transition metal complexes and will be the primary transition metal chromophore discussed in this dissertation work. N3 has garnered much attention by its use within DSSC devices and is regarded as one of the most efficient dyes for DSSC applications.⁹⁻¹² Described previously in chapter 1, in the introduction to DSSCs, N3 performs as the sunlight absorber component within the device. The central purpose of the sensitizer is to absorb incident light and transfer an electron to the semiconductor. Moreover, the electron transfer that takes place after absorption initiates the generation of electrical current within the DSSC device. This electron

transfer is directly influenced by the molecular and electronic structure that N3 undergoes with the semiconductor.

Of all the transition-metal chromophores, there are advantages of choosing N3-dye to be the primary chromophore discussed within this dissertation. N3 is popular within the field and has been studied extensively due to its efficiency as a photocatalyst and wide application within light-driven devices.¹³ Investigating and understanding the photophysical properties of this efficient chemical system will hope to inform the design and fabrication of newer, higher performing photocatalytic and photovoltaic systems.¹⁴

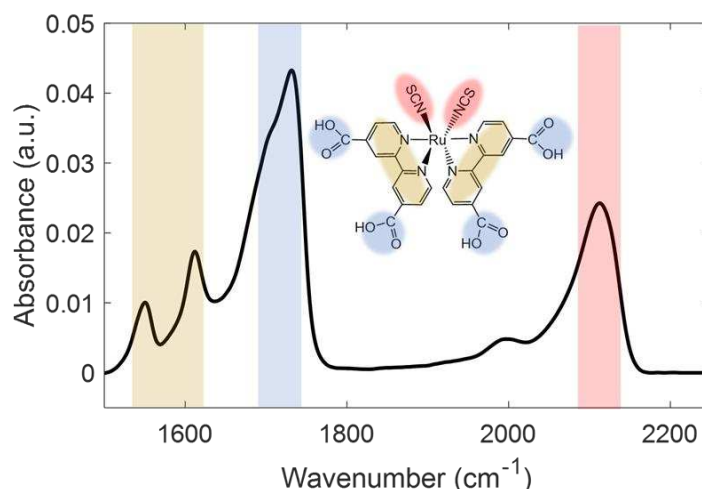


Figure 2.2 ATR-FTIR spectrum of N3 on a CaF_2 plate. From lower to higher energy vibrational modes, the ring modes are highlighted in yellow, the carbonyl of the carboxylic acid is highlighted in blue, and the cyanate stretch of the isothiocyanate is shown in red. The slight resonant feature at approximately 2000 cm^{-1} is an isothiocyanate group that is unbound from the ruthenium complex (discussed more in chapter 4).

Additionally, the N3 complex contains unique functional groups that are of chemical interest. The isothiocyanate ligands are extraordinary molecular oscillators, containing rich vibrational information that yields information regarding local structure.¹⁵ Figure 2.2 displays the resonant vibrational modes of N3 taken using attenuated total-internal reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Moreover, the carboxylic acid groups of N3 offer unique acid-

base chemistry opportunities to explore regarding practical applications, environmental pH conditions, and protonated/deprotonated molecular species.^{14–17} The applications, efficiency, functional groups, and intriguing chemistry of the N3 complex make it a fantastic system to investigate.

N3 is used as a sensitizer and is often situated on a substrate in practice. The orientation and molecular structure on the substrate are important parameters that govern the photophysical properties and performance of N3-based devices.^{14,18–21} Therefore, a surface sensitive experimental technique is needed to study N3 on the substrate. Discussed in section 2.3 of this chapter, is the development and implementation of vibrational sum frequency generation, which is a surface sensitive, interfacial selective technique utilizing nonlinear optical spectroscopy.

2.1.2 Monolayer Molybdenum Disulfide

Transition metal dichalcogenides (TMDs) are type of semiconductor that encompasses a variety of materials with the specific chemical structure MX_2 , where M is a transition metal and X is a chalcogenide.^{22–25} TMD crystals form in 2D nanosheets, composed of a metal center (M) with two hexagonal sheets of the chalcogenide (X) sandwiching the metal. In their bulk form, TMDS are composed of stacks of these 2D sheets held together by van-der-Walls forces. However, a single TMD 2D sheet, or monolayer, possesses very interesting and unique photophysical properties compared to their bulk counterparts.

Monolayer TMDs have been researched for their strong light-matter interactions, photoluminescence, and excitonic effects.^{26–29} The fascinating photophysical properties of monolayer TMDS make them desirable for use in optoelectronic, photovoltaic, and photochemical devices. When a monolayer TMD absorbs an incident photon, excitons form within the material and can be used to do work within operational photo-driven devices. Therefore, understanding the

underlying photo-physics of these excitons is the key to informing the fabrication of 2D monolayer TMD devices, including a PEC.

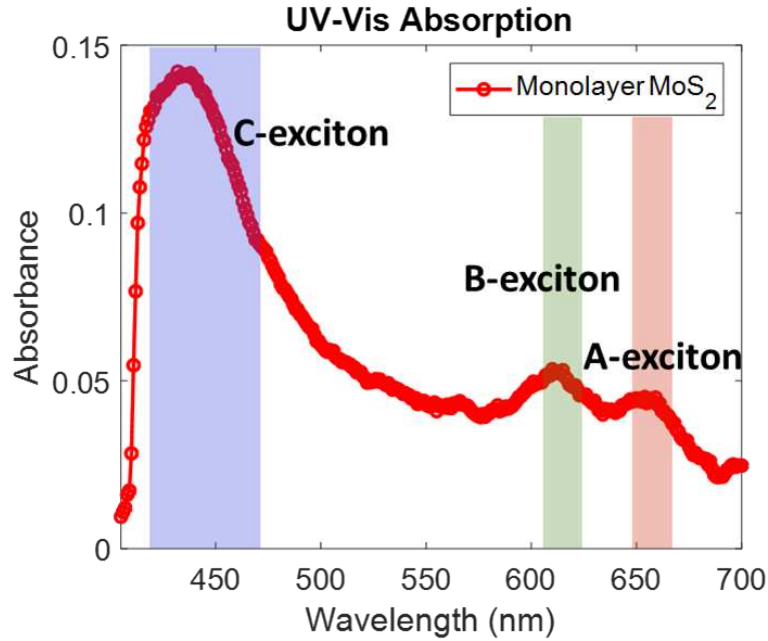


Figure 2.3 Ultraviolet-Visible (UV-Vis) absorption spectrum of MoS₂ on a glass substrate. The resonant exciton features are highlighted in blue, green, and red corresponding to the C-, B-, and A-exciton, respectively.

Here, we investigate the photo physics and excitonic properties of monolayer molybdenum disulfide (MoS₂). It is common and a unique trait of monolayer TMDs to have multiple exciton species that are resonant within the visible spectrum of light. First, a UV-Vis of monolayer MoS₂ on a glass substrate reveals the different exciton species that exist in the material in Figure 2.3. There are three exciton species, referred to as the A-, B-, and C-excitons resonant with the 655 nm, 620 nm, and 435 nm wavelengths of light, respectively.

The photophysical properties of these three exciton species of MoS₂ have been extensively researched.^{23,30–32} However, to truly understand the nature of the excitons within a device, the investigation of the exciton photophysics within an operational device is paramount. Therefore,

we have fabricated a PEC utilizing MoS₂ photoanodes and studied the exciton population and dynamics while operating the PEC using ultrafast pump probe transient absorption spectroscopy.

2.2 Sample Preparation

The work presented within this section describes the methods of fabricating the chemical systems for the pH dependent orientation of N3 on two different substrates, gold and titanium dioxide (TiO₂), the design of an [acetonitrile/N3/TiO₂] sample cell, and the integration of MoS₂ photoanodes in an operational PEC.

2.2.1 N3 Sensitizing Solution

N3-dye (99.7%) is purchased from Sigma-Aldrich and used without any further purification. Sensitizing solutions are prepared using a 0.2mM solution of N3 in a 1:1 water/ethanol solution. Total volume of the sensitizing solution is 10mL. Titration of the N3 sensitizing solution is done using dilute stock solutions of hydrochloric acid (HCl, pH $\approx$ 0.6) and sodium hydroxide (NaOH, pH $\approx$ 12). Small amounts (<300 μ L) of HCl and NaOH stock solutions are added to the N3 sensitizing solution to titrate the solution to desired pH conditions. The sensitizing solution's pH is measured using a pH probe (Orion Star Benchtop pH meter) and allowed to equilibrate for 5 minutes upon addition of acid/base stock solutions.

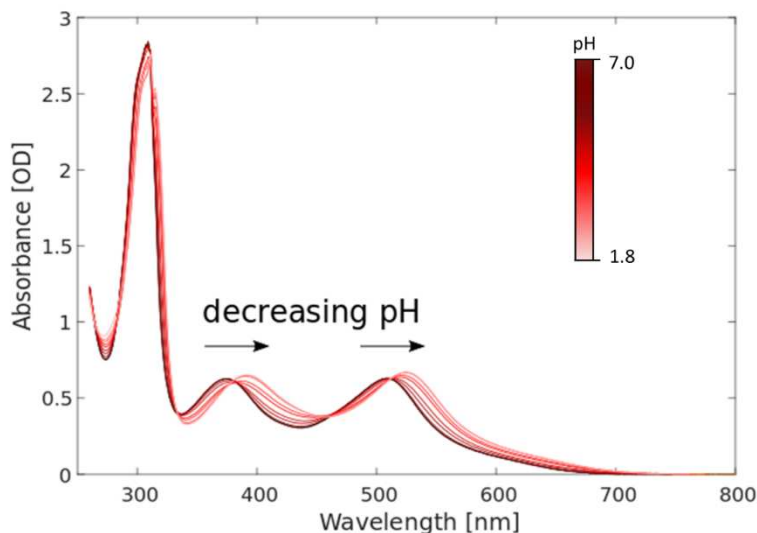


Figure 2.4 The UV-Vis absorption spectrum of N3 ($42\ \mu\text{M}$ in a 1:1 water:ethanol solvent) for a series of pH conditions ranging from 1.8 to 7.0. A slight red shift as the pH is brought down is observed and is a result of protonating the carboxylate groups of N3. The absorption profile of N3 showcases the chromophore's ability to absorb a wide range of visible wavelengths of from sunlight.

Previous studies have investigated the protonation states of N3 that exist in a water:ethanol solution and have determined the pKa values for each protonation state using UV-Vis and DFT.^{16,17} The UV-Vis absorption spectrum of a $42\ \mu\text{M}$ solution of N3 in water:ethanol was titrated with dilute HNO_3 to repeat the previous studies for pH conditions of N3, shown in Figure 2.4. N3-dye has 4 carboxylic acid groups, with 4 acidic protons. As the pH conditions of the sensitizing solution are changed, the carboxylic acid groups of N3 can be deprotonated/protonated. This means that there are five different protonation states of N3 that can exist in solution, the fully deprotonated state (N3^{4-}), the monoprotonated (N3H^{3-}), the diprotonated (N3H_2^{2-}), the triprotonated (N3H_3^{-}), and the fully protonated (N3H_4). The protonation states of N3 are described further within chapters 3 and 4.

2.2.2 N3 on a Gold Substrate

Uncoated gold mirrors (1”) were purchased from Thorlabs and are used as the substrate for the deposition of N3-dye. Gold surfaces are described to have an Au(111) face, and are polished, uniform, and flat. The gold surfaces are rinsed with methanol and wiped clean using lens tissue. The gold mirror is then secured by a clamp attached to a retort stand. To sensitize the gold mirror, the sensitizing solution is decanted into a shallow petri dish (2-inch diameter) and is placed on a stage with a vertical translation. The stage is then raised vertically to meet the petri dish filled N3 sensitizing solution with the clamped and secured gold mirror. Half of the gold mirror is submerged in the sensitizing solution for approximately 1 hour to adsorb N3 molecules onto the surface, while the other half is clean. Afterwards, the sensitized gold is left to air dry, secured in a 1” optic holder, and is placed in the x, y, z sample translation stage in our HD-VSFG spectrometer.

2.2.3 N3 on TiO₂ Thin Films

Calcium Fluoride (CaF₂) windows (Cystran, UV-grade) are used as the substrate to support the TiO₂ nanoparticulate thin films. The fabrication of the thin films is adapted from a previous methodology from the Shutlz group.^{33,34} TiO₂ nanoparticles, (anatase, 5nm) were purchased from US Research Nanomaterials, Inc and used without any further workup. The nanoparticles were dispersed in water with a concentration of ~1mg/mL and sonicated for approximately 15 minutes.

The CaF₂ windows were cleaned and wiped with methanol using optical grade tissue paper. Additionally, one side of the CaF₂ mirrors have a strip of gold that has been deposited onto the surface, which remains clean and serves as a reference signal for the heterodyne detection scheme. The gold strip was made by covering the CaF₂ plate with Kapton tape and exposing a rectangular strip of approximately 0.5cm in height and the length of the plate to have gold grown on using a

physical vapor deposition process. The strip of gold was grown to a thickness of approximately 200 nm.

Approximately 7 μL of the dispersed nanoparticle solution was dropped onto the cleaned CaF_2 window (avoiding the PVD-grown gold strip) and gently spread with the micropipette tip to spread the droplet to a diameter of about 1 cm and then left to dry in air. The resulting film is transparent with a thickness of <200nm and placed on a hot plate set to 300°C for 30 minutes while shining a UV flashlight (365nm, <1.3W) to clean and remove any hydrocarbons and residual water from the TiO_2 surface.^{35,36} The film is cooled to room temperature before submerging into an N3 solution for sensitization. Only the TiO_2 portion of the CaF_2 plate is submerged in the solution, and the PVD-grown gold is left out of the sensitizing solution to remain bare. TiO_2 films are submerged for approximately 1 hour, then lifted out of solution and cleaned with a water:ethanol solution to remove any unbound N3 molecules. The dried film is secured in a 1" optic holder and transferred to the sample stage in the HD-VSFG spectrometer.

2.2.4 Fabrication of an acetonitrile/N3/ TiO_2 Cell

The construction of a sample cell that closely resembles real device chemical environments is ideal for investigating the properties of a functional devices. Described here is the development of a sample that includes the N3-dye, TiO_2 , and acetonitrile in order to mimic the chemical environments of a DSSC or similar PEC device. Acetonitrile (ACN) is used because it is a common solvent to use within electrolyte solutions.^{37,38}

To start, one CaF_2 plate with a gold strip and a TiO_2 film sensitized with N3-dye is made using the procedure described in section 2.2.3. A separate CaF_2 is placed into a 1" optic window holder with a 50 μm spacer (1" in diameter) is placed on the CaF_2 plate. Using a micropipette, approximately 20 μL of HPLC grade ACN is dropped in the center of the clean CaF_2 plate and

spacer that is situated in the sample holder. The CaF_2 plate with the N3/ TiO_2 is then placed on top of the CaF_2 plate with the ACN/spacer and is lightly pressed down and secured in the sample holder.

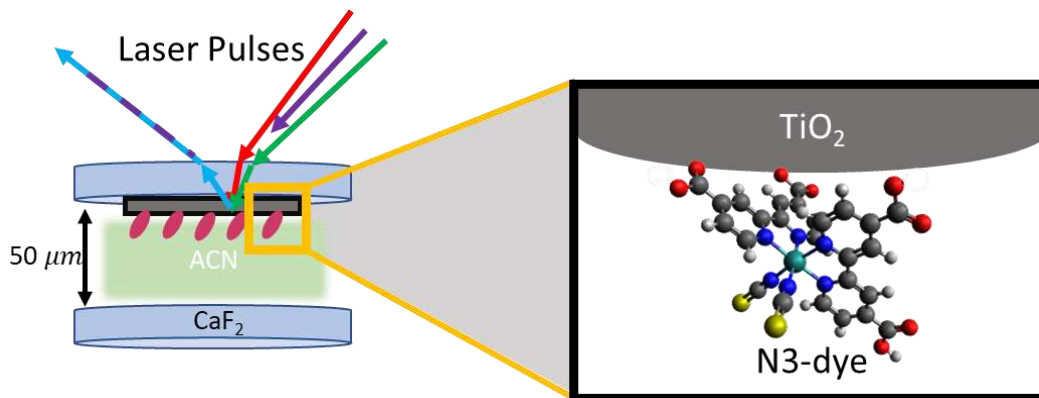


Figure 2.5 A cartoon diagram of the sample cell designed to mimic the chemical conditions that N3 experiences in a DSSC/photoelectrochemical cell. The figure to the right shows a close-up scheme of the N3-dye adsorbed onto the nanoparticulate TiO_2 .

A depiction of the resulting sample cell is shown in Figure 2.5. The N3/ TiO_2 is facing inward in the sample cell and is in direct contact with the ACN. The sample geometry is situated in a way such that the laser pulses come in from the “back-side” of the sample, that way, the incident light does not travel through the ACN.

2.2.5 MoS_2 Monolayer TMDs

The monolayer MoS_2 samples (1 cm x 1 cm) are prepared via chemical vapor deposition (CVD) on sapphire and then mechanically transferred using a PMMA stamp to glass slide and indium tin oxide (ITO) coated glass slide substrates, purchased from 6Carbon Technology, China. Glass samples are an insulating substrate, while the ITO samples are conductive. Photoluminescence spectra of the MoS_2 glass and ITO samples is taken to verify the TMD is a monolayer, this is because any multi-layer TMD does not have photoluminescent properties.

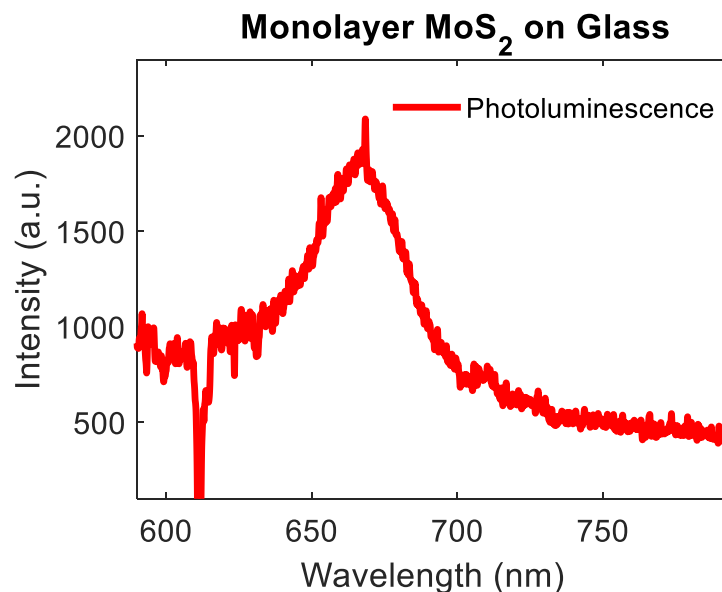


Figure 2.6 A photoluminescence spectra of the MoS₂ sample on glass. The measured intensity at the wavelength corresponding to the A-exciton energy is indicative of a direct recombination of the electron in the conduction band and the hole in the valence band. The direct recombination can only occur for monolayer samples.

Observing the photoluminescence of our samples at the same wavelength of the band edge exciton absorption feature is evidence that our samples are indeed monolayer MoS₂. This is because only direct bandgap semiconductor materials will be photoluminescent, and TMDs like MoS₂ are only direct bandgap semiconductors in their monolayer form.^{23,30,39}

2.2.6 Photoelectrochemical Flow Cell

MoS₂ samples on the conductive ITO substrate are used for the construction of the PEC flow cell for steady state and ultrafast spectroscopic experiments. The conductive ITO surface is needed for the flow cell because the conductive substrate allows for the transport of electrons through the electrochemical cell. The cell is constructed using a three-electrode microfluidic-like device that has been extensively used and researched within Justin Sambur's group at the CSU Department of Chemistry.^{40,41} The MoS₂/ITO serve as the “working” electrode, platinum is used as the counter electrode, and a silver/silver iodide is the reference electrode. The three electrodes

are integrated into the flow cell and hooked up into an Ivium Compactstat potentiostat shown in Figure 2.7.

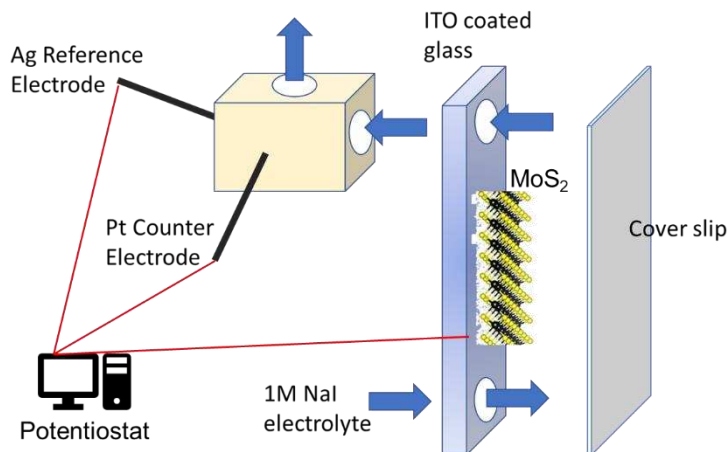


Figure 2.7 Schematic showing the individual components of the PEC flow cell. The monolayer MoS₂ is represented in a ball-stick structure with the black balls representing molybdenum and yellow balls for sulfur.

The ITO/MoS₂ slide has holes drilled through them to allow for the inlet/outlet of electrolyte to flow through the PEC. A cover slip is placed on top of the ITO/MoS₂ slide with polytetrafluoroethylene spacers of 50 μm to allow space for the liquid electrolyte to flow through the sample cell. A cubic chamber containing the platinum and silver electrodes is attached to the outlet port of the sample cell. All components are sealed using Loctite® epoxy.

The electrolyte used here is an aqueous solution of 1 M sodium iodide (NaI) and is flowed through the cell at a constant rate of 0.5 mL/hr using a Kent Scientific® syringe pump. This electrolyte is chosen because it is optically transparent to the spectroscopic experiments and the electrochemistry of the TMD and NaI system has been studied previously. MoS₂ forms excitons upon incident light, and with the correct applied voltage potential to the system, the oxidation of $[\text{I}]^-$ to form $[\text{I}_3]^-$ occurs at the working electrode (MoS₂ surface). Additionally, the reduction of $[\text{I}_3]^-$ to $[\text{I}]^-$ happens at the Pt counter electrode at specific applied voltages. To characterize the

electrochemical behavior and verify that the constructed monolayer MoS₂ flow cell is operational, cyclic voltammetry (CV) measurements are performed using the Ivium Compactstat. The CV shows the oxidation potential and reduction potential of the cell shown in Figure 2.8. Once constructed and operational, the sample cell is held by a slide holding optic on an x, y, z sample stage in the transient absorption spectrometer.

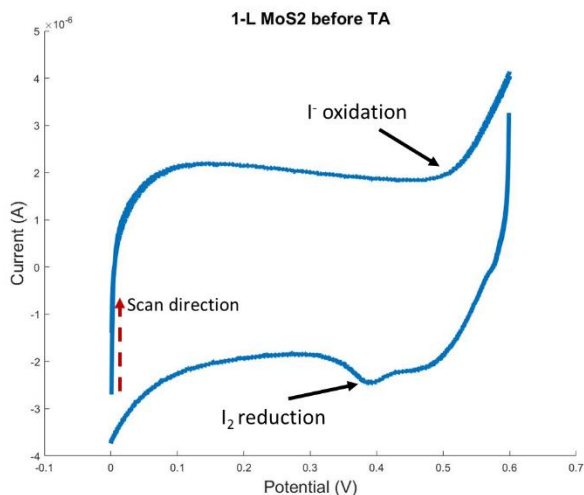


Figure 2.8 A cyclic-voltammetry curve of the PEC flow cell while under illumination. The identification of the electrolyte redox reactions is an indication of cell's successful operation.

2.3 Nonlinear Optical Spectroscopic Methods

When a molecule is subjected to incident light, the force of the electromagnetic field interacts with the valence electrons of the molecule and induces a dipole moment, $\vec{\mu}_{ind}$, within the molecule. The induced dipole is described by the molecule's inherent dipole moment, $\vec{\mu}$, and its polarizability, α . In the condensed phase, an ensemble of molecules in response to incident light is described by the summation of induced dipole moments per volume, referred to as the bulk polarization $\vec{P}$.^{42–45} In the linear regime with non-coherent light (E fields with random amplitude

and phase) and small light intensity, and the condensed phase system has no static dipole moment, $\vec{P}$ is described by the following equation,

$$\vec{P} = \epsilon_0 \chi^{(1)} \vec{E} \quad (2.1)$$

where ϵ_0 is the vacuum permittivity, $\chi^{(1)}$ is the first order electric susceptibility, and $\vec{E}$ is the electric field of the incident light. The molecular information is encoded within $\chi^{(1)}$ as it is related to the molecular system's macroscopic polarizability (α). Here, $\chi^{(1)}$ in equation 2.1 would describe linear spectroscopic processes, for example, UV-Vis absorption and FTIR. When the incident light becomes significantly stronger, like from a coherent pulsed laser source, non-linear effects become significant. Nonlinear effects to the system can be described by expanding $\vec{P}$ in a power series expansion

$$\vec{P} = \epsilon_0 (\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \dots \chi^{(n)} \vec{E}^n) = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots \vec{P}^{(n)} \quad (2.2)$$

From the expansion, higher n -order bulk polarizations arise from nonlinear interactions between light and matter. The n^{th} -order nonlinear polarization of the molecular system is described by the corresponding electric susceptibility, $\chi^{(n)}$. Vibrational sum frequency generation is a second order process and transient absorption is a third order process, both of which are utilized to study PEC systems and described in the following sections.

2.3.1 VSFG Theoretical Framework

Vibrational sum frequency generation (VSFG) is a second order nonlinear optical process that yields molecular vibrational information exclusively at non-centrosymmetric chemical environments, this includes interfaces.^{42,46,47} VSFG was first demonstrated by Ron Shen wherein the vibrational modes of monolayer Coumarin 504 were observed on a fused quartz substrate.⁴⁸ VSFG experiments were soon implemented to determine the molecular structure and orientation at interfaces. Now, 35 years after its development, VSFG has become an influential field of

nonlinear spectroscopy and an invaluable technique to study the vibrational modes of molecules situated at interfaces including the vapor/liquid,⁴⁹ vapor/solid,⁵⁰ liquid/liquid,⁵¹ liquid/solid,⁵² and solid/solid⁵³ interfaces. The reason why VSFG, and SFG in general, is interface specific is due to the second order nature of this nonlinear spectroscopy method.

All even-ordered $\chi^{(n)}$ terms in the expansion shown in equation 2.2 are zero except in chemical systems without a center of inversion symmetry.⁴² Chemical systems that contain no inversion symmetry are said to be noncentrosymmetric and occurs in specific crystal structures, chiral structures, and in environments with an interface. For example, the first demonstration of a nonlinear second order signal (and the first demonstration of a laser induced nonlinear response) was done in a quartz crystal in 1961.⁵⁴ Quartz (SiO_2) has a tetrahedral unit cell, and thus, is noncentrosymmetric and $\chi^{(2)} \neq 0$. The experiment was able to produce second harmonic generation (SHG), which a specific type of SFG where the generated light's frequency is double that of the incident frequency.

An explanation as to why second order signal can be generated in noncentrosymmetric media can be explained by considering $\chi^{(2)}$ in a centrosymmetric environment with a center of inversion. Simply put, $\chi^{(n)}$ is a tensor that relates the input electric field(s) $\vec{E}$ (the incident light) to the induced polarization $\vec{P}$. The $\chi^{(2)}$ is a third rank tensor described by the indices I, J , and K . An inversion acting on $\chi^{(2)}$ in a centrosymmetric environment would have the following relation

$$\chi_{IJK}^{(2)} = \chi_{-I-J-K}^{(2)} \quad (2.3)$$

that is, flipping the sign of each index must be equivalent to the starting value of $\chi_{IJK}^{(2)}$. This relationship holds true for any $\chi^{(n)}$ if the chemical system is centrosymmetric. However, a property of tensors is that each sign change of an index changes the sign of the entire tensor and consequently

$$\chi_{IJK}^{(2)} = (-1)(-1)(-1)\chi_{-I-J-K}^{(2)} = -\chi_{-I-J-K}^{(2)} \quad (2.4)$$

To satisfy both equations 2.3 and 2.4 for $\chi_{IJK}^{(2)}$ in a centrosymmetric environment, $\chi_{ijk}^{(2)}$ must be equal to zero. The same rationale can be used to explain why every even ordered nonlinear process should also be zero in centrosymmetric environments. Therefore, it is only in *non*-centrosymmetric chemical environments that second order signal can be generated.

Noncentrosymmetric environments can be introduced into a condensed phase system by the introduction of an interface. In a typical condensed phase liquid molecular system, the molecular species are randomly distributed around any given point, this system is referred to as isotropic. The isotropic condition is symmetric about every point and the system is centrosymmetric. Indeed, the inversion of “random” is still equal to “random”. In turn, this means that no macroscopic second order polarization can be observed within the system because $\chi_{IJK}^{(2)} = 0$. However, if an interface is introduced to the liquid system, for example, a solid phase substrate, the molecules will adsorb onto the surface of the substrate. Given that the substrate is relatively uniform in chemical composition and lacks a large amount of defects, the liquid molecules will generally take on a preferential orientation on the substrate. This would “break” the isotropic conditions of the condensed phase system, like the example shown in Figure 2.9. The collective molecules that adsorb onto the surface no longer are randomly distributed and will produce a second order signal. Moreover, the chemical system would *exclusively* produce a second order that originates at the interface. It is this reason that even ordered nonlinear spectroscopies are inherently selective to probing molecules at interfaces.

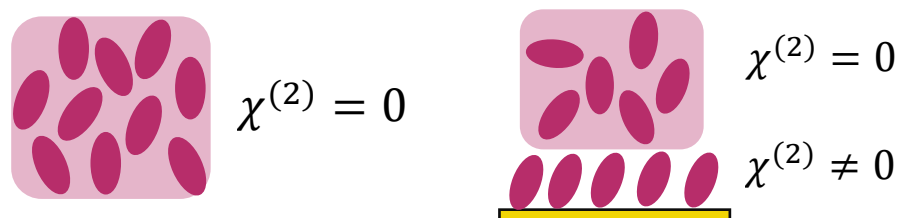


Figure 2.9 An example of how the isotropic environment of molecular oscillators in solution would give no measurable second order susceptibility (left). However, introducing an interface (right), the molecular oscillators would have a non-zero second order molecular susceptibility.

Two incident electric fields are required to generate the second order polarization term described in equation 2.2. To accomplish VSFG, light with frequencies corresponding to the infrared (IR) and visible (Vis) required. IR and Visible pulses are overlapped temporally and spatially at the molecular interface to generate the VSFG signal. The IR pulse is resonant with the vibrational mode of the oscillator, and the visible pulse upconverts the system to a nonresonant electronic state. The molecular system then relaxes to the ground state and emits a photon with a frequency that is the sum of the two incident frequencies ($\omega_{SFG} = \omega_{IR} + \omega_{vis}$) hence the name *sum frequency* generation.

Development of VSFG over the years has eventually made broadband measurements very common in the field. Broadband VSFG uses an ultrafast, broadband IR pulse, which allows for multiple resonant vibrational modes to be probed simultaneously. The visible pulse is a narrowband pulse with a temporal FWHM of a few picoseconds (>3ps). The spectral resolution of broadband VSFG is determined by the bandwidth of the visible pulse; and so, having a longer temporal duration (smaller bandwidth) for the visible pulse is desirable for increased spectral resolution.

VSFG signal is typically detected by a square law CCD detector and reported as intensity versus frequency. The detected signal is directly proportional to the absolute magnitude square of the second order susceptibility, $I_{sig}(\omega) \propto |\chi^{(2)}(\omega)|^2$.

2.3.3 Heterodyne Detected VSFG

Recently, heterodyne detected VSFG (HD-VSFG) has been developed to directly capture the second order susceptibility of a molecular system, rather than the absolute magnitude square.^{55–58} The second order susceptibility is complex, containing both real and imaginary parts, and can be described by the following equation

$$\chi^{(2)} = Re(\chi^{(2)}) + iImag(\chi^{(2)}) \quad (2.5)$$

With HD-VSFG experiments, the real and imaginary parts of the second order susceptibility can be resolved. The molecular susceptibility of a system is represented as a complex number with the real part describing the dispersive component of the susceptibility (ie, the wavelength dependent speed of light) and the imaginary part describing the absorptive component of the susceptibility (ie, the resonant transition energy between states).

In a typical VSFG experiment, the signal detected is the absolute value of the second order susceptibility squared and information regarding the complex nature of the signal is not trivially accessible. This is disadvantages for two primary reasons. One, the second order susceptibility scales with the number of molecular oscillators. Reducing the number of molecular oscillators decreases the signal by a square factor. For samples with poor surface coverage or disperse packing efficiencies, it becomes increasingly harder to detect and measure VSFG. And two, the +/- sign of the real and imaginary components inform on the up vs. down orientation of the vector

describing the dipole moment. This makes it impossible to discern the precise orientation of the molecular oscillator at an interface.

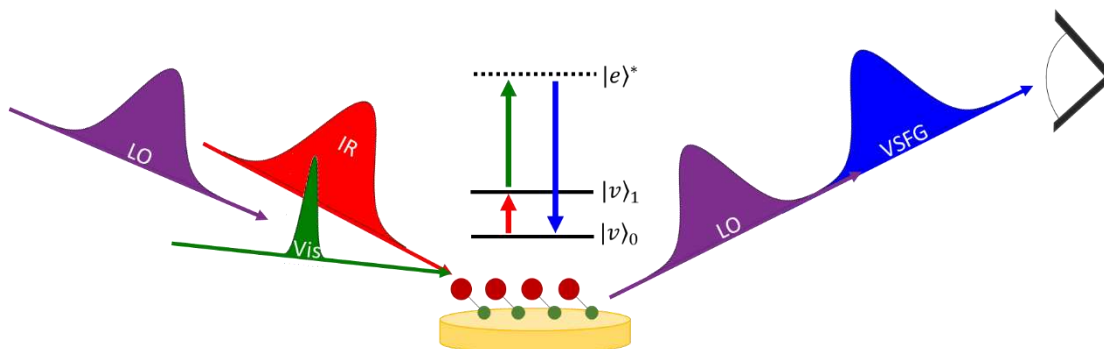


Figure 2.10 Typical beam geometry and pulse sequence heterodyne-detected vibrational sum frequency generation. The ground state, resonant vibrational mode, and virtual electronic energy levels are shown in the center with the color of the transitions associated with the color of the laser pulse/signal.

To resolve the real and imaginary parts of the second order susceptibility, information regarding the phase of the signal is needed.^{55,57,59} HD-VSFG incorporates the use of an external reference electromagnetic field with a known phase to retrieve the signal's phase, and thus, the real and imaginary parts of the detected signal. The external field is typically called the local oscillator (LO) in HD-VSFG experiments. Detailed in the section 2.4 of this chapter is the laser table set up of our HD-VSFG spectrometer where the generation and detection of the LO and VSFG signal is described to acquire a HD-VSFG spectrum.

2.3.4 Transient Absorption Theoretical Framework

Transient absorption (TA) spectroscopy is a third order nonlinear optical process that yields information on the time-dependent relaxation process and chemical dynamics of a system. The third order process is described by the third order molecular susceptibility $\chi^{(3)}$ in the expansion shown in equation 2.2. Ultrafast UV-Vis transient absorption spectroscopy has been used for decades to study the ultrafast photoinduced processes associated with the electronic excited states

of light-driven systems.^{18,60–62} A common use of TA is the study of the lifetime of excited state populations and the population relaxation kinetics. To this extent, TA is an ideal spectroscopic technique to study the excited state lifetimes and populations of the exciton species of MoS₂.^{23,62}

In general, TA uses two pulses separated by time T (or similarly noted as τ in some texts). The first pulse is often referred to as the “pump” and the second pulse is referred to as the “probe”. The pump pulse is an ultrafast short pulse, typically on the order of femtoseconds, and the probe pulse is often a broadband white light pulse to spectrally resolve multiple wavelengths of light across the visible spectrum. By stepping the time between the two pulses, one can retrieve time resolved spectroscopic data from the molecular system. The pump pulse is used to electronically excite the molecular system. This first pulse causes a coherence, or a superposition, between the ground and excited states of the molecular system. The molecular system resolves the coherence to have either population in the ground or excited state. Therefore, the pump pulse causes two interactions within the system, the coherence, and the collapse of the super position to form populations in the ground and excited states. The probe pulse is the third interaction, and the third order NLO signal travels collinearly with the probe pulse where it is spectrally resolved on a detector.

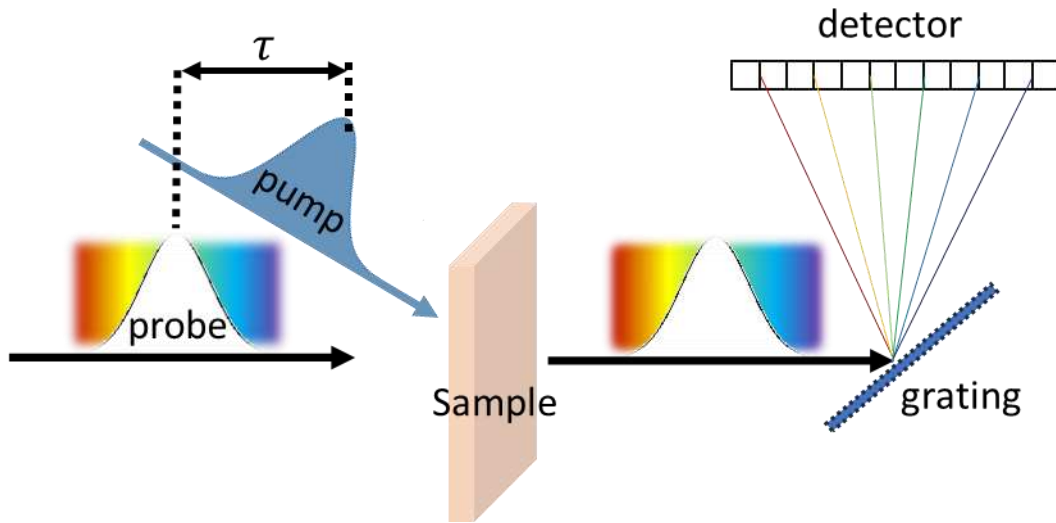


Figure 2.11 Typical pulse sequence for ultrafast transient absorption experiments. The multicolored probe is delayed in time from the probe by τ . Only the probe pulse is collected by the detector. Changes to the absorption within the probe pulse is reported as ΔA for TA spectra.

TA data is reported as a difference spectrum between pumped and unpumped chemical systems, described by the following equation

$$\Delta A = A_{pump} - A_{unpump} \quad (2.6)$$

and recalling that the absorption of a system is expressed as

$$A = -\log_{10} \left(\frac{I}{I_0} \right) \quad (2.7)$$

where I is the intensity of light going through the sample, and I_0 is the intensity of light that is not passed through the sample. Equation 2.6 above can be rewritten as

$$\Delta A = -\log \left(\frac{I_{pump}}{I_0} \right) + \log \left(\frac{I_{unpump}}{I_0} \right) = -\log \left(\frac{I_{pump}}{I_{unpump}} \right) \quad (2.8)$$

The derivation in equation 2.8 is written in a compact form and does not show the dependent variables, however, it should be noted that ΔA is a function of both wavelength (λ) and time (τ). From this derivation, the reported TA difference spectrum is simply the wavelength resolved

intensity of the probe pulse for pumped and unpumped systems, and there is no need for the collection of an I_0 spectrum.

There are different molecular responses that contribute to the difference spectra ΔA of transient absorption, such as excited-state absorption and stimulated emission; however, the one spectroscopic feature that will be the center of discussion throughout this dissertation is the ground state bleach. The ground state bleach feature appears due to the depletion of photo-excitable carriers in the ground state due to the pump pulse. Essentially, the pump pulse excites the sample, promoting a fraction of ground state population to an excited state. When the probe follows after the pump, the sample absorbs “less” light due to carriers already in the excited state. The result is a negative signal for ΔA according to the subtraction defined in equation 2.6.⁶⁰

The bleach feature indicates the presence of photo-excited populations. As the pump and probe pulses are separated in time, the excited state population is given time to relax back down to the ground state. As population goes to the ground state, they are again able to be photo-excited, resulting in a depletion of the intensity of the bleach feature. Therefore, the intensity of the bleach feature indicates photoexcited population, and the depletion of the intensity with time reports on the relaxation of the photoexcited population.

Resolution of the transient absorption system must be considered for the two domains: wavelength and time. Wavelength resolution is determined by the spectral resolution of the grating and pixels of the detector used within the experiment. The temporal resolution of the TA experiment is set by what is commonly referred to as the instrument response function (IRF). The IRF is determined by the cross correlation of the pump and probe pulses, and typically for broadband TA experiments, the IRF is set to the temporal FWHM of the pump pulse used within

the experiment. Detailed in the next section, 2.4, is the laser table set up of our TA spectrometer where the generation of pump pulses and probe pulses is outlined.

2.4 Nonlinear Optical Laser Table

The nonlinear optical spectrometer laser table can be divided into two main components. The first is the initial generation of the ultrafast, 1kHz amplified pulses of light. The second component is the manipulation of the amplified light, such as controlling the wavelength, timing, and polarization, to generate the desired HD-VSFG or TA signal.

For the first part of the table, a KM Wyvern 1000 series titanium:sapphire cryogenically cooled amplification system is used to generate amplified light pulses. The Wyvern amplifier is controlled using the user interface program from KM Labs called the DragonMaster™. A p-polarized, 532nm continuous wave (CW) source (Sprout-H, Lighthouse Photonics®) operating at 3.5 W is used to pump a Kerr-lens KM titanium:sapphire oscillator (Gryffon-W) to create 6 nJ gaussian pulses at a 80MHz repetition rate, with a wavelength centered at 790nm and FWHM of approximately 60nm. Two prisms in the oscillator can be translated using the DragonMaster™ program and are used to control the dispersion within the optical cavity. The modelocked light can be made by manually translating the 2nd prism in the cavity. The mode locked light coming from the oscillator is referred to as the seed.

The seed then exits the cavity through the output coupler optic within the oscillator and is sent to the stretcher stage to temporally stretch the pulse. Stretching the pulse lowers the peak power and ensures that the light will not damage any optics during the amplification process. The stretcher stage is composed of gratings in a 4f configuration to add a positive temporal chirp to the pulse, such that the “red-er” colors of light are in front of the “blue-er” colors of light. The stretched seed is directed into a cavity with a cryogenically cooled titanium:sapphire gain media

where it is overlapped with a pump pulse. The amplifier pump pulse is a 532 nm Q-switched light source (~100 nanoseconds) and is generated from a Lee Laser®.

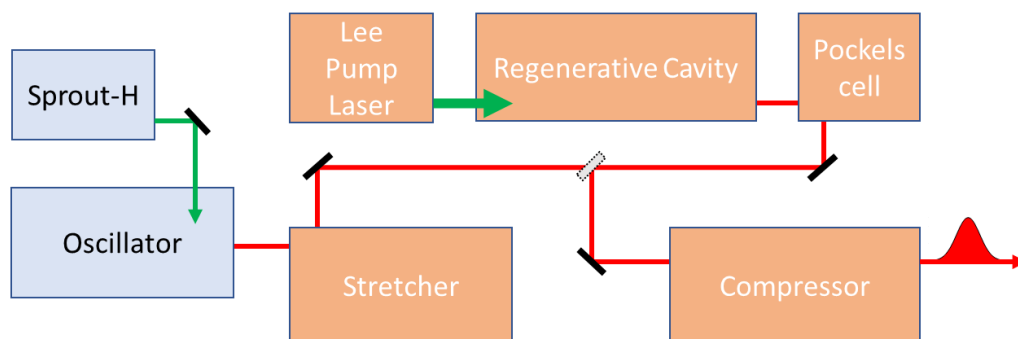


Figure 2.12 Simplified diagram showing each step in the seed generation and pulse amplification procedure.

Both seed and pump are overlapped and travel back and forth within the cryogenically cooled Ti:sapphire cavity where amplification of the seed occurs. The amplified light is ejected from the cavity controlled by a Pockels cell. The number of passes in the regenerative cavity is specified by the timing of the Pockels cell, when it is “on” the seed is trapped within the cavity, and only leaves the cavity when the Pockels cell is “off”. The polarization of the amplified light is then rotated and then directed to a compressor stage by a thin film polarizer. The compressor is needed to compensate for the temporal stretch that was applied by the stretcher stage. By adding a negative temporal chirp to the pulse, the compressor effectively reverses the positive temporal chirp that the stretcher stage added to the pulse. After the compressor, the result is 1kHz, <50fs, 3.3mJ gaussian shaped pulses of light centered at 790nm, verified by frequency resolved optical gating (FROG) measurements.

2.4.1 HD-VSFG Spectrometer Table Layout

The method for generating the mid-IR, visible, and the local oscillator to collect HD-VSFG spectra is described herein. After the amplification system, the light is split utilizing an 80/20

beam splitter. The 80-fraction is sent to an optical parametric amplifier (OPA) to generate tunable mid-IR broadband pulses of light. The OPA system used is the TOPAS-prime from Light Conversion®.

Within the TOPAS, the initial input light is split up to two paths, one path containing 97% of the light to serve as the pump line, which is used to amplify the signal at the second stage BBO crystal. The remaining 3% of the light is split into two additional lines, with one line being used to generate a white light continuum in a sapphire crystal and the other used as the pump on the first stage BBO crystal. The white light and pump are overlapped in the first stage BBO crystal in a noncollinear geometry for easy separation of the signal, idler, and pump fields. The idler and pump residual fields are blocked but the signal is expanded, collimated, and sent to the second stage BBO crystal and amplified by the pump, which is the initial 97% fraction.

The amplified signal is sent to the difference frequency generation (DFG) mixing stage, which is an external attachment to the TOPAS prime. The external mixing stage is controlled by the TOPAS program, in addition to the timing and angle position of the first two BBO stages. An output wavelength of light from the DFG stage can be specified within the TOPAS program. For VSFG experiments, it is important to have the wavelength of the IR light resonant with the vibrational mode of interest. The resulting pulse of infrared light is 25 μJ when centered at 5000 nm.

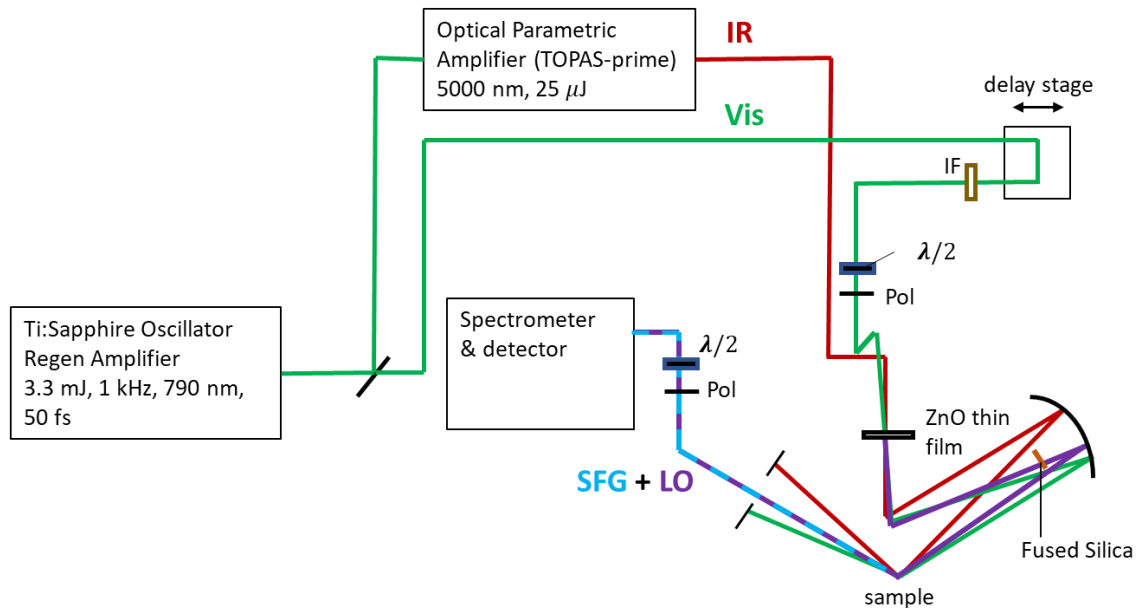


Figure 2.13 Beam path for the HD-VSFG spectrometer. The green line is the visible pulse (790 nm), the red line is the tunable mid-IR light, the blue line is the generated SFG signal, and the purple line is the local oscillator. Other components of the spectrometer are discussed in the main text.

The remaining 20-fraction of amplified light is used as the visible $\vec{E}$ field for the upconversion process to generate the VSFG signal. First the light travels through a delay stage to control the timing of the pulse, followed by a pass through an interference filter (Andover). The interference filter is composed of two coated filters with a small gap of separation to create an etalon effect. The certain wavelengths of light within the broadband pulse destructively interfere, resulting in a narrowband ($\sim 0.5\text{nm}$) visible (790nm) pulse ($\sim 3\text{ps}$) of light.

Both IR and visible pulses of light are overlapped and focused down on a single crystal zinc oxide (ZnO) thin film to produce a broadband non-resonant SFG field. ZnO crystal structure, similar to quartz, is a tetrahedral unit cell with a noncentrosymmetric environment and produces a non-resonant broad SFG field that is used as the external local oscillator (LO) for the HD-VSFG experiment. The LO is then sent through a fused quartz window to temporally delay the LO from the visible and IR pulses by 5ps. The temporal separation of the LO is necessary for the data

processing of the heterodyne signal. Data processing of the HD-VSFG signal is detailed in a later section. All three beams (LO, vis, and IR) are focused down on the sample by a spherical mirror to produce SFG at the sample.

Collection of SFG signal is done in a reflection geometry. The produced SFG field travels collinearly with the local oscillator from the sample. Before reaching the detector, the SFG and LO are collimated and focused down to the entrance slit of a iHR550 Horiba spectrometer equipped with a 1200 lines/mm grating to disperse and wavelength resolve the signal on a CCD detector (Synapse, Horiba).

Polarization experiments can be done using the HD-VSFG spectrometer. There are two linear polarizations one can choose in these experiments, either P or S polarization. P-polarized light has the vector of the electric field parallel with the plane of incidence, while the S-polarized light is perpendicular to the plane of incidence. The polarization of incident IR is P-Polarized and kept consistent throughout all HD-VSFG experiments. Polarization of the visible and collected VSFG fields can be selected using the waveplate and polarizer combinations shown in the laser table diagram. The $\lambda/2$ waveplate is used to rotate the light to the desired polarization, and the polarizer is used to ensure the passing of only the desired polarized light.

2.4.3 TA Spectrometer Table Layout

The transient absorption beam path, generation of frequency doubled light, and white light generation are described herein. Light from the regenerative amplifier is dropped in intensity ($<10 \mu\text{J}$) by taking the front reflections of a beam splitter and wedged CaF_2 plate. The light is then sent to a half waveplate and polarizer to split the light into pump and probe lines. A fraction of the light is sent through a delay stage controlled by a Newport motion controller driver (XPS model) to control timing and a 1mm BBO crystal to frequency double the light by second harmonic

generation (SHG) to approximately 390 nm to create the pump pulse. The probe is created by taking the remaining portion of light that was split and focusing it down in a 2 mm quartz cuvette filled with 18 M Ω water to create a white-light continuum. Water was chosen as the media for white light generation because the bandwidth is large enough to capture the C-exciton resonant energy of MoS₂ at approximately 430 nm and the A-exciton at 660 nm. The half-wave plate and polarizer combination can be used to adjust the intensity of the fraction of light sent to the pump versus probe line.

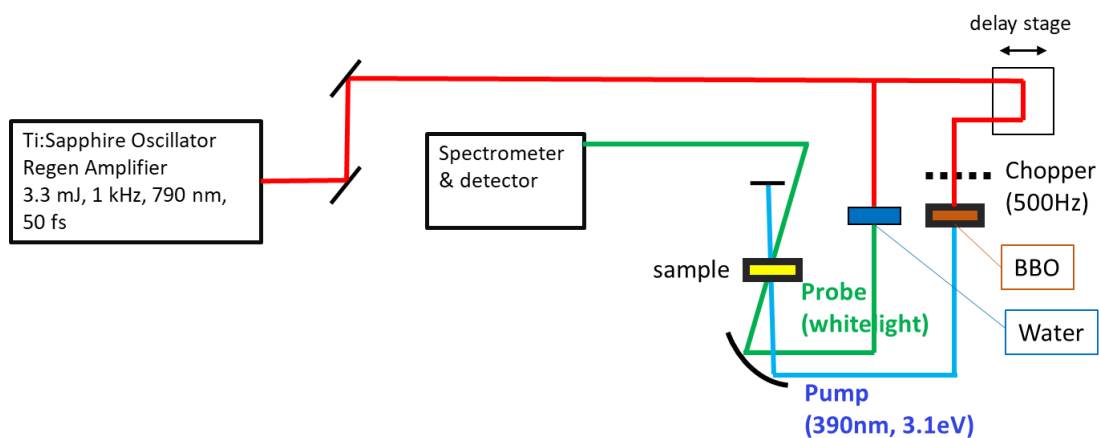


Figure 2.14 Beam path for the TA spectrometer. The red line is the original pulse that originates from the regenerative amplification system. The green line is the white light continuum used as the probe, and the blue line is the pump pulse which has been frequency doubled in a BBO crystal. The remaining components of the spectrometer are detailed within the main text.

The pump and probe are then non-collinearly focused and overlapped on the sample using a parabolic mirror. The pump pulse is blocked after the sample. The probe is collected, collimated, and focused into a spectrometer (iHR550, Horiba) with a 200 mm slit opening, equipped with a 100 line/mm grating (450 blaze), and detected by a single line 2048 element array detector (OctoPlus, Teledyne e2V). Resulting spectral and temporal resolution are 0.6nm and ~50fs, respectively. The pump pulse is modulated by a triggered, optical chopper (Thorlabs) operating at 500 Hz to acquire “pumped” and “unpumped” pulse sequences used to calculate ΔA .

Both the pump and probe pulse have a spatial FWHM of $\sim 100 \mu\text{m}$ and fluence of $75 \mu\text{J}/\text{cm}^2$ at the sample. A variable neutral density filter wheel can be placed before the sample to control the power and resulting fluence of the pulses. Fluence calculations are done by measuring the power using a power meter (ThorLabs®) and using a USB Mightex camera to image the pulse at the sample. The fluence for the MoS_2 experiments was chosen to be in the linear response of the bleach intensity for each exciton.

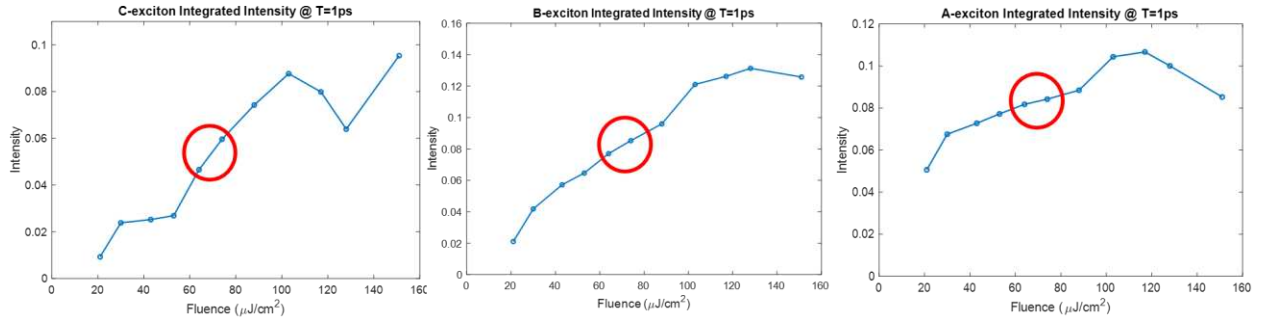


Figure 2.15 Integrated TA bleach intensity of the C-, B-, and A-excitons of MoS_2 as a function of pump fluence. The red circle highlights the pump fluence of $75 \mu\text{J}/\text{cm}^2$ that was chosen and can be seen to be within the linear regime of the excitonic bleach signal. Notice, at fluences $>100 \mu\text{J}/\text{cm}^2$, the exciton bleach signal deviates from the linearity.

To mitigate any undesirable higher-order photophysical processes in the material, the intensity of the pulses used in the TA experiment is kept within a linear regime of the chemical system's photophysical response.^{23,30} Measuring the integrated intensity of the bleach features of each exciton as a function of pump fluence intensity can be done to identify the linear regime. The results of the bleach feature as a function of pump fluence is shown in Figure 2.15. From these results, we have chosen to hold the pump fluence at $75 \mu\text{J}/\text{cm}^2$, which is in the linear response regime for A-, B-, and C-excitons of MoS_2 .

2.5 Signal Collection and Data Processing

The nonlinear signal for both HD-VSFG and TA experiments are collected by detectors (described in the previous sections) that are hooked up to a computer with a LabVIEW® program for each spectroscopic technique. The LabVIEW® code for each technique is shown in Appendix A. In this section, an overview of the signal collection in the LabVIEW® software, further signal processing in Matlab®, and the methodology for data processing is presented for each NLO experiment. The methodology here can be used across different samples, however, the primary examples discussed are the N3-dye and MoS₂ chemical systems.

One of the first steps of data collection for both HD-VSFG and TA experiments is the calibration of the detector. The specific grating and detector can be chosen with the monochromator program in LabVIEW® called “JY Mono USB” shown in Appendix A. Under the current table set up, as of Spring 2022, the “front” outlet port goes to the detector for HD-VSFG and the “side” outlet port goes to the TA detector. Additionally, the center wavelength is specified using this program. After inputting the desired wavelength for detection, a calibration is done with a neon lamp. Emission lines for a typical neon light source can be found on the Newport® website. The emission lines at specific pixel numbers of the detector are assigned to the corresponding wavelength of light, and a linear function is applied to assign each pixel to a wavelength. During the calibration, the entrance slit to the monochromator should be kept small (<0.05 mm) to make emission lines narrow and to not saturate the detector.

2.5.1 HD-VSFG Signal Processing

The emitted VSFG field is visible light (approximately 600-700nm) and appears as an interferogram in the LabVIEW® program for the detected signal. The fundamental visible frequency (~792.1 nm) is noted in the program, and the pixels are calibrated to the visible light by

use of a neon lamp. By subtracting the fundamental visible frequency from the acquired data, the signal intensity can be plotted as a function of IR frequency reported in wavenumber (cm^{-1}).

The integration time (typically between 5-30 seconds) for the signal collection is dependent on the intensity of the signal and is set as to not saturate and harm the detector's pixels. For a typical experiment, 30 acquired spectra are accumulated on the LabVIEW® program, and this data is taken directly from the LabVIEW® program to Matlab® to average the 30 data sets to produce a “raw” spectrum. From here, the rest of the data analysis is done via Matlab®. An example of the raw detected signal is shown in Figure 2.16, the term “raw” meaning that no manipulation has been applied to the data set other than calibration of wavenumber axis and averaging.

The emitted SFG field and the LO constructively and destructively interfere and yields oscillatory fringes as the detected signal. Light detected can be expressed using the following equation:^{55,63,64}

$$\begin{aligned} I_{det} &= |E_{det}|^2 = |E_{sig} + E_{LO} \exp(i\omega\Delta t)|^2 \\ &= E_{sig}^2 + E_{LO}^2 + E_{sig}^* E_{LO} \exp(-i\omega\Delta t) + E_{sig} E_{LO}^* \exp(i\omega\Delta t) \end{aligned} \quad (2.9)$$

Here, the Δt term represents the time delay between the LO and SFG signal fields, which is 5ps from the LO passing through the fused silica window. The electric fields in the equation above are a function of frequency, ω .

To extract the heterodyne detected data, a Fourier transform is applied to the data to shift the data from the frequency domain to the time domain. In the time domain the shown in Figure 2.16, the diagonal and cross terms can be visually distinguished within the HD-VSFG data. The feature centered at time zero is the DC component of the field (ie, the non-oscillatory intensity of the detected signal), and is represented as the first two terms in the expression shown in equation 2.9.

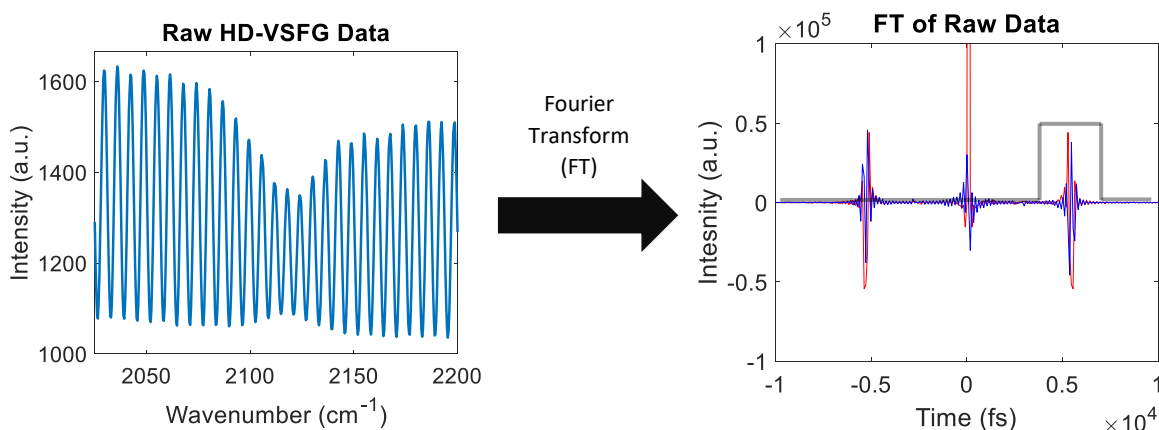


Figure 2.16 The acquired data from an HD-VSFG spectra without any data processing (left) and the Fourier transform of that data (right). The filtering function applied to the data on the right is shown as the gray line that resembles a top hat.

The cross terms of equation 2.9 are represented in Figure 2.16 as the nonzero features at ± 5 ps. A filter is applied to the data by use of a window function. The data showed in the time domain is multiplied by zero everywhere except within the defined region shown by the gray outline in Figure 2.16, where it is multiplied by one. A typical window, for example, would multiply all data points by zero, except for the region between 4ps to 7ps. For data processing, the window is held relatively constant without much variation to the size of the window (± 1 ps). Too large of a window can add unwanted spectral features, like the DC component, into the final spectrum; too small of a window can result in the loss of spectral information by clipping some of the data. Additionally, as a note, the window function can be applied to the -5ps feature, however,

since this is the complex conjugate of E_{sig} (equation 2.9) the imaginary party needs to be multiplied by -1. Moreover, the information in the positive and negative features are identical, and taking the positive feature eliminates the need to keep track of the sign of the E_{sig} complex conjugate.

After the filter/window function is applied, an inverse Fourier Transform is applied to shift the data from the time domain back into the frequency domain. The resulting data of the FT^{-1} is shown in Figure 2.17. From the FT, both the real and imaginary parts of the detected signal are resolved and is directly proportional to the second order susceptibility of the molecular system. The data is still represented as an interferogram due to the E_{sig} and E_{LO} fields beating against one another, expressed by the equation inset in figure 2.17. To remove the E_{LO} field, a reference signal is required.

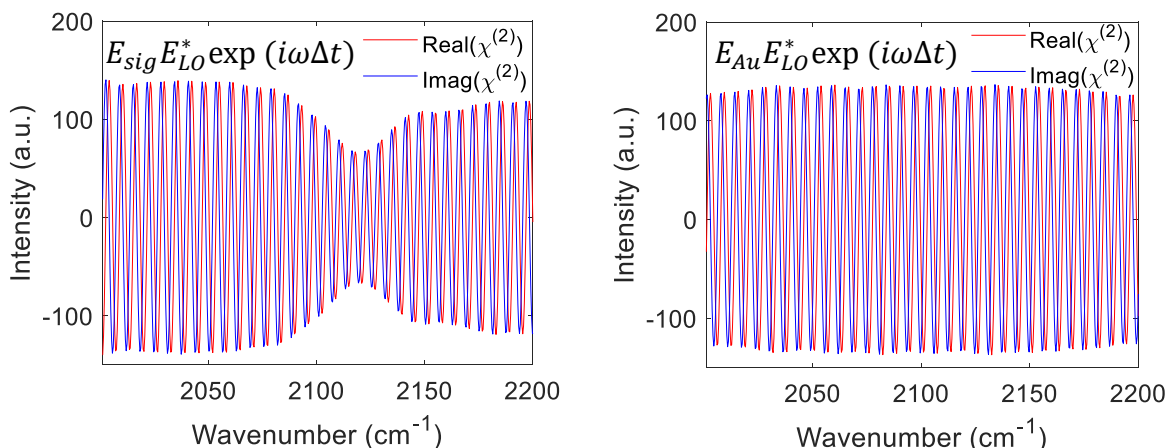


Figure 2.17 The result of taking the inverse Fourier transform of the filtered HD-VSFG data. Data is in the frequency domain with both real and imaginary components. The signal (left) and the gold reference (right) both have oscillatory features due to the interference with the local oscillator signal, defined by the equation inset within each plot.

The HD-VSFG experiments presented within this dissertation all utilize a clean gold surface as the reference signal. Any substrate that gives a large non-resonant background can be used as a reference, for example, quartz can be used as a reference signal.⁶⁴ Gold has a significant nonresonant SFG signal due to the surface plasmon resonance (SPR) with the visible pulse and

emitted SFG fields. Additionally, as a note, noble metals that have SPR characteristics typically give nonresonant SFG signals, such as silver and platinum, and can also be used as references.

Gold is a convenient reference to use in the gold/N3 chemical system because half of the gold mirror has been sensitized by the N3 solution, while the other half has been left clean and can be used as a reference. For TiO₂/N3 samples, the strip of gold that has been applied to the CaF₂ plates is used as the reference gold signal. By translating the sample stage laterally, the gold SFG signal can be acquired with minimal movement of the sample within the focal plane of the incident laser pulses. It is ideal to have minimal movement of the sample because changing the position in the beam path can alter the angle of incidence, phase, and overall signal intensity. The detected gold SFG signal still travels collinearly with the LO and creates an interferogram. A Fourier transform, filter window, and inverse Fourier transform are applied to the gold signal, identical to the procedure used for the sample signal.

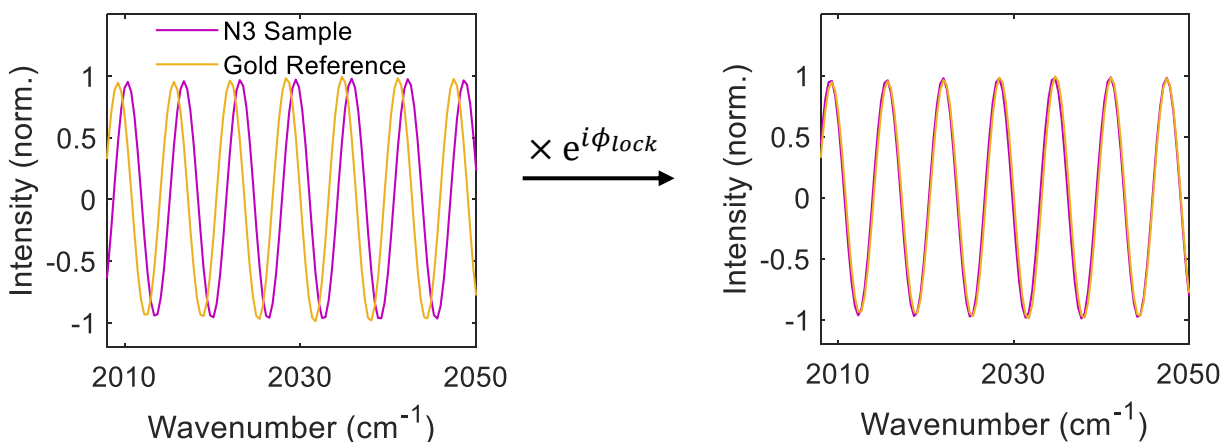


Figure 2.18 The phasing procedure used to match the phase of the sample to the reference. The left plot is an overlay of the real components of the acquired interferograms shown in Figure 2.17. The phase mismatch of the two detected signals is corrected by applying a phase factor to either the sample or gold signal.

Dividing the sample and reference signals shown in Figure 2.17 and 2.18 is represented by the equation 2.10 and removes the LO contribution to the signal. To correctly divide out the LO contribution, the phase of the interferograms must be matched or “locked” into one another.

Locking into the phase of the interferograms is done through a phasing procedure,⁵⁵ wherein the sample signal is multiplied by an exponential factor shown within Figure 2.18. The phase, ϕ_{lock} , within the exponential factor is determined by qualitative alignment of the sample signal and the reference signal. An example of the phasing procedure for N3 on gold using a gold reference signal is shown in Figure 2.18. Once the phase of the interferograms of the sample signal and reference signal are matched, division of the sample by the reference is done to acquire the second order susceptibility as a function of frequency and normalized to a gold background.^{55,57,63,65}

$$\frac{E_{sig} E_{LO}^* \exp(i\omega\Delta t)}{E_{Au} E_{LO}^* \exp(i\omega\Delta t)} = \frac{E_{sig}}{E_{Au}} \propto \frac{\chi_{sig}^{(2)}(\omega)}{\chi_{Au}^{(2)}(\omega)} \quad (2.10)$$

The last step in the data analysis is to account for the phase of the nonresonant background, which here is the phase of the gold SFG signal. The nonresonant background has its own phase offset, for example, quartz has a phase of 115° , silver has a $\frac{\pi}{4}$ phase, and gold has a phase of $\frac{\pi}{2}$ or 90° .^{42,57,66} Therefore, one last phase factor is applied to the processed data to account for the $\frac{\pi}{2}$ phase shift of gold by multiplying the denominator of equation 2.10 by $e^{(\frac{i\pi}{2})}$, or identically, i .

Finally, the $\chi^{(2)}$ of the N3 dye can accurately be plotted to investigate the vibrational modes of N3. Figure 2.19 shows an example of the resulting HD-VSFG spectra after the Fourier filter and phasing procedures are applied. The real and imaginary components of the second order susceptibility of the molecular system are resolved and plotted as a function of frequency. As described previously, the imaginary part refers to the absorptive component of $\chi^{(2)}$, while the real part refers to the dispersive component.

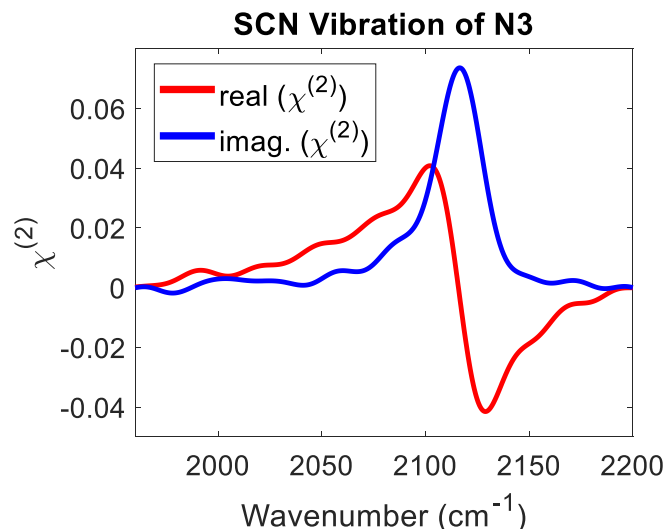


Figure 2.19 The end result of the Fourier filter and phasing procedure. The example HD-VSFG spectrum here is the $\nu(\text{NC})$ vibrational mode of the SCN group of N3. Both the real and imaginary components of the signal are shown.

2.5.2 TA Signal Processing

TA collection is done using the LabVIEW® program detailed in Appendix A. After calibrating the detector with the program and a neon lamp, one of the first steps required for a TA experiment (and for time-dependent experiments in general) is to define what is the “zero” time. Following the definition used here for time τ for our TA experiments, $\tau = 0$ s is when there is no temporal separation between the pump and probe pulses, meaning that they are overlapped temporally.

Finding $\tau = 0$ s is done by spatially overlapping the pump and probe pulses at a scattering sample and detecting the scattered light of both pump and probe pulses at $\sim 790\text{nm}$. Both pulses share this light in common because this is the fundamental wavelength used in both pump and probe lines and is still present in the pump and probe pulses. An interferogram is collected in the LabVIEW® program by collecting the and displaying the intensity of light as the motorized delay stage steps the pump pulse across a specified range. Interference fringes can be seen and grow in

intensity as the pump and probe pulses are brought closer in time with one another. At a certain delay stage position, the fringes reach a maximum, and the fringes will appear to “reverse” in direction as the delay stage continues to step. At the midpoint when the fringes appear to switch direction is the delay stage position that corresponds to $\tau = 0$ s. At this point, the user can put in the position into the program, define the motor positions for the start and ending position to define the temporal range of the TA experiment, and define the step sizes of the delay stage to designate how many data points (time steps) should be collected in the TA experiment.

The first step of data processing happens at each time step by the LabVIEW® program with the assistance of a data acquisition (DAQ) card. At each time step, the detector collects a number of pulses, specified by the user within the program. For our nonlinear optical spectrometer operating at a repetition rate of 1 kHz, this would mean that acquiring 1000 pulses of light takes approximately 1 second. The detected pulses of light, or shots, are taken consecutively with pumped and unpumped shots alternating in the collected signal. To determine which shots are the pumped versus the unpumped. Meanwhile, the DAQ card is reading the output signal from the chopper wheel, a voltage square wave that is read by the card as either a 1 or 0 for pump “on” and “off”. The chopper wheel is operating at 500 Hz, half the repetition rate of the spectrometer, and is being externally triggered by the timing clock used in the Wyvern 1000™ Laser Amplifier System. The after the consecutive collection of the specific number of shots, the DAQ card reads the final position of the chopper wheel signal, either being “on” or “off”. With the last shot being identified as the pump being “on” or “off”, the collected shots can be assigned as pump “on” or “off”. The data array of consecutive shots is then separated into two arrays, corresponding to “on” and “off” shots, and the logarithm and division of each on-off consecutive pairs is implemented. And finally, an averaging of the collected shot pair divisions is done to get the transient absorption

spectrum at one specific time point, $\Delta A = \langle -\log_{10} \left(\frac{pump}{unpump} \right) \rangle$. The DAQ card reading, pump “on-off” assignment, division, and averaging are all done at individual time steps by the LabVIEW® program. Stitching together multiple time steps gives a “full” transient absorption data set that is wavelength and time resolved. The data displayed in the program after running the TA experiment is saved and transferred to Matlab® for further data processing.

Importing data into Matlab® and general processing of the TA data is done using the code found in Appendix A. TA data is imported into Matlab® in the form of a two-dimensional array, with one dimension corresponding to the pixel number of the detector (wavelength) and the number of steps the delay stage position has taken (time). A wavelength axis is made by using the calibrated wavelength axis and the number of pixels (2048). The time axis is created by taking the zero position, starting position, and the step sizes and calculating the time it takes light to travel between the different stage positions.

Typical TA experiments performed herein take multiple TA spectra with different time steps, so it is important to stitch together the different TA experiments and correctly account for variate time steps when analyzing data. For example, an experiment with 30 time steps between 0 to 5 picoseconds and an experiment with 20 time steps between 5 to 50 picoseconds would need to be stitched together to have a complete TA experiment spanning 0-50 picosecond temporal window.

Once the imported TA data is stitched together, the entire array is smoothed along the frequency axis and averaged with other corresponding TA data arrays if the data set was acquired multiple times. Herein, TA experiments on MoS₂ were repeated 5 times. The first few time steps of the averaged data are typically “negative” time where there is no TA signal. These first few time steps are averaged together, and the array is subtracted across all other time steps to do a background subtraction. There is no molecular response at negative times, and therefore, averaging and subtracting the negative time “signal” allows for the removal of background noise from the detector. After stitching, smoothing, averaging, and background subtraction steps the resulting spectrum of a complete TA experiment will have data corresponding to the data set shown in Figure 2.20.

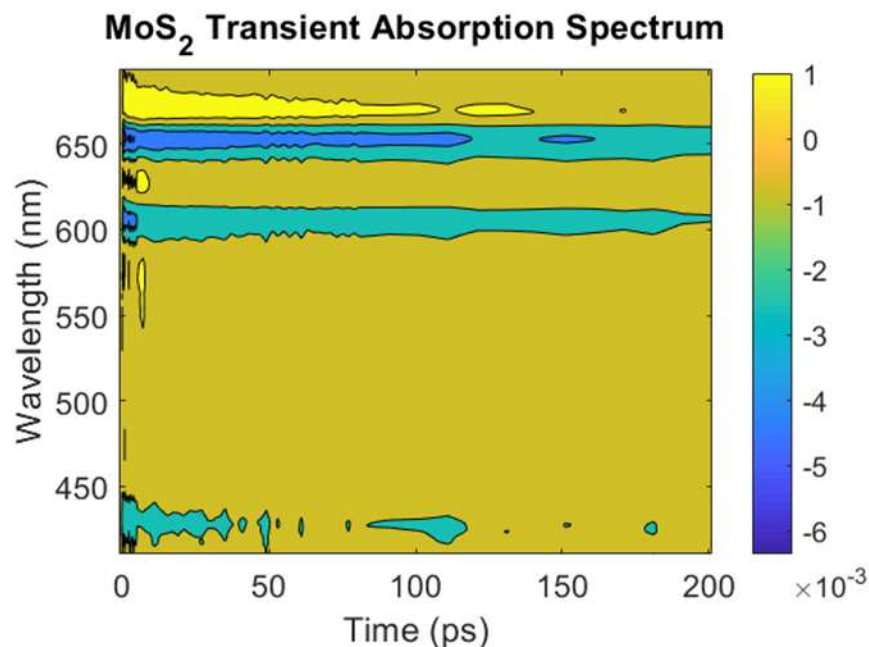


Figure 2.20 An example of a final TA spectrum that shows ΔA as a function of both wavelength (nm) and time (ps). The spectrum shown here is of MoS₂ and the bleach features for the A-, B-, and C-exciton species can be identified at 655 nm, 610 nm, and 430 nm, respectively.

2.5.3 Fourier Detection Method for TA

Presented in this section is the development of a Fourier filtering method to acquire the TA data in LabVIEW®. The LabVIEW code can be found in Appendix A. Data collection outlined in section 2.5.2 required the collection of N number of shots at each time step. The $N \times 2048$ array that is collected is split into two $\frac{1}{2}N \times 2048$ arrays, corresponding to the “pump” array and the “unpumped” array. The program then proceeds to divide element by element each of these two arrays and takes a logarithm, as outlined in the previous section. Problems with this method occur when N becomes large (>3000 consecutive shots) and the program becomes sluggish and data acquisition is slowed as a result. Using Fourier analysis and the fact that the TA signal occurs at 500 Hz, a Fourier filtering method can be done to speed up data acquisition.

At each time step, the LabVIEW® program stores the $N \times 2048$ array of shots at each time step in the TA experiment. The program then proceeds a $\log_{10}$ of the data followed by a fast-Fourier transform (FFT) along the pixel axis of the array, such that the program does the FFT of the one-dimensional array of $N \times 1$ for each of the 2048 pixels of the detector. The time step axis, N , is in the time domain with the detection the TA signal in time with a sampling frequency of 1 kHz, which is the repetition rate of the spectrometer. Performing a FFT brings the TA data into the frequency domain with the largest resolvable frequency at half the sampling frequency at 500 Hz, also known as the Nyquist limit. The ΔA transient absorption data can be resolved at precisely the pump “on-off-on-off” frequency, which is at half of the repetition rate of the spectrometer precisely at the Nyquist limit. The program then plots the intensity of the point at 500 Hz for each of the 2048 arrays that the program has performed an FFT. The 500 Hz amplitude is the value for ΔA of that pixel. The resulting graph is a plot of intensity versus the wavelength calibrated 2048 pixels.

The key takeaway from this detection scheme is that the data acquisition program struggles to create $N \times 2048$ arrays and do $\frac{1}{2}N \times 2048$ division and $\log_{10}$ operations for every time step when N is large. It is much quicker for the program to do 2048 FFT operations. Take for example a TA experiment with $N = 5000$ shots, this would be equivalent to 2500 pump and 2500 unpumped shots. The traditional data acquisition technique outlined in 2.5.2 would take between 20-30 seconds to process the 5000 shots and create a TA spectrum at a single time step; on the other hand, the Fourier detection method would take only 5 seconds. The Fourier detection method produces TA spectra almost instantaneously with respect to the repetition rate of the laser. A final note, the data acquisition technique presented in this section is a recent development to our TA spectrometer and the TA experiments shown within this dissertation do not utilize this Fourier detection scheme. However, future experiments should utilize this detection method for faster data collection.

2.6 Modelling and Fitting Spectroscopic Data

2.6.1 HD-VSFG Data Modelling

The goal of the modelling is to reproduce the spectral response of the molecular system for different polarization conditions. Then, the model can be applied and compared to the experimental data to acquire molecular information, specifically regarding the orientation. HD-VSFG signal can be modeled to acquire the orientation of the molecular oscillator at the interface. Polarization experiments are conducted to measure the second order signal as a function of polarization. The different incident polarizations, IR and Vis, will interact with the molecular system differently depending on the incident polarization. Similarly, the system will emit an SFG field that has a specific intensity which is polarization dependent. By modelling how the different polarizations

interact with the molecular system and the intensity of the second order signal, the orientation of the vibrational mode within the molecular system can accurately be determined.

The experimental data is reported as $\chi^{(2)}(\omega)$; therefore, a molecular model that describes the second order polarizability as a function of frequency is necessary. A commonly used line shape function in VSFG analysis is a Lorentzian line shape which has the functional form:^{47,67}

$$\chi^{(2)}(\omega) = \frac{\chi_q^{(2)}}{\omega_q - \omega_{IR} - i\Gamma_q} \quad (2.11)$$

Where subscript q denotes the vibrational mode, ω_q is the frequency of the resonant mode, ω_{IR} is the dependent variable, and Γ_q is damping constant of the molecular oscillator and determines the half width half max of the resonant spectral feature. The $\chi_q^{(2)}$ in the numerator governs the intensity of the spectral feature and is dependent on many criteria, including the polarization and transition dipole moment orientation.

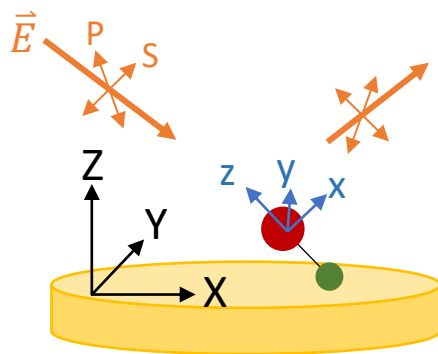


Figure 2.21 A cartoon molecular system describing the different coordinate systems used to model the HD-VSFG experimental system. Lowercase x, y, z coordinates are for the molecular frame, uppercase X, Y, Z are for the laboratory frame, and P and S represent the propagation and direction of the laser pulse polarization utilized in the experiment.

Briefly recalling $\chi_{IJK}^{(2)}$ is a 3rd rank tensor, the tensor elements are described by cartesian coordinates X, Y, and Z, with 27 elements in total (3x3x3).⁴² The X, Y, Z cartesian coordinates refer to the frame of reference of the molecular system within the laboratory, referred to here as the lab frame coordinates. The lab frame coordinates typically have the Z-axis lie along surface

normal and is shown within Figure 2.21 on a gold mirror as an example. The lab frame N3 system studied here has an azimuthally isotropic system, meaning the X and Y directions are identical, while the Z direction is not. The result is that $X = Y$, $X = -X$ and $Y = -Y$, but $Z \neq -Z$.

The symmetry conditions of the molecular system have consequences to the unique element values of $\chi_{IJK}^{(2)}$. Specifically, of the 27 tensor elements, there are only four non-zero and unique elements, being:

$$\chi_{ZXX}^{(2)} = \chi_{ZYY}^{(2)}, \chi_{XZX}^{(2)} = \chi_{YZY}^{(2)}, \chi_{XXZ}^{(2)} = \chi_{YYZ}^{(2)}, \chi_{ZZZ}^{(2)} \quad (2.12)$$

Therefore, it is important to implement polarizations that specifically select for these tensor elements. S-polarized light has an electric field vector that lies along the Y-axis of the laboratory frame shown in Figure 2.21 and will drive the molecular response along the Y-axis. Similarly, P-polarized light has both X and Z components and will drive the molecular response in both the X and Z direction.

The HD-VSFG performed in the work presented here utilizes PPP and SSP polarization schemes, with the first, second, and third letter corresponding to the sum frequency, visible, and IR polarizations, respectively. The measured, or effective, susceptibility can be expressed for each polarization scheme used as follows.^{42,56,68,69}

$$\begin{aligned} \chi_{PPP}^{(2)} = & -|L_{XX,SF}L_{XX,Vis}L_{ZZ,IR}| \cos(\gamma_{SF}) \cos(\gamma_{Vis}) \sin(\gamma_{IR}) \chi_{XXZ}^{(2)} \quad (2.13) \\ & - |L_{XX,SF}L_{ZZ,Vis}L_{XX,IR}| \cos(\gamma_{SF}) \sin(\gamma_{Vis}) \cos(\gamma_{IR}) \chi_{XZX}^{(2)} \\ & + |L_{ZZ,SF}L_{XX,Vis}L_{XX,IR}| \sin(\gamma_{SF}) \cos(\gamma_{Vis}) \cos(\gamma_{IR}) \chi_{ZZX}^{(2)} \\ & + |L_{ZZ,SF}L_{ZZ,Vis}L_{ZZ,IR}| \sin(\gamma_{SF}) \sin(\gamma_{Vis}) \sin(\gamma_{IR}) \chi_{ZZZ}^{(2)}, \end{aligned}$$

$$\chi_{SSP}^{(2)} = |L_{YY,SF}L_{YY,Vis}L_{ZZ,IR}| \sin(\gamma_{IR}) \chi_{YYZ}^{(2)}. \quad (2.14)$$

Here, γ is the angle from surface normal (angle of incidence) and L are the Fresnel coefficients. The equations here are identical to the ones presented in Chapter 3. Now, however, a brief overview of the calculation of the Fresnel coefficients is described.

The Fresnel coefficients, L , describes the light's reflective and transmissive properties when encountering a change in refractive index, such as encountering an interface like the N3/gold or N3/TiO₂ system. Equations for the Fresnel coefficients are expressed as^{56,69,70}

$$L_{XX} = \frac{2n_1 \cos(\theta)}{n_1 \cos(\theta) + n_2 \cos(\rho)} \quad (2.15a)$$

$$L_{YY} = \frac{2n_1 \cos(\rho)}{n_1 \cos(\rho) + n_2 \cos(\theta)} \quad (2.15b)$$

$$L_{ZZ} = \frac{2n_1 \cos(\rho)}{n_1 \cos(\theta) + n_2 \cos(\rho)} \left(\frac{n_1}{n'}\right)^2 \quad (2.15c)$$

where n_1 and n_2 are the refractive index of air and the substrate, respectively, and n' is the refractive index of the monolayer. Here, for N3, $n' = 1.2$. The angle of incidence of the light, θ , is related to the refracted angle, ρ , using Snell's law, $n_1 \sin(\theta) = n_2 \sin(\rho)$. Within the methodology presented here, and implemented within other groups,^{56,65,70} the complex nature of the refractive index is included in the calculation of the Fresnel coefficients.

The angle of incidence used in the Fresnel coefficient calculations are taken from the beam geometry outlined in the laser table setup for the HD-VSFG spectrometer. For the incident IR angle is $\theta_{IR} = 60.7$, for the visible the angle is $\theta_{Vis} = 66.2$. The output angle of the sum frequency field is calculated by considering conservation of momentum using the following equation

$$n_{SF}\omega_{SF} \sin(\theta_{SF}) = n_{Vis}\omega_{Vis} \sin(\theta_{vis}) + n_{IR}\omega_{IR} \sin(\theta_{IR}) \quad (2.16)$$

All angles and refractive indices can therefore be determined and input into the equations for the Fresnel coefficients. The Fresnel coefficients, once calculated, can be used in equations 2.13 and 2.14 to calculate the either $\chi_{PPP}^{(2)}$ or $\chi_{SSP}^{(2)}$.

The method above relates the polarization of the experiment to the lab frame coordinates. Next, for modelling data, the lab frame coordinates are related to the molecular frame coordinates of the oscillator, defined by the axis in Figure 2.21 as x, y, and z (lowercase). The molecular frame coordinates and second order molecular response is described by the molecular hyperpolarizability, β_{ijk} . By use of an Euler rotation matrix, the molecular frame can be projected into the laboratory frame. The resulting equations that relate the molecular frame hyperpolarizability of a linear molecular species (depicted in Figure 2.21) to the laboratory frame macroscopic second order susceptibility of the system are as follows:^{69,71,72}

$$\chi_{XXZ}^{(2)} = \chi_{YYZ}^{(2)} = \frac{1}{2}\beta_{zzz} \left(\langle \cos \theta \rangle \left(1 + \frac{\beta_{xxz}}{\beta_{zzz}} \right) - \langle \cos^3 \theta \rangle \left(1 - \frac{\beta_{xxz}}{\beta_{zzz}} \right) \right) \quad (2.17a)$$

$$\chi_{XZX}^{(2)} = \chi_{ZXX}^{(2)} = \frac{1}{2}\beta_{zzz} \left(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle \left(1 - \frac{\beta_{xxz}}{\beta_{zzz}} \right) \right) \quad (2.17b)$$

$$\chi_{ZZZ}^{(2)} = \beta_{zzz} \left(\langle \cos \theta \rangle \frac{\beta_{xxz}}{\beta_{zzz}} + \langle \cos^3 \theta \rangle \left(1 - \frac{\beta_{xxz}}{\beta_{zzz}} \right) \right) \quad (2.17c)$$

Here, θ is the Euler angle describing the angle between the molecular frame z-axis and the lab frame Z-axis and the brackets indicate an orientational average. The average accounts for the distribution of molecular oscillators in a chemical system; and, indeed, it is the collective response of the oscillators in a chemical system that gives the observable, macroscopic second order susceptibility. β_{zzz} and β_{xxz} are individual elements of the 3x3x3 hyperpolarizability tensor. Solving equations 2.17a-c and substituting them into equations 2.13 and 2.14 with the Fresnel coefficients (equations 2.15a-c), the effective second order susceptibility of the system for each

polarization condition can be solved for $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$. Plugging in these values to the line shape function in equation 2.11, an HD-VSFG spectra can be calculated for each polarization condition,

$$\chi_{PPP,calc}^{(2)}(\omega) = \frac{\chi_{PPP,q}^{(2)}}{\omega_q - \omega_{IR} - i\Gamma_q} \quad (2.18)$$

$$\chi_{SSP,calc}^{(2)}(\omega) = \frac{\chi_{SSP,q}^{(2)}}{\omega_q - \omega_{IR} - i\Gamma_q} \quad (2.19)$$

2.6.2 HD-VSFG Fitting Procedure

HD-VSFG experiments presented here probes the $\nu(NC)$ vibrational mode of the N3 isothiocyanate [SCN] group, which is a linear molecular species with a transition dipole moment, $\vec{\mu}$, that points from the carbon to the nitrogen. The dipole moment lies along the z-axis of the molecule. From equations 2.17a-c above, we can relate the molecular frame z-axis to the lab frame Z-axis through the Euler angle, θ . Therefore, the goal of the fitting procedure outlined here is to acquire the angle, θ , to get the orientation of the molecular frame z-axis, which is also conveniently the axis that the transition dipole moment lies along. Utilizing the equations outlined in the previous section 2.6.1, experimental data acquired can be fit with the HD-VSFG model equations to determine the transition dipole moment of SCN and elucidate orientation of N3-dye on the substrate

The fitting procedure is nearly identical for N3/gold, N3/TiO₂ and acetonitrile/N3/TiO₂ systems, the only key difference the refractive index, n , of the substrate needs to be accounted for when calculating the Fresnel coefficients. For gold, the refractive index values are $n_{IR} = 2.96 + i33.0$, $n_{Vis} = 0.1414 + i5.05$, $n_{SF} = 0.158 + i4.0$, and for TiO₂ the refractive index values are $n_{IR} = 2.1403 + i0$, $n_{Vis} = 2.3432 + i0$, $n_{SF} = 2.3729 + i0$.

First, the imaginary component of the acquired spectra is fit with the imaginary component of the Lorentzian line shape function using the Matlab® Fitting Toolbox. The default settings using the nonlinear least squares method in the toolbox are used to initially fit the spectrum. The parameters for the fit are the amplitude ($\chi^{(2)}$), the center frequency, ω_q , and the damping constant, Γ . This “pre” fit is simply done to set the center frequency and width of the line shape function. Once acquired, the ω_q and Γ are fixed during the simultaneous multi-fitting procedure to solve for the amplitude, $\chi^{(2)}$.

A simultaneous multi-fitting method is used to determine the transition dipole moment angle of the $\nu(NC)$ mode for each pH sensitizing condition. The simultaneous multi-fitting procedure is adapted from the open-source code on the Matlab® forums website with the title “nlinmultifit”. This code, shown in Appendix A, is a wrapping function that fits multiple sets of data with shared parameters. For equations that describe $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$, there are 3 parameters that are shared, being the transition dipole moment angle θ , the hyperpolarizability β_{zzz} , and the $\frac{\beta_{xxz}}{\beta_{zzz}}$ term which is simplified as a ratio term, r , for the fitting procedure.

For each pH sensitizing condition, the real and imaginary components of the experimental spectra of $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$ are fit to the calculated $\chi_{PPP,calc}^{(2)}$ and $\chi_{SSP,calc}^{(2)}$ equations for each vibrational mode. The N3/Gold samples have two vibrational modes, labeled as “low” and “high”, therefore there are a total of six parameters for the fit. The results for the parameters are tracked for each pH condition and used to investigate the pH-dependent orientation of N3 on gold and TiO₂ substrates.

2.6.3 TA Global Fitting and Population Dynamics

The aim of the TA experiments described in this dissertation is to monitor the MoS₂ exciton population, lifetime, and dynamics within an operational photoelectrochemical cell. There are

three photophysical processes that contribute to the detected transient absorption signal, ΔA , being the ground state bleach, stimulated emission, and excited state absorption. Ground state bleach intensity of the MoS₂ exciton species directly reports on the exciton population.^{32,60,62,73} Moreover, by monitoring the intensity increase/decrease of the exciton bleach in time, the exciton lifetime and photophysical dynamics can be studied. Therefore, the goal of the data analysis and fitting procedure is aimed at capturing the transient absorption bleach signal for all excitonic species of MoS₂.

Since it is the bleach feature that is of interest for understanding the exciton photophysical nature of MoS₂, the first step in the global fit is to fit the TA bleach features. Global fit here follows the following workflow: 1) fit each exciton bleach feature and every time point with a line shape function, 2) trace the fitted parameter in time, 3) fit the parameter with a functional form that captures photophysical processes as a function of time. This workflow is applied to the MoS₂ monolayer TMD sample on glass, ITO, and in flow cell conditions at different applied potentials. Keeping a routine workflow for each chemical sample is important for not introducing user bias to the fitting process in order to capture the photophysical and dynamic response of MoS₂ excitons. The following discussion is focused on the fitting and modelling of the TA data, and the Matlab® code that implements the following methodology is provided in Appendix A.

To begin, each exciton bleach feature of MoS₂ TA spectrum is fitted using a nonlinear least-squares regression model in the Matlab® fitting toolbox. This is done by taking the wavelength resolved spectrum of a TA experiment at each time point, specifying boundary conditions, and fitting with a gaussian function with amplitude, center wavelength, and peak width. An example of fitting at a single time point is shown in Figure 2.22.

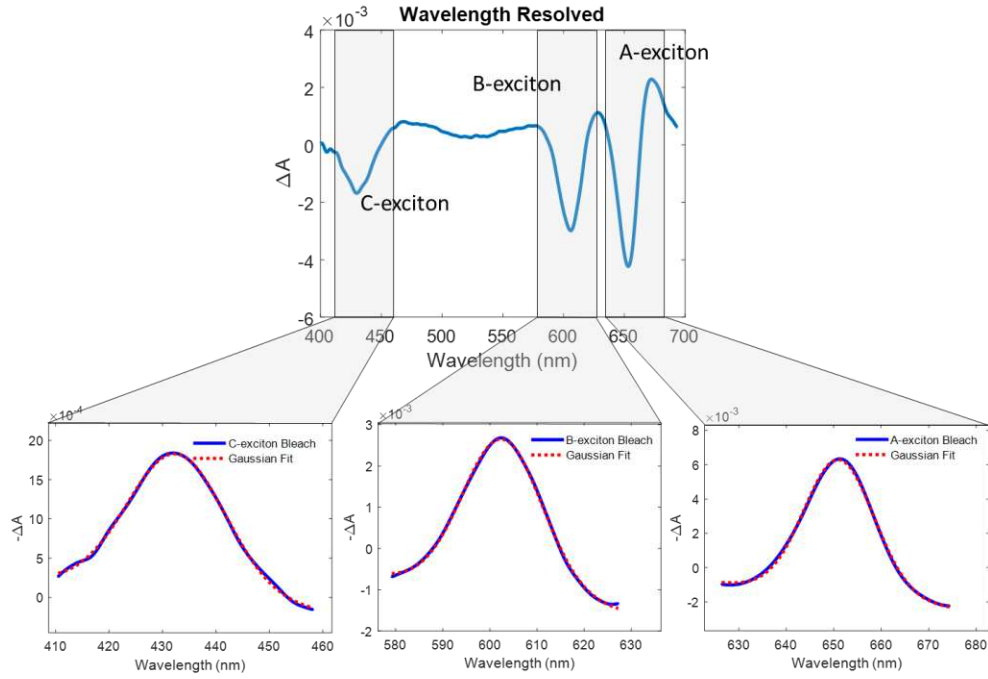


Figure 2.22 An example of the spectral fitting procedure done at every time step of the TA experiment to C-, B-, and A-exciton features. The wavelength resolved spectra is shown on top, and each exciton region is truncated and fit with a gaussian and linear polynomial. The plots on the bottom show the data (blue) with the fit (red). Plots on the bottom are flipped from the original spectrum, but the fitted results are the same except that the amplitude is positive instead of negative.

The fit applied to each exciton bleach feature is a linear combination of a Gaussian function with a linear polynomial (a line). The fitting function takes on the following form:

$$y(\lambda) = a_1 \exp\left(\left(\frac{(\lambda - b_1)}{c_1}\right)^2\right) + (d_1 * \lambda + f_1). \quad (2.20)$$

The first part of the equation is the Gaussian function. Here, a_1 is the amplitude of the bleach feature, b_1 is the center wavelength of the bleach corresponding to the resonant energy of the excitonic species, and c_1 corresponds to the width of the lineshape function related to the FWHM of the Gaussian. The second part of the fitting function, shown in equation 2.20, is the linear polynomial. The addition of a linear polynomial is to account for any baseline offset in the

spectra.⁷⁴ Each of the parameters (a_1, b_1, c_1, d_1, f_1) are recorded for each time point for each exciton.

The intensity of the gaussian function, a_1 in equation 2.20, is plotted versus the delay time, τ , of the TA experiment. Plotting the exciton bleach intensity versus time yields time resolved TA data for an individual exciton. An example of time resolved intensity decay for the A-exciton is shown as an example in Figure 2.23.

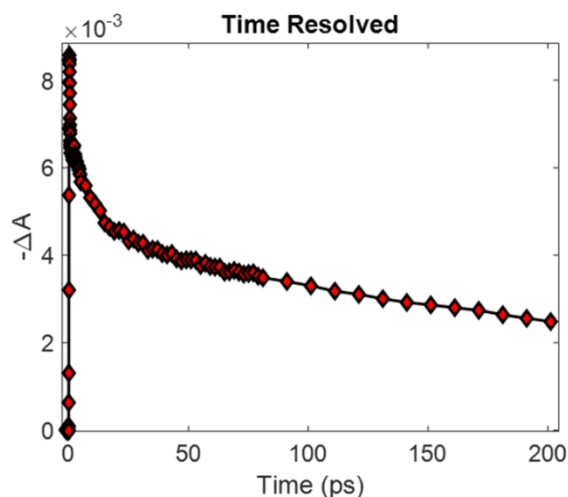


Figure 2.23 The resulting fitted amplitude of the gaussian for each time step plotted as a function of time. In this example, it is the decay of the A-exciton in time (red diamonds). The black line models the decay of the A-exciton population in time described by equation 2.21.

The intensity decay in time directly relates to the exciton population decay dynamics. With exciton lifetime and population dynamics, understanding the photophysical properties of the excitons in the presence of different applied potential within the photoelectrochemical cell can be investigated. By modelling the time resolved data set using a linear combination of exponential decay functions, the population and lifetime of each exciton can be realized.

Exciton intensity decay is modeled with a rising exponential function and a tri-exponential decay function for the A and B exciton species. The functional form of the applied model for the A- and B-exciton is shown in equation 2.21 below.^{73,75}

$$y(t) = \left(a_1 \exp\left(-\frac{t}{b_1}\right) + a_2 \exp\left(-\frac{t}{b_2}\right) + a_3 \exp\left(-\frac{t}{b_3}\right) \right) * \left(a_4 - \exp\left(-\frac{t}{b_4}\right) \right) + c \quad (2.21)$$

The first part of the function is the tri-exponential decay with amplitudes a and time constants b with subscripts 1, 2, and 3. The rising exponential function is for the fast, initial formation of the A- and B-excitons which happens on the order of approximately 200 femtoseconds. Additionally, an offset is applied to remove any residual non-zero offset of the TA exciton intensity; essentially, ensuring that as $t \rightarrow \infty$ the exponential decays go to zero intensity. The functional form for this fit is commonly used throughout TA analysis, but specific application to ultrafast TA of monolayer TMDs has been shown from other groups.^{29,60,73}

The tri-exponential is chosen for three reasons. First, a bi-exponential function is not able to capture the ultrafast dynamics of the exciton decay at times less than 1 picosecond and the long-time decay at times greater than 100 picoseconds. Second, the bi-exponential residuals are effectively reduced by applying a tri-exponential, indicating that fitting with a tri-exponential is not “over” fitting the temporal decay traces. And third, each of the exponential decay functions can be attributed to a known photophysical process of the exciton within the MoS₂ monolayer.^{29,30,73,75}

C-exciton intensity decay traces are modelled differently than the A and B excitons. The C-exciton is modeled using a bi-exponential decay that is convoluted with a gaussian instrument response function (IRF).⁷⁶ The functional form of the C-exciton fit is shown below in equation 2.22.

$$\begin{aligned}
y(t) = & \left(\frac{a_1}{2} \exp \left(- \left(\frac{1}{b_1} \right) \left((t - t_0) - \frac{c^2 \left(\frac{1}{b_1} \right)}{2} \right) \right) \right) \left(1 + \operatorname{erf} \left(\frac{\left((t - t_0) - \frac{c^2}{b_1} \right)}{\sqrt{2} * c} \right) \right) \\
& + \left(\frac{a_2}{2} \exp \left(- \left(\frac{1}{b_2} \right) \left((t - t_0) - \frac{c^2 \left(\frac{1}{b_2} \right)}{2} \right) \right) \right) \left(1 + \operatorname{erf} \left(\frac{\left((t - t_0) - \frac{c^2}{b_2} \right)}{\sqrt{2} * c} \right) \right)
\end{aligned}
\tag{2.22}$$

In equation 2.22, a and b are parameters that correspond to the exponential amplitude and the time decay, respectively. The value for t_0 sets the horizontal offset of the IRF function and the value for c is the width of the gaussian convolution that defines the IRF, which is typically near the FWHM value of the pump pulse of the TA spectrometer at approximately 50 fs. The C-exciton fit sufficiently fits the decay for all experiments and utilizes previous fitting methods within the literature. The convolution with the gaussian IRF is done only with the C-exciton because the pump pulse used in the TA experiments is at a similar wavelength to that of the C-exciton versus the A-, and B-excitons that are at lower resonant energies.

The exponential fits for the A- and B-excitons with equation 2.21 and C-exciton with equation 2.22 are done individually utilizing the fitting toolbox in Matlab®. The fitted parameters from the fits for the exciton bleach intensity decays can be compared side-by-side to identify exciton population dynamics. For example, the potential dependent decay dynamics of each exciton can be investigated for the MoS₂ photoanode used within the photoelectrochemical flow cells. Trends in the data can be identified to reveal potential dependent pathways and photophysical

responses of each exciton within the photochemical cell. This is discussed in more detail in chapters 6 and 7.

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CHAPTER 3 – THE pH-DEPENDENT ORIENTATION OF N3 DYE ON A GOLD SUBSTRATE IS REVEALED USING HETERODYNE-DETECTED VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

The work presented in this chapter is a publication of the American Institute of Physics in the Journal of Chemical Physics from March 2021. Authors of the paper are Yusef R. Farah and Amber Krummel from the department of Chemistry, Colorado State University, Fort Collins, CO. This paper was part of the Journal of Chemical Physics special collection in honor of women in Chemical Physics and Physical Chemistry.

3.1 Synopsis

We report systematic changes to the adsorption geometry of the dye, N3 ([cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II))], on a gold substrate as the pH of the deposition environment is altered. Protonation states of the four -COOH groups of the N3 dye change accordingly to modified pH conditions, affecting the number of -COOH and -NCS functional groups that participate in the adsorption to gold. Here we use heterodyne detected vibrational sum frequency generation (HD-VSFG) spectroscopy to obtain surface specific vibrational information on both -COOH and -NCS groups as a function of pH of the deposition conditions. Polarization-dependent HD-VSFG yields sets of complex $\chi^{(2)}$ spectra enabling us to perform a simultaneous fitting procedure to the polarization-dependent real and imaginary components, and thus, extract detailed structural information of the N3/gold interface. Our results show that N3 preferentially adsorbs to gold either with two -COOH groups and one -NCS group in more acidic conditions, or with one -COOH group and two -NCS groups in more basic conditions.

3.2 Introduction

Visible light harvesting chromophores have attracted widespread attention for their use in photocatalytic systems and photovoltaic devices. Specifically, transition-metal chromophores have been investigated for their application in organic syndissertation,^{1,2} water-splitting,³⁻⁵ carbon dioxide reduction,⁶⁻⁸ and dye-sensitized solar cells (DSSC).⁹⁻¹¹ The molecule commonly known as N3 dye ([cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II))], is a popular chromophore in the well-known family of Ru(bpy) transition-metal photocatalysts. N3 is often used in the fabrication of dye-sensitized solar cell devices and is regarded as one of the most efficient dyes to use in a DSSC.¹²⁻¹⁵ As new dyes are developed and studied for DSSC fabrication, N3 remains the benchmark to which new chromophores are often compared. Figure 3.1 shows the structure of N3 along with DFT geometry optimized structures illustrating the electron density corresponding to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). When N3 is photoexcited, electron density is transferred from the HOMO to the LUMO.¹⁶ The spatial separation of the HOMO and LUMO across N3 dye emphasizes the importance of molecular orientation of the dye in a photochemical device, because the location of the orbitals accepting or donating electrons will influence electron transfer kinetics within the photochemical device.^{17,18} Therefore, it would be advantageous to be able to control the orientation of the dye to promote desired chemical reactions and/or electron transfer kinetics within device architectures that use a light harvesting chromophore such as N3. To understand the parameters that influence the orientation of the dye molecule on an interface relevant to photochemical systems, such as an electrode surface, a technique to deduce the orientation of N3 at the electrode surface is required.

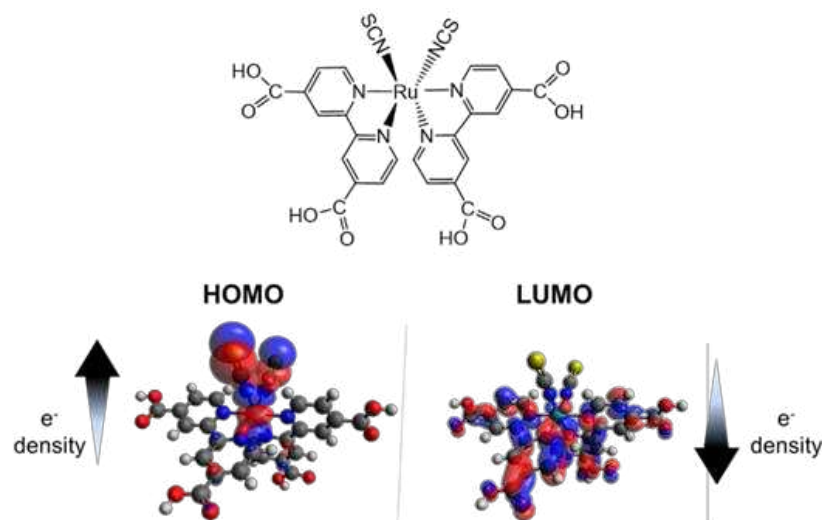


Figure 3.1 (Top) Chemical structure of N3 dye. (Bottom) N3 geometry optimized structure and molecular orbitals calculated using density functional theory under B3LYP functional and LANL2DZ basis set calculated with Gaussian09.^{36,58} The electron density corresponding to each molecular orbital is illustrated by the grayscale arrow, with a darker shade indicating a larger electron density. Colors for the atoms in the optimized N3 structure are: white = hydrogen, gray = carbon, red = oxygen blue = nitrogen, yellow = sulfur, and teal = ruthenium.

Previous studies have used methods such as ATR-FTIR and X-ray spectroscopic techniques to tease out the adsorption geometry of N3 on device-relevant substrates like gold and various metal-oxide semiconductors.^{19–25} ATR-FTIR yields information on molecular vibrational modes that can be used to hypothesize the binding motifs of N3; such experiments have been used to determine that the carboxylic acid groups of N3 are used to anchor the dye to a TiO₂ surface.²⁵ X-ray techniques, like glancing angle x-ray diffraction and x-ray photoelectron spectroscopy, have also been useful to study the binding modality of N3 on different substrates. These x-ray investigations reveal that choice of substrate and deposition conditions of the N3 dye can alter the resulting binding orientation and interfacial structure.^{19,23} However, the precise geometry of N3 binding orientations are still ambiguous and questions regarding the number of ligands bound to the substrate remain unanswered. Herein, we use heterodyne detected vibrational sum frequency generation (HD-VSFG) to monitor the adsorption geometry of N3 dye as a function of solution-

phase pH. Our results and analysis provide a more detailed description of the dye/substrate interfacial structure and the deposition conditions that impact the adsorption geometry of N3.

Vibrational sum frequency generation (VSFG) spectroscopy is a nonlinear spectroscopic technique that yields IR spectra of molecular species exclusively in non-centrosymmetric environments; the non-centrosymmetric environment here being the dye/electrode interface.^{26–30} Unlike conventional VSFG, the heterodyne detected or phase sensitive counterpart uses a local oscillator as a reference electric field to both preserve the phase information of the acquired signal and increase signal intensity.^{31–33} Phase sensitive detection gives a more detailed description of molecular adsorbates at a surface and an increased signal-to-noise ratio.³⁴ HD-VSFG has proven to be a useful technique to study the adsorption geometry of transition metal complexes on substrates such as gold and TiO₂.^{35–38} Previous studies using HD-VSFG attain a detailed molecular picture of the interfacial structure by determining the binding orientation and tilt angle of the transition metal complex to the substrate. The combination of surface specificity and phase information encoded in the acquired spectrum makes HD-VSFG spectroscopy a powerful approach for elucidating the binding geometry of N3 on a substrate unambiguously. In this work, we use HD-VSFG spectroscopy to investigate chemical parameters that influence the adsorption geometry of N3 on a gold electrode.

N3 has four auxiliary carboxylic acid groups, which in solution can individually be either protonated or deprotonated; consequently, there are up to five different protonation states of N3 that can exist in a solution.³⁹ A solution of N3, referred to as the sensitizing solution, is used for the fabrication of dye-sensitized photoelectrochemical cells and dye-sensitized solar cells. Once a substrate is introduced to the N3 sensitizing solution, N3 deposits onto the surface. The auxiliary carboxylic acid groups make up a majority of the N3 complex's periphery and are most likely

participating in the adsorption geometry of N3 to the substrate. Significant efforts have been made to understand the impact of the N3 protonation state on the binding geometry of N3 to a substrate, however this question remains unanswered. Previous studies investigated how N3 protonation states and relative acidity of the solvent might change the adsorption geometry, but an unequivocal understanding of the intricacies that influence N3 binding orientation due to the protonation/deprotonation of the carboxylate/carboxylic acid groups has not yet been realized.^{20,25,40} Herein, we investigate how incremental changes to the sensitizing solution's pH affects the protonation state of N3, which in turn influences the binding orientation onto a substrate, specifically, a gold electrode.

The protonation state of N3 in the deposition process is largely dictated by the pH of the sensitizing solution containing N3. For this investigation, we change the pH of the sensitizing solution to tune the distribution of N3 protonation species during the deposition process. We utilize the power of HD-VSFG spectroscopy measurements to identify preferential adsorption geometries for different protonation species of N3 to a gold electrode. The changes in observed dye orientation are expected to alter the electronic structure of the N3/gold interface, which can directly impact the photophysical processes in a light-driven chemical system.

3.3 Methods

3.3.1 N3 Sensitization on Gold Substrates

Unprotected gold mirrors were used as the substrate for all samples. N3 dye was purchased from Sigma Aldrich and used without any further purification processing. N3 dye was dissolved in a 1:1 mixture of deionized water and 200 proof ethanol to make sensitizing solutions held at 0.2 mM of N3 dye. Stock acid and base solutions were made by diluting HCl and NaOH in a 1:1 mixture of deionized water and 200 proof ethanol. Small amounts (10-275 μ L) of these stock

solutions were added to the 0.2 mM N3 sensitizing solution until the desired pH was achieved and measured using a Thermo Scientific pH probe (Orion Star Benchtop pH Meter). Sensitizing solutions were allowed to equilibrate upon addition of the acid/base for 5 minutes before measuring and recording the resulting pH.³⁹ Changes to the concentration of the sensitizing solution due to the addition of acid/base stock solutions were <5% of the starting concentration, and negligible to the dye loading conditions. A portion of the gold mirror was dipped in the resulting sensitizing solution for approximately 45 minutes at room temperature; the bare portion of the substrate was used as a reference for spectroscopic experiments. After sensitization the sample is left to air-dry for 5 minutes; thus, measurements are made of the N3/gold interface in air. The concentration of the sensitizing solution and sensitizing time duration were chosen to mimic dye loading procedures performed in previous studies.^{41–43}

3.3.2 Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy

HD-VSFG measurements were collected on our home-built SFG spectrometer described previously.³¹ Briefly, a Ti:sapphire-based regenerative amplifier (Wyvern 1000, KM Laboratories) is used to generate 3.4 mJ, <50 fs pulses centered at 790 nm at a repetition rate of 1 kHz. A beam splitter directs 80% of the output to an optical parametric amplifier (OPA, TOPAS Prime, Light Conversion) to generate tunable mid-IR short pulses carrying pulse energies of 25 μ J centered at 4760 nm, and 18 μ J centered at 5880 nm. The remaining 20% is used as the visible source and is passed through an interference filter (Andover Corporation) to create visible pulses with a FWHM of 0.5 nm (FWHM pulse duration of approximately 2 picoseconds assuming a transform limited pulse) centered at 790 nm. These pulses are overlapped in a 150 nm thick ZnO film deposited on a CaF₂ window to produce a local oscillator (LO) field with the wavelength centered at the sum frequency of the mid-IR and visible pulses.⁴⁴ The ZnO film on CaF₂ generates

a LO field that is comparable in magnitude with the SFG signal field generated from the sample and the gold reference. The LO pulse is passed through a 3 mm thick fused silica window to delay the LO field 5 picoseconds with respect to the visible and mid-IR pulses. The LO, visible, and mid-IR pulses are subsequently refocused onto the sample with incident angles of 65.6° , 66.2° , and 60.7° , respectively, relative to surface normal. Visible and IR fields are spatially separated from the VSFG signal that travels collinearly with the LO. The collinear VSFG signal and LO fields are dispersed in a spectrometer (iHR550, Horiba) equipped with a 1200 lines/mm grating and detected on a thermoelectrically cooled CCD camera (Synapse 2048 $\times$ 512, Horiba). Spectral resolution of our HD-VSFG spectrometer is limited by the bandwidth of our narrowband up-conversion visible pulse, giving our spectrometer a spectral resolution of 0.5 nm (8.2 cm^{-1}). The polarization of the signal field and incident visible and IR pulses are controlled using a half wave plate/wire grid polarizer combination. Polarization of the fields are denoted by P and S; P indicates a polarization that is parallel to the plane of incidence and S indicates a polarization that is perpendicular to the plane of incidence with respect to the sample. Polarization schemes used in this study were PPP and SSP, where the letters correspond to the VSFG signal, visible, and IR fields, respectively. PPP experiments were performed with a $15 \text{ }\mu\text{m}$ slit entrance into the monochromator, and measurements were averaged over 30 spectra with an acquisition time of 5 seconds for each spectrum. Experiments done with the SSP polarization scheme had a much lower signal; therefore, for SSP experiments, the entrance slit to the monochromator was set to $50 \text{ }\mu\text{m}$ and measurements were averaged over 10 spectra with an acquisition time of 30 seconds for each spectrum. The spectral resolution of PPP and SSP experiments (approximately 0.16 nm and 0.35 nm, respectively) are not affected by the different slit widths because the bandwidth of the visible up-conversion pulse (0.5 nm) is the limiting factor for the spectral resolution for both polarization

schemes. Furthermore, any change in intensity of the PPP and SSP experiments due to the change in slit width and integration time is inconsequential due to our normalization process. Each polarization experiment is normalized to the signal from a bare gold reference using identical experimental and acquisition methods for each respective polarization scheme.

3.3.3 Fourier Filtering and Normalization

The phase of the sum frequency signal field provides valuable information about the transition dipole moment of the oscillator at the surface, specifically the ‘up’ or ‘down’ orientation with respect to the surface normal.^{45,46} Here, a local oscillator impinging on a bare gold surface is used as a reference to preserve phase information of the VSFG signal generated at the N3/gold interface.^{33,34,37,41,47} Delaying the LO by 5 picoseconds allows for a Fourier filtering process to be performed to extract the heterodyned VSFG signal from the total VSFG signal field.

A complete description of the Fourier filtering process can be found in previous work by our group and others.^{34,41} Briefly, the raw data acquired appears as an interferogram in the frequency domain due to the LO and signal fields interfering with each other. A Fourier transform of the data into the time domain allows for the separation of the heterodyne signal from the homodyne signal using a filtering process. An inverse Fourier transform of the filtered signal brings the information back into the frequency domain. The resulting heterodyned signal from N3 on the gold substrate is normalized by dividing the signal with the reference signal, which in this case is the non-resonant sum frequency signal of gold, shown in equation 3.1. The normalized electric field acquired is directly proportional to the second order polarization, $\chi^{(2)}$, of the sample.

$$\frac{E_{sample}E_{LO}}{E_{gold}E_{LO}} = \frac{E_{sample}(\omega)}{E_{gold}(\omega)} \propto \frac{\chi_{sample}^{(2)}}{\chi_{gold}^{(2)}}, \quad (3.1)$$

$$\chi^{(2)} = \text{Re}(\chi^{(2)}) + i\text{Im}(\chi^{(2)}). \quad (3.2)$$

The phase of the substrate must also be considered in this data analysis. $\chi_{gold}^{(2)}$ has approximately $\frac{\pi}{2}$ phase shift in its signal due to the surface plasmon driven SFG signal. The surface plasmon contributes a non-resonant term that has been approximated by ourselves and others using phase-sensitive measurements to have a shifted phase of $\frac{\pi}{2}$.^{31,41,48–50} Thus, a 90° phase factor is also included in the denominator of the normalization step shown in equation 3.1. To ensure a consistent phase relationship in our normalization process, the interferogram of the sample is phased to that of gold.³⁴ The Fourier filtering and normalization process allows for the real and imaginary components of the second-order susceptibility, $\chi^{(2)}$ in equation 3.2 to be observed.

The resulting normalized HD-VSFG spectra of N3 on a gold surface has both real and imaginary components that describe the molecular susceptibility. The real part of the susceptibility refers to the dispersive component of the macroscopic polarization of the material, while the imaginary component refers to the absorptive property of the material. The HD-VSFG signal intensity is a function of the probed infrared intensity with an absorption maximum at the resonant frequency of the vibrational mode.

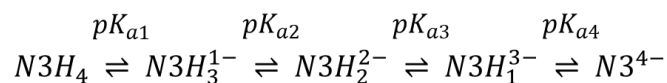
Our tunable infrared source allows us to probe different functional groups of the N3 dye, such as the carboxylic acids or the isothiocyanates. As we will show in the next section, probing these two functional groups of the adsorbed N3 dye yields different information; specifically, the protonation state of the adsorbed N3 species and the binding orientation of the dye on gold.

3.4 Results and Discussion

The spatial orientation and electronic structure of the N3 dye's HOMO and LUMO affects the performance of photocatalytic and photochemical systems. It is expected that the binding motif

of the N3 dye to the gold surface will depend on the protonation state of the N3 dye. The protonation state of the N3 dye can be controlled by changing the pH of the sensitizing solution used during the deposition of N3 onto a substrate.

Previous works identify up to five protonated species using UV-Vis spectroscopy in combination with DFT calculations.^{39,51} The possible five protonated species of N3 being the fully deprotonated N3^{4-} in solution at $\text{pH} > 7$; upon lowering the pH, N3H^{3-} , N3H_2^{2-} , N3H_3^{-} , and the fully protonated N3H_4 were identified. We performed similar pH dependent UV-Vis experiments and acquired spectra identical to previous reports used to identify the 5 protonation states of N3 in a water/ethanol solution. Four pK_a values, were determined in the previous study, one for each carboxylic acid of N3, shown in scheme 1. Reported pK_a values are $\text{pK}_{a1} = 1.33$, $\text{pK}_{a2} = 2.24$, $\text{pK}_{a3} = 3.45$, $\text{pK}_{a4} = 4.20$, and reflect the water/ethanol solvent conditions used within this chemical system.³⁹ Concentrations of each protonation state at a given pH can then be calculated from the pK_a values, as shown in the SI. It should be noted that UV-Vis studies were carried out using nitric acid to lower the pH of the bulk N3 solutions. For our HD-VSFG experiments we used hydrochloric acid to lower the pH of the sensitizing solutions because HCl will not contribute to the SFG spectra, whereas HNO_3 might contribute undesired signal to acquired SFG spectra. From the spectroscopic study, the dynamic range which captures all five protonation states of N3 falls between pH values of 1 and 7 for the sensitizing solution. Thus, the work presented here operates within the pH range from 1 to 7.



Scheme 1. Equilibria equation of N3 with showing different pKa values for each of the four carboxylic acids.

The 0.2 mM N3 dye sensitizing solution has a pH of 3.8 before any addition of HCl or NaOH. The pH of the sensitizing solution is tuned in order to change the protonation species of N3 adsorbed to the gold surface. Concentrations of protonation species in the sensitizing solution are calculated using pKa values. The HD-VSFG spectra shown in Figure 3.2 report on the carboxylic acid groups of N3 species adsorbed to the gold surface and reveal any changes to the adsorbed N3 protonation states as the pH of the sensitization solution is altered. The spectra here and throughout this report only show the resonant HD-VSFG features of the N3 and any offset due to the non-resonant contribution of gold has been accounted for and removed. Change in the carboxylic acid spectral response reports on the protonation state of N3 because the double bond $\nu(C=O)$ response is present in the carboxylic acid group ($-COOH$). However, when a carboxylic acid group is deprotonated, the double bonded $C=O$ is no longer present, and instead, a resonance structure between the two oxygens and carbon is formed in the carboxylate group ($-COO^-$).

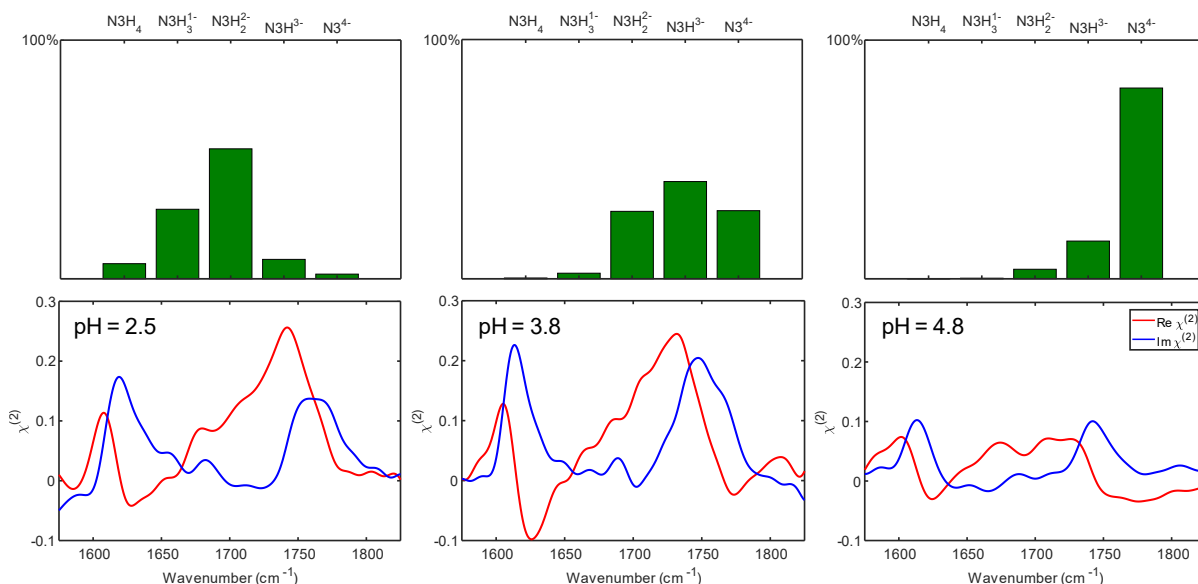


Figure 3.2 HD-VSFG spectra of N3 on gold using different pH sensitizing conditions, collected in a PPP polarization scheme. Red traces correspond to the real $\chi^{(2)}$ spectra and blue traces correspond to the imaginary $\chi^{(2)}$ spectra. Inset in the spectra are the pH values of the N3 sensitizing solution. The corresponding concentration of each protonation species existing in solution, shown here as a percentage, is noted above the spectra.

Two modes for the $\nu(\text{C}=\text{O})$ carbonyl stretch of the carboxylic acid are observed at 1750 and 1768 cm^{-1} in the HD-VSFG spectra corresponding to a pH = 3.8. The ring mode of the bipyridyl group is also present in the spectra at 1617 cm^{-1} . The two modes of the carbonyl are attributed to two environments, a carboxylic acid group adsorbed to the gold surface and a carboxylic acid group that is not adsorbed to the gold surface. The adsorbed carbonyl is assigned to the lower energy vibrational mode due to the decrease of electron density of $\nu(\text{C}=\text{O})$.⁵² The carbonyl that not adsorbed is assigned to the higher energy vibrational mode.

Addressed first is the intensity of the high-frequency (1768 cm^{-1}) carbonyl mode across the pH range in Figure 3.2. Deprotonating N3 by changing the sensitizing solution to pH = 4.8 makes the high-frequency carbonyl response disappear because the double bond character of the carbonyl

is no longer present once the carboxylic acid is deprotonated, forming the carboxylate. Decreasing the pH of the sensitizing solution (pH = 2.5) increases the detected signal of this high-frequency carbonyl mode, indicating a larger presence of the carboxylic acid groups of the N3 dye.

The low-frequency (1750 cm^{-1}) carbonyl mode remains present throughout the different pH conditions shown in Figure 3.2. This is because the adsorbed N3 species always has at least one carboxylic acid group in which the carbonyl is participating in the adsorption of the N3 species onto the gold substrate. When all carboxylic acids of N3 deprotonate to carboxylates at higher pH's, it is preferential for the dye to be solvated in the sensitizing solution rather than deposition onto the surface. Previous studies have arrived at a similar conclusion; suggesting that it is the carboxylic acid group that participates in the adsorption to a gold surface.^{21,23} The other carboxyl groups not adsorbed to the gold surface can be either carboxylic acids or carboxylates depending on the sensitizing pH conditions, resulting in the pH dependent high-frequency carbonyl mode shown in Figure 3.2.

Calculated concentrations of N3 protonation species validate our assignment of carboxylic acid modes contributing to the HD-VSFG spectra. For the pH=4.8 condition, over 95% of the N3 species existing in solution are the mono-protonated and fully deprotonated. Therefore, the spectral response of the carboxylic acid shown in Figure 3.2 at a pH of 4.8 is expected to originate from the monoprotonated species; and the lone protonated carboxylic acid of the monoprotonated species being adsorbed to the gold surface. Concentrations of di- and tri-protonated N3 species increase as the pH of the sensitizing solution is lowered, with the concentration of these species being approximately 84% of the N3 species present in a solution with a pH of 2.5. The increase of the di- and tri-protonated species explains the amplitude increase of the high-frequency, unadsorbed carboxylic acid relative to the low-frequency, adsorbed carboxylic acid.

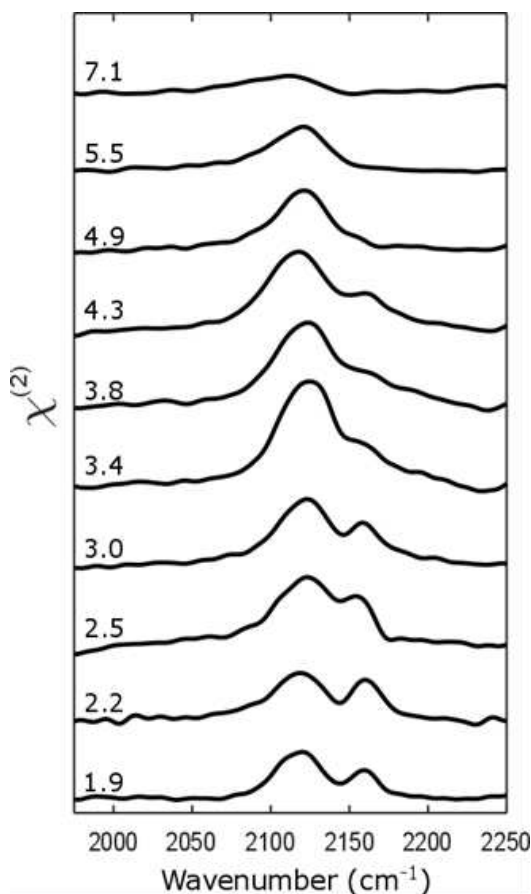


Figure 3.3 HD-VSFG spectra of N3 sensitized onto a bare gold mirror in different pH conditions. Spectra shown here are the imaginary component of $\chi^{(2)}$ and were all collected with a PPP polarization scheme. The real component is omitted and the spectra are offset for clarity. The pH of the sensitizing solution is tabulated to the left of each spectrum.

Changes in the carboxylic acid HD-VSFG spectra due to the pH of the sensitizing solution allows for the investigation of the protonation species of N3 adsorbed to the gold surface. However, to get a complete picture of the dye's orientation on gold with respect to the sensitizing solution's pH, we investigate the two isothiocyanate groups of N3. The isothiocyanate (NCS) ligands are convenient for elucidating the molecular orientation of N3 because the NCS ligand is linear and the resonant vibrational frequency $\nu(\text{NC})$ of NCS is in a convenient spectral window, with no spectral contributions from other molecular species.

The $\nu(\text{NC})$ stretch of the isothiocyanate on N3 is monitored to observe any changes in molecular orientation that are pH dependent. The imaginary component of the HD-VSFG spectra across a pH range are shown in Figure 3. Only the imaginary component in the PPP polarization scheme for each are displayed for clarity.

The HD-VSFG spectrum of N3 sensitized gold with no addition of HCl or NaOH (pH = 3.8) is shown in Figure 3 and exhibits a peak centered at 2120 cm^{-1} with a broad shoulder centered at 2169 cm^{-1} . The lower energy mode is attributed to an isothiocyanate group chemisorbed to the gold surface with a larger reduced mass contributing to the lower energy vibration.^{21,23,41} The shoulder at the higher energy is assigned to the second isothiocyanate, which is not bound to the surface. These assignments for the surface-bound, low-frequency vibrational mode and unbound, high-frequency vibrational mode for the isothiocyanate remain the same when interpreting spectra for all pH conditions shown in Figure 3.3.

When the sensitizing solution has a pH of 7 and greater, over 99% of the N3 species in the sensitizing solution are fully deprotonated. It is more energetically favorable for the fully deprotonated N3 species to be solvated than to be adsorbed onto the substrate. Therefore, the HD-VSFG signal of N3 decreases as we increase the pH from 3.8 and disappears once the sensitizing solution has a pH of 7 and greater. Figure 3.3 shows that altering the pH of the sensitizing solution changes the line shapes for both low- and high-frequency vibrational modes with little to no change in center frequencies, this result is attributed to different binding orientations of N3 protonation species on the gold substrate.

There are two NCS groups in the N3 complex and two spectroscopic features (low- and high-frequency modes) in the spectra in Figure 3.3. Therefore, we treat both vibrational modes as two independent linear oscillators when interpreting most of the resulting HD-VSFG spectra, the

exception being when there is only one spectroscopic feature. The acquired spectra shown in Figure 3.3 were fitted using a Lorentzian line shape function.²⁶ From the Lorentzian fit, the center frequencies across all pH conditions showed insignificant variation, however, the relative intensities as well as the full width at half maximum (FWHM) linewidths of the low- and high-frequency modes changed as a function of pH.

The two spectral features assigned to the bound and unbound NCS groups in Figure 3.3 have the smallest FWHM values when the sensitizing solution pH=1.9. As the pH of the sensitizing solution is increased from pH 1.9 to pH 3.8, the FWHM of both the low- and high-frequency vibrational modes broaden from 14 cm⁻¹ to 20 cm⁻¹ and 7 cm⁻¹ to 19 cm⁻¹, respectively. The broadening of the low- and high-frequency modes could arise from the larger distribution of protonation states existing in the sensitizing solution as the pH is adjusted. This would allow for more diverse binding environments of N3 to the gold surface, leading to inhomogeneous broadening of the spectra. At low pH, the protonation states are restricted to the more protonated N3 species, resulting in a narrow distribution of binding environments, thus resulting in narrower linewidths. Though Lorentzian linewidths are typically used to reflect homogeneous broadening, we acknowledge that both inhomogeneous and homogeneous broadening contribute to the FWHM of our fitted Lorentzian functions. The same fitting procedure was used for experiments set at pH of 4.9 and above, however, the amplitude for the high-frequency mode was < 0.01% compared to the low-frequency mode. Therefore, we assume no contribution to the spectrum from the unbound mode. The abrupt drop in intensity of the vibrational mode attributed to the unbound NCS indicates that the N3 is orienting differently on the gold surface such that this mode is no longer present, not to be associated with the gradual intensity decrease of the entire spectrum as the pH approaches 7

due to the favorability of N3 being fully solvated and hence leading to desorption of the N3 from gold.

To retrieve the orientation of the N3 dye on the gold surface, we model the intensity of our HD-VSFG spectra $\nu(\text{NC})$ stretching modes. Specifically, the relative intensity of the PPP and SSP spectra can be used to determine the direction and angle of the $\nu(\text{NC})$ transition dipole moment for each pH condition in this study. In order to extract quantitative information we use mathematical relationships derived for each polarization condition in order to retrieve the transition dipole moment angle from the acquired spectra.^{26,49,53,54}

Signal from the SFG or HD-VSFG experiment arises from the second order susceptibility, $\chi^{(2)}$, of the system. The second order susceptibility can be expressed for the specific polarization scheme used within the experiment, $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$. The subscripts describing the polarization scheme refer to the polarizations of the detected sum frequency (SF) signal, the incident visible (Vis) pulse, and the incident infrared (IR) pulse, respectively. Only certain elements of the molecular susceptibility, $\chi_{IJK}^{(2)}$, contribute to the total signal acquired according to the following expressions

$$\begin{aligned} \chi_{PPP}^{(2)} = & -L_{XX,SF}L_{XX,Vis}L_{ZZ,IR} \cos(\gamma_{SF}) \cos(\gamma_{Vis}) \sin(\gamma_{IR}) \chi_{XXX}^{(2)} \\ & - L_{XX,SF}L_{ZZ,Vis}L_{XX,IR} \cos(\gamma_{SF}) \sin(\gamma_{Vis}) \cos(\gamma_{IR}) \chi_{XXZ}^{(2)} \\ & + L_{ZZ,SF}L_{XX,Vis}L_{XX,IR} \sin(\gamma_{SF}) \cos(\gamma_{Vis}) \cos(\gamma_{IR}) \chi_{ZXX}^{(2)} \\ & + L_{ZZ,SF}L_{ZZ,Vis}L_{ZZ,IR} \sin(\gamma_{SF}) \sin(\gamma_{Vis}) \sin(\gamma_{IR}) \chi_{ZZZ}^{(2)}, \end{aligned} \quad (3.3a)$$

$$\chi_{SSP}^{(2)} = L_{YY,SF}L_{YY,Vis}L_{ZZ,IR} \sin(\gamma_{IR}) \chi_{YYZ}^{(2)}. \quad (3.3b)$$

Fresnel coefficients, L , are calculated for each input and output electric fields and depend on the refractive indices at the interface and the angle of incidence, γ , with respect to the lab frame

coordinates X, Y, and Z. Each element in the lab frame second order susceptibility tensor, $\chi_{IJK}^{(2)}$, can be expressed in terms of the molecular frame hyperpolarizability tensor elements, β_{ijk} , through rotational averaging and Euler rotation matrices. The hyperpolarizability can be described as the dot product of the molecular transition polarizability, α_{ij} , with the transition dipole moment, μ_k , where i, j , and k index the molecular frame Cartesian coordinates. Expressions for $\chi_{IJK}^{(2)}$ are then simplified under the approximation that the vibrational mode is azimuthally isotropic at the surface and each NCS group is a linear species,⁵⁵

$$\begin{aligned}\chi_{XXZ}^{(2)} &= \chi_{YYZ}^{(2)} = \frac{1}{2}\beta_{zzz}(\langle \cos \theta \rangle(1+r) - \langle \cos^3 \theta \rangle(1-r)), \\ \chi_{XZX}^{(2)} &= \chi_{ZXX}^{(2)} = \frac{1}{2}\beta_{zzz}(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle(1-r)), \\ \chi_{ZZZ}^{(2)} &= \beta_{zzz}(\langle \cos \theta \rangle r + \langle \cos^3 \theta \rangle(1-r)),\end{aligned}\tag{3.4a-c}$$

where $r = \frac{\beta_{xxz}}{\beta_{zzz}}$ and θ is the tilt angle of the transition dipole moment of the vibrational mode from the surface normal, Z, in the lab frame coordinates. A schematic of the tilt angle with respect to the lab frame coordinates is shown in Figure 3.4. With azimuthally isotropic symmetry considerations applied to the system, there are only three nonzero hyperpolarizability elements β_{zzz} and $\beta_{xxz} = \beta_{yyz}$; additionally, $\chi_{XXZ}^{(2)} = \chi_{YYZ}^{(2)}$ and $\chi_{XZX}^{(2)} = \chi_{ZXX}^{(2)}$.

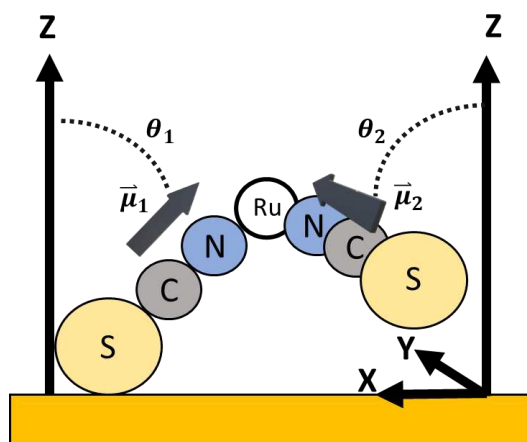


Figure 3.4 Representative schematic of each isothiocyanate group of N3 on a gold surface. The transition dipole moment μ of the $\nu(CN)$ stretch is pointing from the carbon to the nitrogen. Theta is the angle of rotation from the transition dipole to the lab frame Z axis. The surface bound NCS group (left) is in the XZ plane and the unbound NCS group (right) is in the YZ plane. Azimuthal symmetric considerations for each linear oscillator allow for any twist angle to be ignored and lab frame X or Y coordinates to be equivalent; thus, each dipole moment for each oscillator can be projected into the lab frame coordinates using its respective tilt angle θ_1 or θ_2 to the Z axis without any dependence on its position along the X or Y axis.

A Lorentzian line shape function (Eq. 5) is used to model the HD-VSFG spectra along with Eq. 3 & 4 shown above,

$$\chi^{(2)} = \chi_{NR}^{(2)} + \sum_q \frac{\chi_q^{(2)}}{\omega_q - \omega_{IR} - i\Gamma_q}. \quad (3.5)$$

Here, $\chi_{NR}^{(2)}$ is written explicitly into the expression and represents the non-resonant background generated from the substrate. Gold contributes a non-resonant background to the detected signal, however, for simplicity, this term is set to zero throughout the fitting.⁵⁶ The subscript q denotes the resonant vibrational mode and Γ is the damping constant, which gives the values of the FWHM discussed previously. The equations above are used in our fitting procedure to model the $\nu(NC)$

stretch and elucidate the molecular orientation of N3 dye as a function of the sensitizing solution pH.

To use the equations presented above for an orientational analysis both polarization experimental data, SSP and PPP, are utilized. Polarization intensity ratio (PIR) is a common method of VSFG analysis that is used to determine the orientation of a dipole moment using polarization experiments.^{26,49,53} Here, we implement identical equations used for a PIR analysis, but take advantage of the shared parameters between SSP and PPP by implementing a fitting strategy to simultaneously model the SSP and PPP experimental data.

Equations 3.3-3.5 are used to model the PPP and SSP experimental data of the $\nu(\text{NC})$ mode with β_{zzz} , r , and θ as fitting parameters. A simultaneous fit of these parameters to the real and imaginary components of the PPP and SSP spectra is carried out for each pH condition. Results of the fit are plotted with the experimental data in Figure 3.5. The spectra shown in this study are normalized and absolute quantities for the hyperpolarizabilities are relative, therefore, we report on the ratio, $r = \frac{\beta_{xxz}}{\beta_{zzz}}$. Typical methods to deduce the hyperpolarizability rely on other spectroscopic methods to extract the transition dipole and Raman polarizability, or alternatively, using calculations methods such as DFT.⁵⁷ Though we do not extract the exact values for the hyperpolarizability, the ratios yield valuable information about the vibrational modes. A small value for r indicates β_{xxz} has less magnitude compared to β_{zzz} , which is likely due to a slight electronic resonant enhancement that lies along the molecule's z-axis. Additionally, the small value for the ratio, r_{low} , seen in Table 1 for the low frequency mode across all pH conditions indicates that $\beta_{zzz} \gg \beta_{xxz}$. This result is anticipated because of an increase in the polarizability or transition dipole moment of the bound isothiocyanate to gold.⁴¹

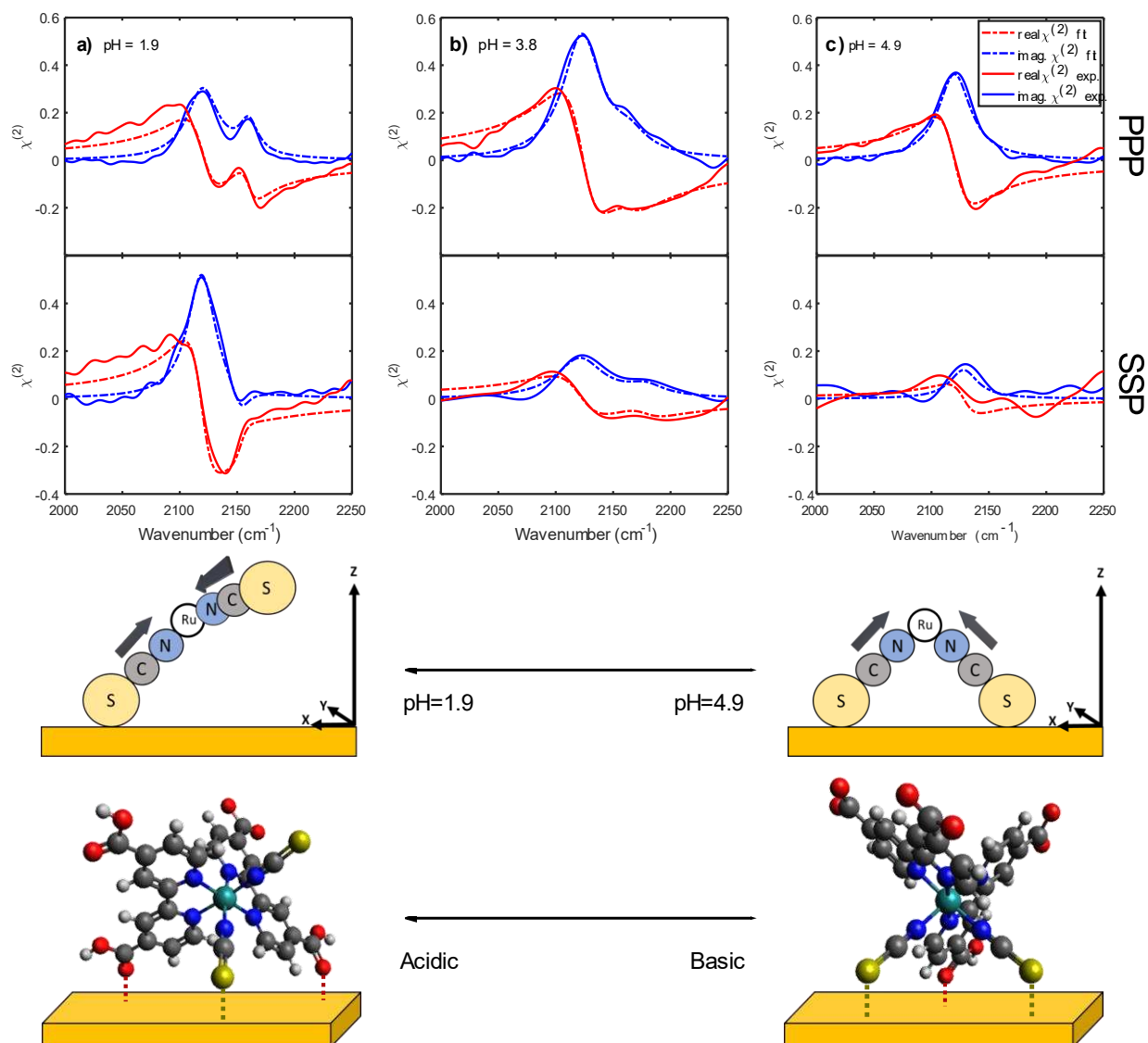


Figure 3.5. HD-VSFG spectra of the $\nu(\text{NC})$ stretch of adsorbed N3 onto a gold substrate in different pH sensitizing conditions. Panel (a) represents the acidic condition of pH = 1.9, panel (b) represents the starting sensitizing condition of pH = 3.8 with no addition of HCl or NaOH, and panel (c) represents the basic condition of pH = 4.9. The spectra on the top row were taken in a PPP polarization setup, while the bottom row was taken with an SSP setup. Solid lines in the spectra are experimental data and the dashed lines are the Lorentzian lineshape fits. Red traces correspond to the real $\chi^{(2)}$ spectra and blue traces correspond to the imaginary $\chi^{(2)}$ spectra. Below the spectra are schema of the N3 species' adsorption geometry onto the gold substrate in different acidic/basic conditions. Colors for the optimized N3 structure are: white = hydrogen, gray = carbon, red = oxygen, blue = nitrogen, yellow = sulfur, and teal = ruthenium.

Elucidating the orientation of the isothiocyanate groups allows us to deduce the adsorption geometry of the N3 dye to a gold electrode. The transition dipole moment of $\nu(\text{NC})$ on the isothiocyanate group is pointing from the carbon to the nitrogen. Fitted tilt angles for the low-frequency transition dipole moment (bound isothiocyanate) are within $72 - 76^\circ$ across all sensitizing pH conditions (Table 1). Indicating that while the protonation state of the N3 molecule is changing, the orientation of the adsorbed isothiocyanate group remains consistent and the transition dipole moment of $\nu(\text{NC})$ points upward with respect to surface normal. This is likely due to a preferential binding orientation of the sulfur on the isothiocyanate to the gold substrate.

Table 1. Fitting results for the tilt angle and hyperpolarizability ratio parameters for the low- and high-frequency $\nu(\text{NC})$ vibrational modes of the isothiocyanate groups. Error bars for transition dipole moment angles report $\pm 5\%$ of $\chi(\omega_q)$ of our fit from experiment.

pH	θ_{low}	r_{low}	θ_{high}	r_{high}
1.9	75.5 ± 0.05	0.0082	135.6 ± 0.04	-1.159
3.8	72.8 ± 0.15	0.0035	82.9 ± 0.34	0.079
4.9	72.0 ± 0.16	0.0076	—	—

Deposition of N3 with the sensitizing condition at $\text{pH} = 3.8$ results in an average fitted angle of 82.9° for the high-frequency $\nu(\text{NC})$ transition dipole moment. This value is consistent with our previous work and illustrates a similar binding geometry for N3 on a gold surface; one surface bound NCS, low-frequency $\nu(\text{NC})$ mode pointing upwards, and one unbound NCS, high-frequency $\nu(\text{NC})$ mode pointing upward, but nearly orthogonal to the surface normal.⁴¹ This binding scheme for the isothiocyanate groups at a $\text{pH} = 3.8$ is shown in Figure 3.4. The

hyperpolarizability ratio r_{high} is larger than r_{low} indicating that the unbound isothiocyanate has a smaller value for β_{zzz} compared to β_{xxz} because it is not bound to the surface, therefore the increase to the polarization or transition dipole moment is weakened by not being directly chemisorbed to gold.

The fitted angle to the high-frequency mode (θ_{high}) for the acidic condition of pH = 1.9 is approximately 135.6°, which suggests that this vibrational mode is oriented downward, unbound, and pointing toward the gold substrate. This validates our assignment of the high-frequency mode in the spectra to an unbound isothiocyanate group. Our determined orientation of the fully protonated N3 species on gold is similar to the proposed orientation of a fully protonated N3 on gold in previous work.²³ Furthermore, the hyperpolarizability ratio for the unbound, high-frequency mode with a pH = 1.9 is drastically different than the bound isothiocyanate. Being oriented away from the gold surface lowers the value of β_{zzz} because the polarizability or the dipole moment is no longer increased by being bound to the gold surface. The negative value of r_{high} also indicates a change in the electronic structure of the N3/gold interface due to the significant reorientation of the dye on the substrate. Therefore, our results show that tuning the pH conditions from 3.8 to 1.9 changes the average molecular orientation of adsorbed N3, and consequently, alters the electronic structure of the N3/gold interface.

With pH conditions of 4.9 and above, only a single peak is present in the HD-VSFG spectra at the same energy corresponding to the low-frequency vibrational mode (Figure 3.3). However, the vibrational mode is no longer a single bound isothiocyanate, but instead, a normal mode corresponding to the asymmetric stretch of the two isothiocyanate ligands. In this case the N3 has oriented on the surface such that both isothiocyanate groups are bound to the gold substrate, resulting in the loss of the high-frequency, unbound isothiocyanate vibrational mode. Performing

our fitting procedure to a sensitizing solution with pH = 4.9 results in 72° for the transition dipole angle, similar to the binding angles acquired for the bound isothiocyanate groups in the other pH conditions. Moreover, the ratio (r_{low}) of the hyperpolarizabilities reflects the same enhancement to the β_{zzz} element for adsorbed isothiocyanate groups.

The complete picture of the adsorption geometries in Figure 3.5 shows that one isothiocyanate is always adsorbed to the surface across all pH conditions. Starting at the most acidic condition of pH=1.9, the unbound isothiocyanate is not adsorbed to the gold substrate and its dipole moment is pointing downward with respect to surface normal. Increasing the pH of the sensitizing solution pivots the deposited N3 dye on the gold substrate, bringing the average orientation of the unbound isothiocyanate closer to the gold surface (pH=3.8, Figure 3.4) while keeping one NCS group bound to the gold surface. Many protonation species are likely contributing to the HD-VSFG signal with deposition conditions of pH=3.8, lending to the spectral broadening of the $\nu(\text{NC})$ signal. Further increasing the sensitizing solution to pH=4.9 brings down the unbound isothiocyanate, until it is bound on the surface, such that both isothiocyanates are adsorbed onto the gold substrate. With both isothiocyanate ligands bound to the surface, the molecular orbital associated with the LUMO of N3 dye is spatially near the gold surface. The electronic structure of the N3/gold interface for sensitizing conditions of pH=4.9 would be advantageous if electron transfer events were desired between a gold electrode and the LUMO of N3. For example, upon photoexcitation of N3 dye, the LUMO is electron deficient; therefore, a gold electrode can replenish this electron deficiency in the LUMO favorably if sensitization of the gold electrode occurred in a pH=4.9.

In the pH=1.9 sensitizing condition, two carboxylic acid groups participate in the adsorption onto gold; carboxylic acid groups situated away from the gold surface lend to the

observed high-frequency carbonyl mode (Figure 3.2). As an example, the schematic in Figure 3.5 that pertains to a pH=1.9 shows a tri-protonated species of N3 with two of the three carboxylic acid groups directly adsorbed to gold. With sensitizing conditions of pH=1.9, the orientation of N3 positions the electron density of the HOMO near the gold surface, this is because the HOMO of N3 resides primarily on the bipyridyl-carboxyl ligands of N3. With a sensitizing solution of pH=4.9, the monoprotated N3 adsorbed to the surface only has one carboxylic acid adsorbed to the surface. The carboxylate groups are oriented away from the surface in a sensitizing condition of pH = 4.9, consequently positioning most of the electron density associated with the HOMO of N3 away from the gold surface. The interpretation of our HD-VSFG experiments reveal that preferential binding orientations of N3 dye and the electronic structure of the dye/gold interface can be influenced by changing the pH during deposition.

3.5 Conclusion

We have shown that the pH of the sensitizing solution determines the protonation species of N3 adsorbed onto a gold substrate, and thus, directly affects the molecular orientation and electronic structure of N3 on gold. The spectra acquired for the carboxylic acid, along with our rigorous orientation analysis of the isothiocyanate groups, allows us to make the following conclusions. The tri-, and fully-protonated species of N3 preferentially adsorb with two carboxylic acid groups and one isothiocyanate group bound to the gold surface. The two adsorbed carboxylic acids retain their acidic proton, while the two carboxylic acid groups not adsorbed can become deprotonated depending on the pH conditions upon deposition. Conversely, the mono-protonated species adsorbs with one carboxylic acid group and both isothiocyanate groups bound to the gold surface. The relatively higher pH of the sensitizing solution (pH=4.9) decreases the amount of carboxylic acid groups available for adsorption onto the gold surface, which allows both

isothiocyanate groups to be bound to the gold surface. The di-protonated species could take either binding motifs proposed here depending on which two carboxylic acid groups are deprotonated.

The change of N3 orientation due to the pH of the sensitizing solution is accompanied with a change in electronic structure of the interface. This has been shown with the changing values of the hyperpolarizability ratios for isothiocyanate groups in different binding orientations due to pH conditions. Additionally, orientation of the dye affects the electronic structure of the interface due to the positioning of the LUMO and HOMO of N3 relative to the surface. A change in electronic structure would have a direct impact on the efficiency of photochemical systems if these structural changes affected electron kinetics, quantum yield, or chemical reactions. This report has focused on using a gold substrate for the N3 sensitization. It is anticipated that pH conditions could also affect the binding orientation of N3 in systems where semiconductors, such as TiO₂ or ZnO, are used as the primary substrate for sensitization processes. HD-VSFG is a powerful spectroscopic technique that provides insight on the conditions that effect the molecular geometry and electronic structure of an interface. Tunability of the electronic structure of photocatalysts like N3 in photochemical and photovoltaic devices is an integral step needed to make these systems more efficient.

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CHAPTER 4 – THE N3/TiO₂ INTERFACIAL STRUCTURE IS DEPENDENT ON THE pH CONDITIONS DURING SENSITIZATION

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4.1 Synopsis

The electronic structure of the N3/TiO₂ interface can directly influence the performance of a dye sensitized solar cell (DSSC). Therefore, it is crucial to understand the parameters that control the dye's orientation on the semiconductor's surface. A typical step in DSSC fabrication is to submerge the nanoparticulate semiconductor film in a solution containing the dye, the sensitizing solution. The pH of the N3 sensitizing solution determines the distribution of the N3 protonation states that exist in solution. Altering the pH of the sensitizing solution changes the N3 protonation states that exist in solution and, subsequently, the N3 protonation states that anchor to the TiO₂ substrate. We utilize the surface specific technique of heterodyne detected vibrational sum frequency generation (HD-VSFG) to determine the binding geometry of N3 on a TiO₂ surface as a function of the sensitizing solution pH conditions. It is determined that significant reorientation of the dye occurs in $\text{pH} \leq 2.0$ conditions due to lack of N3-dye carboxylate anchoring groups participating in adsorption to the TiO₂ substrate. Consequently, the change in molecular geometry is met with a change in interfacial electronic structure that can hinder electron transfer in DSSC architectures.

4.2 Introduction

Dye sensitized solar cells (DSSCs) have garnered attention since their development and modernization with the Gratzel cell in 1991.¹ DSSCs have the potential to be an inexpensive, non-toxic, environmentally friendly source of sustainable solar energy. During the past three decades, there have been many studies aimed towards improving DSSC device performance for its viability as a source of electricity in today's energy economy.²⁻⁸ However, despite ongoing research, DSSCs have yet to exceed an overall efficiency of 13%. It is therefore of paramount importance to study the underlying physics and chemistry involved within DSSC devices to improve performance. Specifically, in this report, we investigate the solution parameters that influence the dye/semiconductor interfacial structure within DSSC architectures.

The working electrode of DSSCs are typically fabricated with a semiconductor thin film, often anatase TiO₂ nanoparticles, deposited on a conducting glass surface (Figure 4.1).^{1,9,10} The semiconductor is sensitized with a visible light harvesting chromophore that, upon excitation of sunlight, transfers an electron to the conduction band (CB) of the semiconductor, which starts the generation of electrical current in the cell. The chromophore studied herein {[*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II))]}, commonly known as N3 dye, is an efficient and popular dye used in photocatalytic, photoelectrochemical, and DSSC devices.¹¹⁻¹⁵ Here, we investigate the N3/TiO₂ chemical system due to the widespread interest, industrial relevance, and vast literature precedent this system holds within DSSC and other photoelectrochemical applications.

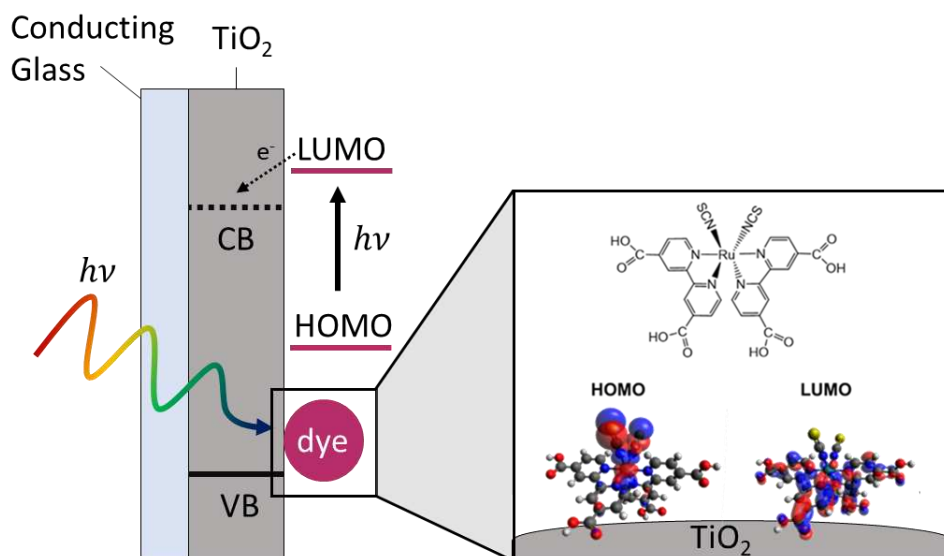


Figure 4.1. Schematic of the DSSC working electrode. The dye absorbs sunlight ($h\nu$) and transfers an electron to the conduction band (CB) of the semiconductor, TiO_2 . The N3-dye molecular structure and the electronic structure of the HOMO/LUMO are shown within the inset. DFT optimized structures were generated using the B3LYP functional and LANL2DZ basis set in Gaussian09.^{40,64} Colors for the atoms in the optimized structure are: white = hydrogen, gray = carbon, red = oxygen, blue = nitrogen, yellow = sulfur, and teal = ruthenium.

N3 dye is an excellent absorber of sunlight with the absorption primarily associated with the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).^{16–18} Once promoted to an electronic excited state, N3 can transfer an electron to the CB of TiO_2 . The electron density of N3 dye's LUMO is ideally positioned near the TiO_2 surface to facilitate favorable electron transfer from dye to semiconductor due to the spatial dependence of electron transfer reactions.^{19–21} Alternatively, if the HOMO is oriented near the semiconductor, back electron transfer (BET) from TiO_2 to N3 is more likely to occur and hinder the generation of electrical current in a DSSC.^{22–24} Therefore, it can be understood that the molecular orientation and electronic structure of the dye/semiconductor interface directly impacts electron transfer efficiency and can influence a DSSC's overall performance.

A multitude of methods have been implemented to elucidate the nature and structure of the N3/TiO₂ interface. ATR-FTIR studies have shown that N3 (and similar organometallic dye analogs) bind using the carboxyl groups and indicate that the binding is primarily through Ti-O bond formation.²⁵ DFT calculations corroborate experimental ATR-FTIR experiments and indicate many possible binding modalities of N3.^{17,26} From these previous studies, it becomes clear that the ambiguity surrounding the structure of N3/TiO₂ is the number of carboxylate/carboxylic acid groups participating in the binding. Additionally, UHV studies have indicated the possible binding of the isothiocyanate group with rutile TiO₂,²⁷ and more recently, studies have alluded to the mixing of binding modalities.^{23,28,29} It becomes problematic to isolate a definitive answer of the interfacial structure when experimental results are not surface sensitive and the experimental conditions vary. In this investigation, we use the interface-selective spectroscopic technique of heterodyne detected vibrational sum frequency generation (HD-VSFG) to identify the structure of N3 on nanoparticulate TiO₂ thin films.

Vibrational sum frequency generation (VSFG) is a second order, non-linear spectroscopic technique that yields molecular vibrational data exclusively in non-centrosymmetric environments; in this case the N3/TiO₂ interface. VSFG has been utilized for decades to study interfacial molecular structures. Heterodyne detected or phase sensitive VSFG spectroscopy in which the phase of the detected signal is retrieved, provides a picture of the absolute molecular orientation.^{30–33} Heterodyned detection of the signal provides the added benefit of increased signal-to-noise compared to conventional VSFG.³⁴ HD-VSFG has proven to be a powerful spectroscopic technique to study transition metal complexes on multiple surfaces.^{35–37} Previously, we reported the absolute orientation of N3 on TiO₂ utilizing HD-VSFG wherein it was shown the orientation of N3 deposited on TiO₂ is significantly different than on gold.³⁸ In this work, we

explore parameters that influence N3 orientation on TiO₂ and unravel the ambiguity surrounding the interplay between dye and semiconductor. Specifically, we are interested in how the acid/base conditions of the sensitizing solution influences N3 binding orientation on TiO₂.

The pH of the sensitizing solution sets the protonation states of the N3 carboxyl groups existing in solution during the sensitization of TiO₂.^{39,40} Since N3 dye anchors to the TiO₂ surface using its carboxyl groups, we hypothesize that altering the pH of the sensitizing solution, and thus the protonation state of the N3 carboxyl groups, will give rise to a specific adsorption geometry of N3 and the electronic structure of the N3/TiO₂ interface. The pH condition of semiconductor film preparation has been studied in previous reports and has been shown to alter TiO₂ surface charge, dye packing efficiency, short-circuit current density, and dye/semiconductor structure.^{3,18,25,29,41,42} However, the interplay between pH conditions, N3 protonation states, and the subsequent binding geometry on TiO₂ remains unknown. Thus, we explore how the sensitizing pH conditions influences the binding geometry of N3 on TiO₂ by utilizing HD-VSFG to unambiguously determine the pH dependent orientation of N3 dye on the semiconductor surface.

4.3 Methods

4.3.1 N3 Sensitization of TiO₂ Nanoparticulate Thin Films

Titanium dioxide nanoparticulate thin films were prepared on calcium fluoride substrates by procedures adapted from previous studies.^{43,44} Anatase TiO₂ nanoparticles (5 nm diameter, US Research Nanomaterials) are dispersed in a 1 g/L suspension in water and sonicated before drop casting 7 μ L of the suspension onto a clean UV-grade calcium fluoride (Crystran, Ltd) 1" diameter window. The CaF₂ window has a ~200nm strip of bare gold, located away from the drop cast area, which has been grown using physical vapor deposition and serves as the reference for the HD-VSFG measurements. The drop cast area is approximately 1 cm in diameter, is dried in air, and

yields a uniform nanoparticulate film that is <200 nm in thickness.⁴³ TiO₂/CaF₂ plates are heated to 300°C on a hot plate and illuminated with 365nm UV light for 30min to clean the TiO₂ thin film.^{45,46}

Sensitizing solutions were made using N3 dye (Sigma Aldrich) dissolved in 1:1 deionized water:200 proof ethanol to make 0.2 mM N3 sensitizing solutions with a pH = 3.8. Small amounts of dilute HCl (<300 μ L) are added to the sensitizing solution to titrate to the desired pH which is measured using a Thermo Scientific pH probe (Orion Star Benchtop pH Meter). The total volume of the sensitizing solution is 10 mL, and therefore, the small addition of dilute HCl negligibly effects the overall concentration of the sensitizing solution. The TiO₂ film portion of the CaF₂ plate is submerged in the N3 sensitizing solution and the gold strip portion of the plate is not submerged. Sensitization is done for approximately 1 hour. The 1-hour time frame allows for sufficient TiO₂ film coverage and equilibrium of sensitizing solution and film to be established.^{25,47} Films are rinsed repeatedly with water:ethanol solutions to remove any unbound N3 and N3 aggregates on the surface. Rinsing solutions have been titrated with dilute HCl to match the pH of the respective sensitizing solution as to not alter the acid-base chemistry of the films.

4.3.2 Heterodyne-Detected Vibrational Sum Frequency Generation Spectrometer

HD-VSFG experiments are done using our home-built spectrometer, described in previous reports.^{48,49} Briefly, 3.3 mJ, <50 fs pulses centered at 790 nm are generated in a Ti:sapphire regenerative amplifier (Wyvern 1000, KM Laboratories) with a 1 kHz repetition rate. 80% of the output is sent to an optical parametric amplifier (OPA, TOPAS Prime, Light Conversion) to generate broadband mid-IR light with pulse energy of 25 μ J for the incident IR field; and the remaining 20% is passed through an interference filter (Andover Corporation) to create narrowband pulses (FWHM = 0.5nm) centered at 790nm to be used as the incident visible field.

The bandwidth of the visible field determines the spectral resolution of our spectrometer which is 8.2 cm^{-1} .

The visible and IR pulses are overlapped on a ZnO thin film deposited on a CaF_2 window to produce a sum frequency field that is used as an external local oscillator (LO). The LO travels through a 3 mm fused silica window to delay the pulse by 5 ps with respect to the visible and IR pulses. All three pulses are overlapped and focused on the sample to produce the SFG signal field, which travels collinearly with the LO, and is directed into a spectrometer (Horiba, iHR550) and detected by a CCD camera (Horiba, Synapse 2048 x 512). The entrance slit width of the spectrometer is $120 \text{ }\mu\text{m}$, and spectra are collected for 20 seconds and averaged over 30 spectra. The polarization of the fields is denoted as P and S to indicate the direction of the E-field with respect to the plane of incidence; P polarization lies parallel to the plane of incidence and S polarization lies perpendicular. HD-VSFG experiments are performed with PPP and SSP polarization conditions, with the indicated polarization corresponding to the SFG, visible, and IR fields, respectively.

Signal analysis of the detected SFG and LO is done using a Fourier filtering and normalization procedure described previously.^{34,38,50} The resulting HD-VSFG signal is acquired by normalizing and phasing the N3/TiO_2 signal to the non-resonant SFG field produced by the strip of bare gold deposited on the CaF_2 . The sample stage is translated laterally to move the N3/TiO_2 or the gold strip in and out of the beam path to minimize any position change within the focal plane and to minimize phase drift. Accounting for the $\frac{\pi}{2}$ phase shift of gold,^{38,48,51–53} and dividing out the contribution of the LO, we obtain the relation

$$\frac{E_{sample}E_{LO}}{E_{gold}E_{LO}} = \frac{E_{sample}(\omega)}{E_{gold}(\omega)} \propto \frac{\chi_{sample}^{(2)}}{\chi_{gold}^{(2)}}, \quad (4.1)$$

to describe the second order susceptibility of the system defined by,

$$\chi^{(2)} = Re(\chi^{(2)}) + iIm(\chi^{(2)}). \quad (4.2)$$

Here, the real and imaginary parts describe the dispersive and absorptive components of the second order susceptibility, $\chi^{(2)}$. HD-VSFG, sometimes referred to as “phase sensitive” SFG, is used to extract the real and imaginary components of $\chi^{(2)}$ by referencing the phase of the signal to an external field; here the external field is the LO. The ability to retrieve the real and imaginary parts of the signal yields the “up” versus “down” orientation of the molecular oscillator and is not trivially accessible for conventional VSFG experiments.^{30,54} Additionally, access to the real and imaginary parts provides more constraints to our molecular model, and thus, yields precise molecular orientation data.

4.4 Results and Discussion

There are five different possible protonation states of N3 dye in solution—the fully protonated (N3H₄), tri-protonated (N3H₃⁺), di-protonated (N3H₂²⁺), mono-protonated (N3H³⁺), and the fully deprotonated (N3⁴⁻). The four pK_a values of the four carboxylic acid groups on N3 in a water:EtOH (1:1) solvent system have been previously identified and utilized here to determine the distribution of N3 protonation states within the sensitizing solution.⁴⁰ Reported pK_a values for the carboxylic acids are $pK_{a1} = 1.33$, $pK_{a2} = 2.24$, $pK_{a3} = 3.45$, and $pK_{a4} = 4.20$ and are used to calculate the relative concentrations of each protonation state in solution at a given pH.

The population distribution of the protonation states that exist in the sensitizing solution is adjusted by titrating with dilute HCl. A specific protonation species can be the primary or most abundant species formed in solution at certain pH conditions. We investigate the pH conditions that predominantly form the mono-, di-, and tri-protonated states of N3 in solution. The pH conditions of approximately 3.8, 3.0, and 2.0, produce the mono-, di-, and tri-protonated species, respectively, as the primary species in the system. The population distribution and relative concentrations are shown in Figure 4.2. We anticipate the more abundant protonation states in solution to be the predominant N3 protonation states to adsorb to the TiO₂ surface during the sensitization process.

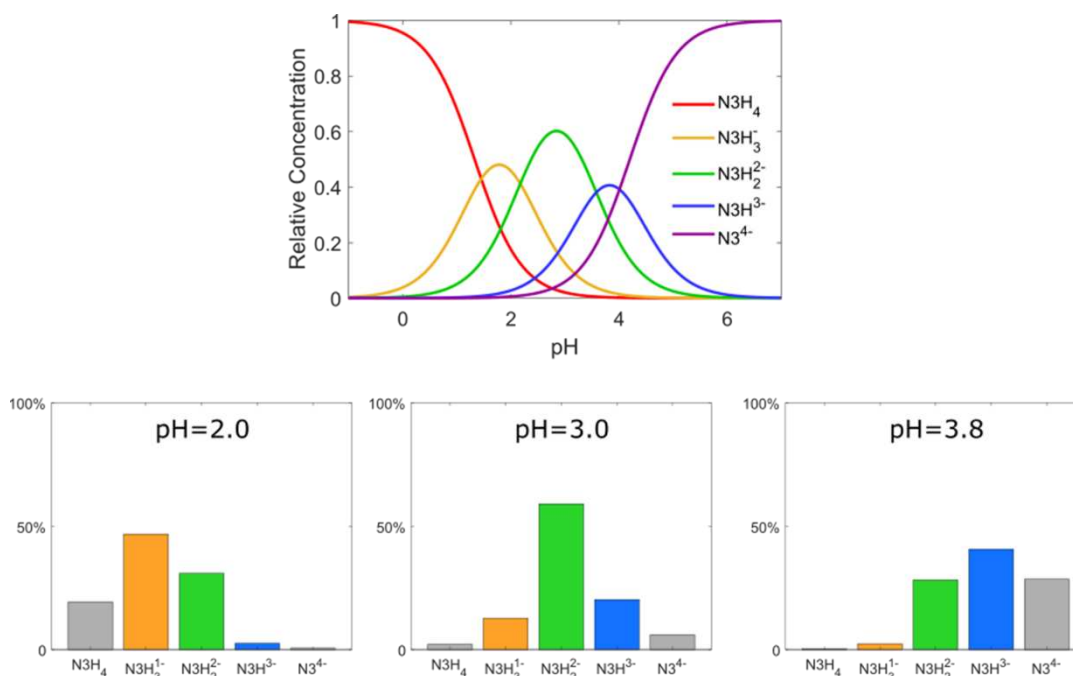


Figure 4.2. (Top) Relative concentrations for each protonation state as a function of the sensitizing solution pH calculated using pK_a values determined by Pizzoli *et. al.* (Bottom) Percentage of each protonation species that exists in solution for pH conditions of (left to right) 2.0, 3.0, and 3.8. The fully protonated and fully deprotonated N3 species (gray) are not expected to bind to TiO_2 , and therefore, not contribute to the HD-VSFG signal. The bar graph (bottom) with colors corresponding to the color legend of the line graph (top).

The pH conditions that primarily form the fully protonated and fully deprotonated N3 species are not investigated as these protonation species are not expected to participate in the adsorption onto TiO_2 . The fully protonated N3 species readily hydrogen bond with one another, leading to aggregation and subsequently crashing out of the sensitizing solution.⁵⁵ Conversely, the fully deprotonated species formed under basic conditions is readily solvated in solution and it is more energetically favorable to be solvated than adsorb onto the substrate.⁴⁸ Additionally, in basic sensitizing conditions, a negative potential is applied to the surface of the TiO_2 that coulombically repels the carboxylate anion of N3 from binding.³ The pH conditions selected here are chosen to

investigate the three dominant protonation species of N3 most likely to contribute to the binding onto the TiO₂ nanoparticulate semiconductor.

We utilize the spectral response of the isothiocyanate (NCS) ligands for determining the adsorption geometry of N3 on TiO₂. Our HD-VSFG spectrometer is tuned to directly probe the vibrational mode $\nu(NC)$ of the isothiocyanate ligands. The acquired HD-VSFG spectra report both the real and imaginary parts of the second order molecular susceptibility, $\chi^{(2)}$, with the imaginary part corresponding to the absorptive component and the real part corresponding to the dispersive component of the molecular susceptibility. Advantages of the sample system used in this work are: 1) the CaF₂ substrate is transparent to the visible and IR wavelengths, and 2) the TiO₂ nanoparticulate thin film is not SFG active and as such, there is no significant non-resonant contribution to the signal.

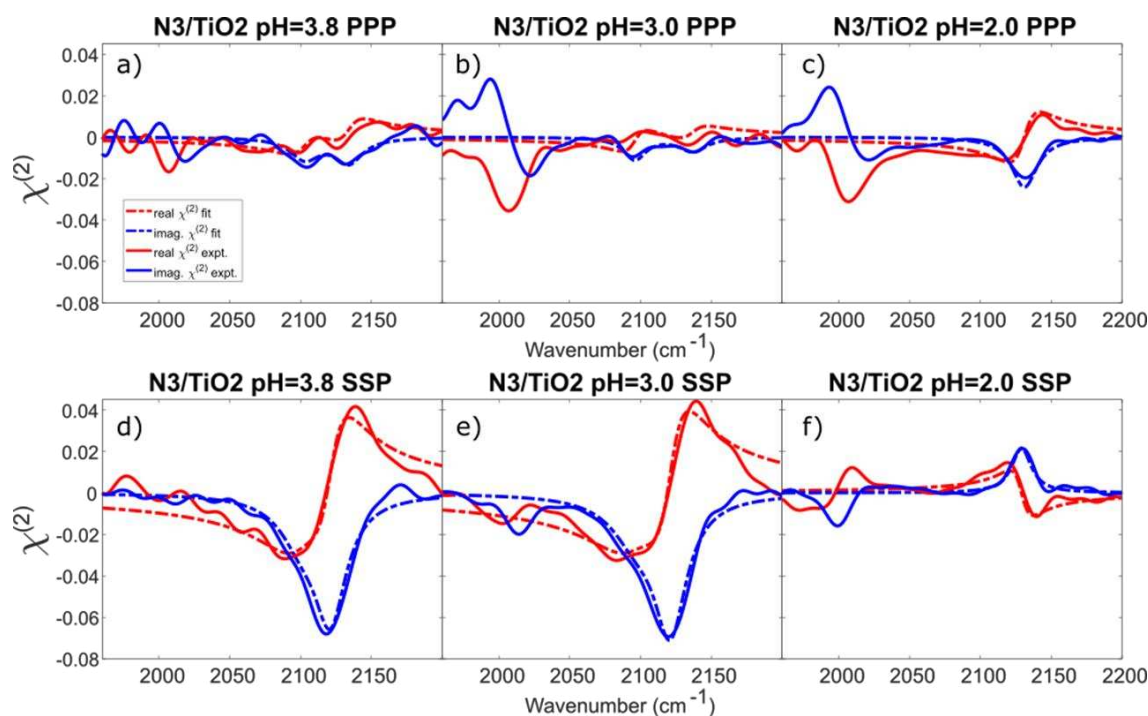


Figure 4.3. HD-VSFG spectra of the $\nu(\text{NC})$ vibrational mode of N3 on TiO_2 (solid) for pH sensitization conditions of 3.8, 3.0, and 2.0. The second order susceptibility is shown as a function of frequency reported in wavenumber (cm^{-1}) with blue lines corresponding to the imaginary part and the red lines the real part. Spectra on the top and bottom row are the PPP and SSP polarization experiments, respectively. The dashed lines are the calculated $\chi^{(2)}$ spectral response for each pH and polarization experiment determined by the fitting procedure.

Figure 4.3 shows the HD-VSFG spectra of N3 adsorbed on TiO_2 for PPP and SSP polarizations. The $\nu(\text{NC})$ resonant vibration of the isothiocyanate is observed in both polarizations and for all three investigated pH sensitization conditions (pH = 3.8, 3.0, and 2.0). The sensitizing solution has a pH = 3.8 without any titration. For simplicity, we focus the discussion to the imaginary component of the HD-VSFG spectra. Two vibrational modes at approximately 2100 cm^{-1} and 2130 cm^{-1} for both SSP and PPP polarization are observed as negative features for pH = 3.8. The appearance of two modes is likely due to residual solvent (water/ethanol) coordinating to the isothiocyanate ligand, which is known to alter the $\nu(\text{NC})$ resonant vibration.⁵⁶ During sample preparation, a rinsing procedure with water:EtOH is conducted to remove any unbound or

aggregated N3 from the TiO₂ surface. The sample is then left to dry in atmosphere before HD-VSFG measurements and residual solvent is most likely present at the interface. The lower frequency ($\sim 2100\text{ cm}^{-1}$) mode is attributed to the solvent-coordinated isothiocyanate.

Similar to the condition pH = 3.8, the condition pH = 3.0 has two negative imaginary features for both polarizations at approximately 2100 cm^{-1} and 2130 cm^{-1} . One significant difference between the pH condition of 3.8 and 3.0 is the spectral feature at 2000 cm^{-1} for the HD-VSFG spectra of condition pH = 3.0. This feature is attributed to the $\nu(\text{NC})$ vibrational mode of a free $[\text{SCN}]^-$ bound to the TiO₂ surface. The formation of free $[\text{SCN}]^-$ is possible due to the removal of the N3 isothiocyanate ligand via a ligand exchange reaction.^{57,58} Side reactions and possible degradation effects at the N3-dye/TiO₂ interface is an interesting problem for DSSC device performance, and we intend to investigate this in a future study. However, for the scope of this study, we limit the discussion to the isothiocyanate ligands that are still within the N3-ruthenium complex.

Clear changes to the measured HD-VSFG spectra for the $\nu(\text{NC})$ mode is observed for conditions pH = 2.0 (Figure 4.3 (c) and (f)). The imaginary PPP signal is negative, while the SSP signal is positive. Additionally, the intensity of PPP and SSP spectra for the pH condition of 2.0 are similar in intensity, which contrasts with the pH conditions of 3.8 and 3.0 where the SSP signal intensity is much larger than the PPP intensity. Also shown in the spectra for condition pH = 2.0 is a single resonant frequency at 2130 cm^{-1} , indicating a local environment of N3 with no solvent coordination to the isothiocyanate ligands. The significant difference in the HD-VSFG for various sensitization conditions is likely due to a pH-dependent structural orientation of N3 on the TiO₂ surface. Determining the dye's interfacial geometry on the semiconductor surface is crucial for understanding the parameters and conditions that affect the structure of the N3/TiO₂ interface.

The HD-VSFG PPP and SSP spectra are used to elucidate the transition dipole moment angle of the $\nu(NC)$ vibration and determine the geometry of N3 on TiO_2 . To do this, we model the HD-VSFG experimental data. Specifically, we calculate the spectral response of the isothiocyanate $\nu(NC)$ vibrational mode using mathematical relationships to describe the second-order susceptibility for PPP and SSP polarization experiments, $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$. The derivation for the polarization dependent $\chi^{(2)}$ is explained by ours and others' previous work.^{48,52,59-61}

Briefly, the transition dipole moment of the vibrational mode is pointing from the C to the N and lies along the linear axis of the isothiocyanate ligand. We use azimuthally isotropic symmetry conditions to simplify the nonzero hyperpolarizability tensor elements β_{ijk} , where i, j , and k are the molecular frame cartesian coordinates. Using rotational averaging and Euler rotation matrices, we can relate the molecular frame hyperpolarizability elements β_{zzz} and β_{xxz} to the macroscopic second order susceptibility through the rotation angle θ . The angle θ is the tilt angle of the transition dipole moment with respect to the lab frame Z axis, which lies along the surface normal. Refractive indices of the system and the polarization and angle of incident fields are used to calculate Fresnel coefficients to properly model PPP and SSP experiments. Lastly, to model the HD-VSFG experimental data, $\chi_{PPP}^{(2)}$ and $\chi_{SSP}^{(2)}$ spectra are calculated as a function of frequency using a Lorentzian lineshape function,

$$\chi^{(2)} = \sum_q \frac{\chi_q^{(2)}}{\omega_q - \omega_{IR} - i\Gamma_q} . \quad (4.3)$$

Here, ω is the resonant vibrational frequency and Γ is the damping constant that describes the half width at half max (HWHM). The subscript q denotes the resonant $\nu(NC)$ vibrational mode. A scheme describing the relation of the net transition dipole moment angle to the lab frame

coordinates is shown in Figure 4.4. The net transition dipole moment of the normal mode, $\vec{\mu}$, is projected to lab frame coordinates X, Y, and Z with a rotation that solely depends on the angle θ .

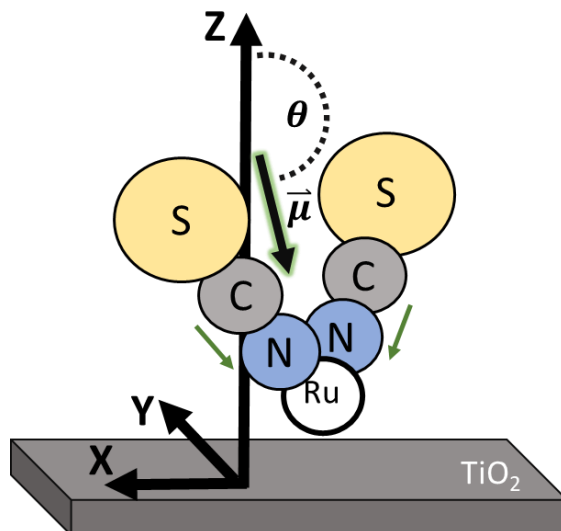


Figure 4.4 Representative schematic of the isothiocyanate groups of N3 on TiO₂. The small arrows pointing from C to N represent the dipole moment vector of each local $\nu(NC)$ stretch. The net transition dipole moment of the $\nu(NC)$ vibrational modes is shown with the black arrow and labeled as $\vec{\mu}$. Theta, θ , is the angle of rotation from the net transition dipole to the lab frame Z axis. Azimuthal symmetric considerations allow for any twist angle to be ignored and lab frame X or Y coordinates to be equivalent; thus, the net dipole moment angle can be projected into the lab frame coordinates using the angle θ .

The resulting equation 4.3 models HD-VSFG data and is used to fit the experimental data with the fitting parameters $\langle\beta_{zzz}\rangle$, θ , and r . The parameter $\langle\beta_{zzz}\rangle$ is related to the normalized signal intensity and the molecular hyperpolarizability tensor element β_{zzz} of the oscillator; θ is the average transition dipole moment angle with respect to the lab frame Z-axis; r is the ratio of the two hyperpolarizability tensor elements β_{zzz} and β_{xxz} , specifically, $r = \frac{\beta_{xxz}}{\beta_{zzz}}$. The equations and parameters used here are identical to the equations outlined for the polarization intensity ratio (PIR) method to determine molecular orientation through polarization dependent VSFG experiments.^{52,62,63} Our fitting procedure takes advantage of HD-VSFG's ability to retrieve the

real and imaginary components of $\chi^{(2)}$. Simultaneously fitting the real and imaginary parts of the SSP and PPP data effectively doubles the input experimental data into our model and constrains our parameters to acquire precise results. Fits are plotted as dashed lines with the experimental data shown in Figure 4.3 and do not include the free SCN⁻ vibrational mode at 2000 cm⁻¹.

The fitted results of the average transition dipole moment angle θ are used to elucidate the binding orientation of N3 for each pH sensitization condition. With the sensitization conditions of pH = 3.8, the lower frequency (2100 cm⁻¹) transition dipole moment angle $\theta_{low} = 177^\circ \pm 3^\circ$ and the higher frequency (2130 cm⁻¹) angle $\theta_{high} = 176^\circ \pm 1^\circ$. This result for the conditions pH = 3.8 indicate that the transition dipole moment of $\nu(NC)$ is pointing downwards with respect to surface normal, toward the TiO₂ surface. Additionally, the similar angles of each $\nu(NC)$ mode indicates that the coordination to residual water and/or ethanol solvent molecules does not drastically change the binding geometry of N3 on TiO₂. The proposed binding geometry for pH = 3.8 is shown in the left-most binding scheme of Figure 4.5. Previous studies indicate that the N3-dye (and similar analogs) primarily adsorb to metal-oxide semiconductors via the carboxylate anion. We propose that N3 binds the TiO₂ using two carboxylate groups from each bipyridyl ligand, which causes the two isothiocyanate ligands to be spatially distant from the TiO₂ surface and the net $\nu(NC)$ transition dipole moment to be pointing downwards. The proposed structure for the sensitization conditions of pH = 3.8 agrees with our previous work of the N3/TiO₂ interface, as well as other previous reports.^{25,28,38}

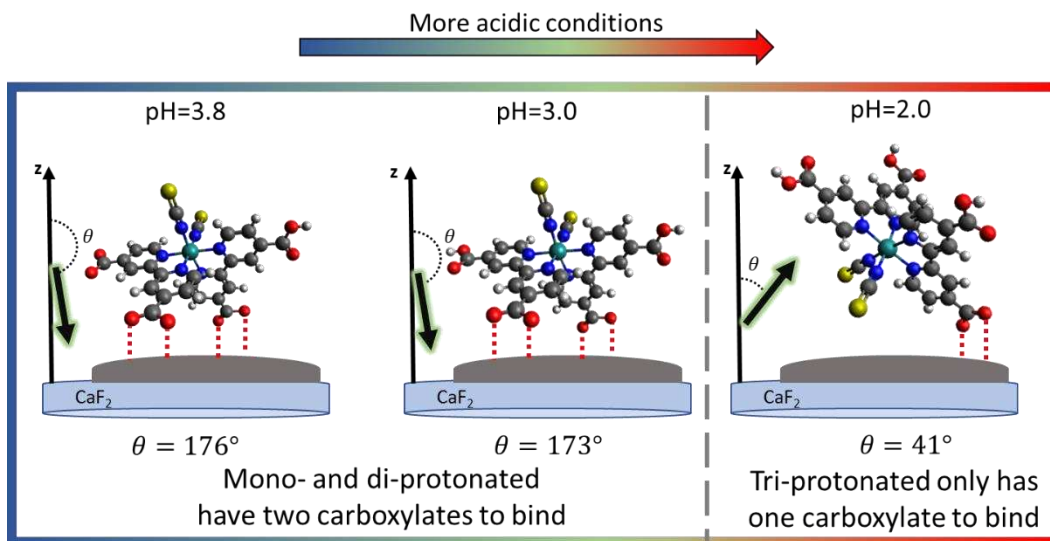


Figure 4.5. Binding scheme of N3 on TiO_2 for each pH condition. The determined net transition dipole moment angle of the $\nu(\text{NC})$ vibrational mode is shown corresponding to the predominant protonation species of each respective pH condition. The angle θ is shown with respect to the Z axis of the lab frame cartesian axis that lies along surface normal.

The sensitization conditions of $\text{pH} = 3.0$ is determined to have $\nu(\text{NC})$ transition dipole moment angle values for the low and high frequency modes of $\theta_{\text{low}} = 175.7 \pm 1.2$ and $\theta_{\text{high}} = 172.7^\circ \pm 0.4^\circ$, respectively. The resulting angles for the condition of $\text{pH} = 3.0$ are similar to the values for conditions of $\text{pH} = 3.8$, and therefore, we propose a similar binding motif of N3 on TiO_2 under both pH conditions. The binding structure of N3 on TiO_2 for the pH condition of 3.0 are shown in Figure 4.5.

The acid-base calculations (Figure 4.2) reveal the most abundant protonated species in solution at a pH of 3.0 is the di-protonated N3 species. Furthermore, for $\text{pH} = 3.8$, the most abundant species is the mono-protonated with significant population also arising for the di-protonated. From our HD-VSFG results, we show that the binding geometry of the $\text{pH} = 3.8$ and 3.0 facilitate similar binding geometries of N3 to the TiO_2 substrate. Therefore, the mono- and di-protonated species of N3 both bind to the TiO_2 substrate with two carboxylates. We suspect that

the two bound carboxylates come from each of the bipyridyl ligands. If the two carboxylates came from a single bipyridyl ligand, then the $\nu(NC)$ transition dipole moment angle would be significantly different, close to an angle of $\sim 90^\circ$. Consequently, the determined angles being $> 173^\circ$ for both pH = 3.8 and 3.0 indicates a binding geometry like the structures depicted in Figure 4.5.

Applying the model and fitting procedure to the conditions of pH = 2.0 is done with specific considerations regarding the number of vibrational modes and protonation states that contribute to the signal. First, there is no significant contribution of the solvent coordinated vibrational mode at the lower frequency 2100 cm^{-1} , thus, only one resonant frequency at 2130 cm^{-1} is used to model the experimental data. Second, the acid-base stoichiometry calculations indicate that a significant amount of protonated population exist as the di-protonated species in solution. Therefore, we model the pH = 2.0 condition to be a linear combination of two binding geometries from the di-protonated species and tri-protonated species. For the di-protonated contribution to the linear combination, we fix the values θ and $r = \frac{\beta_{xxz}}{\beta_{zzz}}$ to the previously acquired values from the pH = 3.0 non-solvated mode and only allow the $\langle \beta_{zzz} \rangle$ parameter to vary within the fit. The tri-protonated contribution to the linear combination is fitted without fixing any parameters. Independent fitting results for the separate di- and tri-protonated species are detailed in the supplementary material.

By accounting for di-protonated signal in the spectra for the sensitization conditions of pH = 2.0, the tri-protonated binding geometry can be independently calculated in our model. The resulting tri-protonated $\nu(NC)$ transition dipole moment angle $\theta = 41.3^\circ \pm 0.7^\circ$. The angle determined for the tri-protonated species indicates the transition dipole moment is pointed upwards with respect to the TiO_2 surface normal. The proposed binding structure of the tri-protonated N3 species on TiO_2 is shown in the right-most binding scheme in Figure 4.5. One carboxylate is available on the tri-protonated N3 species to anchor to the TiO_2 surface. Anchoring to the

semiconductor with the one carboxylate “flips” the N3 molecular orientation on TiO₂ compared to the binding geometries of the mono- and di-protonated species. Moreover, the isothiocyanate ligand position mitigates interaction with residual solvent, and thus, there is no significant contribution to the HD-VSFG spectra of the solvent coordinated $\nu(\text{NC})$ vibrational mode. The interfacial structure of N3/TiO₂ sensitized in pH conditions of 2.0 can have different impacts to DSSC device performance versus the interfacial structure sensitized with pH conditions of 3.8 and 3.0. This is discussed in more detail below.

Table 4.1 Fitting results for the hyperpolarizability, tilt angle, and hyperpolarizability ratio parameters for each pH dependent HD-VSFG spectra. For pH conditions 3.8 and 3.0, the subscript **1** refers to the low frequency, solvent coordinated $\nu(\text{NC})$ vibrational mode, while the subscript **2** refers to the high frequency, non-coordinated $\nu(\text{NC})$ vibrational mode. The subscript **1** for the 2.0 pH condition refers to the di-protonated component of the linear combination used to model the 2.0 pH HD-VSFG spectra. The subscript **2** for the 2.0 pH condition refers to the tri-protonated component of the linear combination. The bolded numbers in brackets are fixed and are determined from the results of the di-protonated non-coordinated $\nu(\text{NC})$ vibrational mode. Error bars for transition dipole moment angles report $\pm 5\%$ of $\chi(\omega_q)$ of our fit from experiment.

pH	$\langle\beta_{zzz}\rangle_1$	θ_1	r_1	$\langle\beta_{zzz}\rangle_2$	θ_2	r_2
3.8	16.875	176.8 ± 3.2	0.5564	33.859	175.8 ± 0.8	0.6126
3.0	17.891	175.7 ± 1.2	0.5865	36.293	172.7 ± 0.4	0.6425
2.0	20.513	[172.7]_{fix}	[0.6425]_{fix}	34.815	41.3 ± 0.7	0.6022

Results from the model and fit are summarized in Table 4.1. An interesting result are the hyperpolarizability ratios, $r = \frac{\beta_{xxz}}{\beta_{zzz}}$. The similar values for r indicate a consistent relationship between the two hyperpolarizability tensor elements for all protonation states, pH conditions, and

binding geometries. This finding supports the N3 binding scheme in Figure 4.5. The local environment and intrinsic properties of the $\nu(NC)$ vibrational mode is not altered by the change in N3 molecular geometry. The only observed change to the mode is coordination to residual solvent, which is reflected by the slightly lower r value for the solvent-coordinated mode (Table 1). In contrast, previous work shows that drastically altering the local environment, such as making and breaking bonds to the substate, can alter the values for r .⁴⁸

The parameter $\langle\beta_{zzz}\rangle$ is a normalized and averaged value that is proportional to the molecular hyperpolarizability β_{zzz} and the number density of oscillators. Because the HD-VSFG signal is normalized to an external reference (gold), the individual value of $\langle\beta_{zzz}\rangle$ is not informative by itself. However, by comparing the ratio of the di-protonated and tri-protonated $\langle\beta_{zzz}\rangle$ we observe a compelling relationship that reflects the acid-base stoichiometry for the pH = 2.0,

$$\frac{\langle\beta_{zzz,di-proton}\rangle}{\langle\beta_{zzz,tri-proton}\rangle} \propto \frac{\langle N_{di-proton} \rangle \beta_{zzz}}{\langle N_{tri-proton} \rangle \beta_{zzz}} \cong \frac{[N3H_2^{2-}]}{[N3H_3^{1-}]} \quad (4.4)$$

Here, individual β_{zzz} values are approximated to be equivalent because of the similar r values. The ratio between $\langle\beta_{zzz,di-proton}\rangle$ and $\langle\beta_{zzz,tri-proton}\rangle$ fitted parameters used in the linear combination to model pH = 2.0 HD-VSFG signal reflect the ratio of the concentration of di- and tri-protonated species that exist in solution at a pH of 2.0. It is compelling evidence that without prior information of weights, amplitudes, or concentrations, the model returns information regarding the relative stoichiometry of the N3 protonation states for a pH of 2.0.

The significant reorientation of the tri-protonated N3 species can arise due to coulombic interactions on the surface. When the TiO₂ thin film is exposed to the acidic conditions, a slight

positive charge exists at the surface of TiO_2 .³ Under typical DSSC device fabrication, this is favorable for coulombically attracting and anchoring the negatively charged carboxylate to the surface; however, with $\text{pH} = 2.0$ conditions, the carboxylic acids of the tri-protonated species are no longer coulombically attracted to the TiO_2 surface, perhaps even repelled. Therefore, the lone carboxylate group on the tri-protonated N3 anchors to the semiconductor and the protonated carboxylic acid groups are positioned away from the TiO_2 surface.

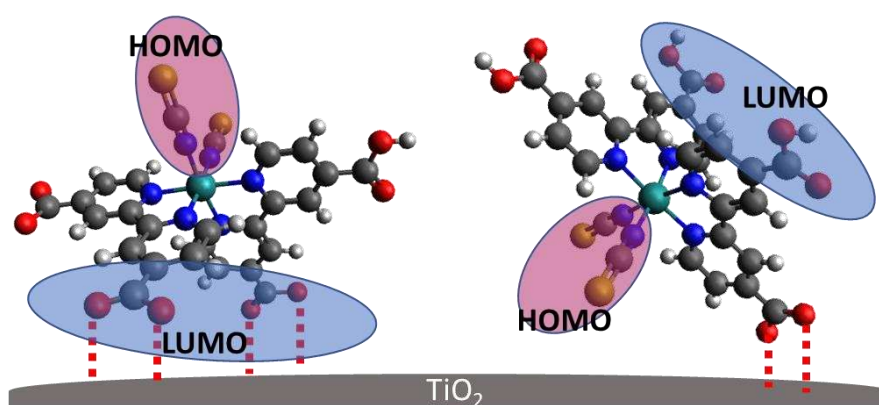


Figure 4.6 Binding modality of the N3 mono-protonated species (left) and the tri-protonated species (right) on TiO_2 . The approximate location of N3's LUMO and HOMO are shown in blue and red, respectively.

The potential consequences of the pH-dependent structural reorientation of N3 for DSSC performance is made apparent considering the position of the N3-dye's HOMO and LUMO in relation to the TiO_2 substrate. To facilitate favorable electron transfer for the N3/ TiO_2 system in a DSSC device, it is advantageous to position the LUMO of the dye spatially near the semiconductor. Electron density associated with the LUMO is mainly distributed across the carboxyl and bipyridyl groups. Furthermore, the electron density of the HOMO is predominantly distributed on the isothiocyanate ligands. To deter electron recombination from the TiO_2 conduction band to the N3-dye and favor redox reactions with the electrolyte of the DSSC, it is preferable to have the HOMO

positioned away from the semiconductor. Considering the electronic structure of the HOMO and LUMO of N3, it can be understood that the two-carboxylate binding mode of N3 on TiO₂ shown on the left in Figure 4.6 is the better interfacial structure for optimizing DSSC device performance. To facilitate the two-carboxylate binding geometry on TiO₂, sensitization must happen in a pH condition that primarily forms the mono- or di-protonated species of N3 dye.

The binding orientation of the tri-protonated N3 sensitized under the pH = 2.0 condition shown on the right in Figure 4.6 would not be ideal for electron transfer from the photo-excited dye to the semiconductor. The LUMO of the tri-protonated N3 is located spatially distant from the semiconductor interface. Additionally, the HOMO that resides on the isothiocyanates are spatially near the TiO₂ would increase undesirable back electron transfer and decrease redox reactions with the DSSC electrolyte system. The conditions of DSSC fabrication, specifically the pH during sensitization, can therefore have dramatic impacts on device performance by altering the molecular and electronic structure of the dye/semiconductor interface.

4.5 Conclusion

We have shown that altering the pH conditions during the sensitization of N3-dye onto a TiO₂ nanoparticulate surface alters the interfacial structure. N3 has multiple protonation states that can exist in solution. Titrating the sensitizing solution to a specific pH controls the distribution of N3 protonation states that exist in solution and subsequently adsorb onto the TiO₂ surface. Using HD-VSFG we have elucidated the N3/TiO₂ interfacial structure produced under different pH sensitization conditions.

Mono- and di-protonated N3 species are primarily formed with a pH of 3.8 and 3.0, respectively, and are oriented on the TiO₂ surface using two carboxylate groups, one from each bipyridyl ligand of N3. The tri-protonated N3 species primarily forms with pH condition of 2.0

and anchors to the TiO₂ surface with one carboxylate group. The different binding geometries associated with the pH conditions arise due to the number of carboxylate groups available to bind and the average surface charge on the TiO₂ surface when exposed to more acidic conditions. Interfacial electronic structure of the binding geometries is discussed, and it is determined that the N3/TiO₂ structure produced under pH conditions of 3.8 and 3.0 is better for DSSC device performance than the structure produced under the pH condition of 2.0. Our study has demonstrated the utility of HD-VSFG for studying the interfacial chemistry of DSSC devices and inform how tuning pH conditions during DSSC fabrication can impact overall device performance.

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CHAPTER 5 – INVESTIGATING BURIED INTERFACES OF PHOTOELECTROCHEMICAL CELLS USING HETERODYNE DETECTED VIBRATIONAL SUM FREQUENCY GENERATION

Presented within this chapter are results and a brief discussion regarding the work done utilizing HD-VSFG for investigating the molecular structure of N3 at the acetonitrile/N3/TiO₂ interface. Acetonitrile (ACN) is a common solvent for electrolyte systems. By employing acetonitrile into the N3/TiO₂ chemical system introduced in chapter 4, device-relevant chemical environments can be replicated, and *in-situ* HD-VSFG measurements can be performed. The work presented here highlights the inherent advantages that HD-VSFG has to offer for probing buried interfaces within photoelectrochemical systems.

5.1 Introduction

Within typical photoelectrochemical cells (PECs) architectures, an electrolyte is used to provide electron transport between the working and counter electrodes via chemical reductive/oxidative reactions. Depending on the type of photoelectrochemical cell, different electrolyte systems can be used to facilitate specific reactions.¹ For example, utilizing an aqueous electrolyte within a PEC is necessary for fabricating a water splitting PEC, and changing the acidity/basicity or integrating different salts and additives in the solution can impact the efficiency of the PEC.²⁻⁴ The electrolyte serves as one of the central components that make up PECs, and therefore, understanding how the electrolyte effects performance is necessary for developing efficient and viable PEC devices.⁵

As discussed previously within this dissertation, dye-sensitized solar cells (DSSCs) are a specific type of PEC with a dye molecule anchored onto a semiconducting substrate. The dye transfers an electron to the semiconductor after photoexcitation and subsequently evolves into an

oxidized state with one less electron. The electrolyte of the DSSC replenishes the dye with an electron via a reduction reaction so that the dye can photoexcite and transfer another electron to the semiconductor. One of the most effective and commonly used electrolyte systems within DSSC devices is the iodide/triiodide redox couple dissolved in acetonitrile.⁶⁻⁸ This electrolyte system interacts favorably with N3-dye (and similar analogs) most likely do to the interactions between the isothiocyanate (SCN) ligand and the redox couple (I^-/I_3^-).^{6,8} It follows, then, that the dye molecule must be oriented on the semiconductor in a way that encourages favorable interaction with the electrolyte system.

Discussed in chapter 4, to facilitate favorable electron transfer from the N3-dye to the semiconductor (TiO_2) the LUMO of N3 must be oriented spatially close to the TiO_2 surface; additionally, the LUMO must be oriented away from the semiconductor to avoid electron recombination and interact favorably with the electrolyte system.^{9,10} However, chapter 4 investigates the N3/ TiO_2 surface without the presence of the electrolyte system. It, therefore, must be asked: to what effect does the electrolyte have on the N3/ TiO_2 structure?

Explored in this chapter is the molecular structure of N3 within a mock DSSC device using acetonitrile (ACN) as the electrolyte, N3-dye as the sensitizer, and nanoparticulate anatase- TiO_2 as the semiconductor. Additionally, the effects of the sensitizing solution's pH to the molecular orientation of N3 is investigated. The molecular structure of N3 can be probed within the ACN/N3/ TiO_2 interface because of the interfacial specificity that HD-VSFG measurements offer.¹¹ While previous studies have investigated this interface using techniques such as X-ray photoelectron spectroscopy,¹² x-ray diffraction,¹³ and neutron reflectometry¹⁴, these techniques require intense radiation from synchrotron sources and the experimental setups do not mimic the operating conditions of DSSC devices. Heterodyne-detected vibrational sum frequency generation

(HD-VSFG), however, has the advantage of investigating the molecular structure of buried interfaces within ambient conditions that mimic operational conditions of DSSC devices.^{15–17} The work presented here 1) showcases HD-VSFG as a powerful spectroscopic technique to study the buried interfaces within DSSC and PEC architectures, and 2) investigates the pH conditions of the N3/TiO₂ sensitization as a parameter that influences the molecular structure of N3 of the ACN/N3/TiO₂ interface within the sample cell.

5.2 Methods

The fabrication and sensitization of the N3/TiO₂ interface on a calcium fluoride (CaF₂) plate has been described within chapters 2 and 4. Briefly, anatase TiO₂ nanoparticles (5nm) are dropcast onto a clean CaF₂ from a 1 g/L suspension in water. The film is dried and cleaned by heating the CaF₂ window on a hot plate at 300 °C and irradiated by a UV flashlight (365nm) for 30 min. A 0.2mM solution of N3 dye dissolved in a 1:1 water:ethanol solvent is used as the sensitizing solution. Submerging the TiO₂ film in the N3 sensitizing solution for 1 hour sensitizes the TiO₂ substrate with N3 dye.^{18,19} The N3/TiO₂ interface is sensitized under different pH sensitization conditions by titrating the sensitizing using dilute HCl (pH $\cong$ 0.6).

Here, the N3/TiO₂ interface is placed in a sample cell with an additional CaF₂ plate, a 50 μ m spacer, and approximately 10-20 μ L of HPLC grade acetonitrile. The two CaF₂ plates are secured together by a set screw within the sample holder. A general scheme of the sample cell is outlined in Figure 5.1. Additionally, the CaF₂ plate that has the N3/TiO₂ surface also has a 200 nm gold strip that has been grown using physical vapor deposition (PVD), described in previous chapters, to use as the gold reference signal for HD-VSFG data analysis.

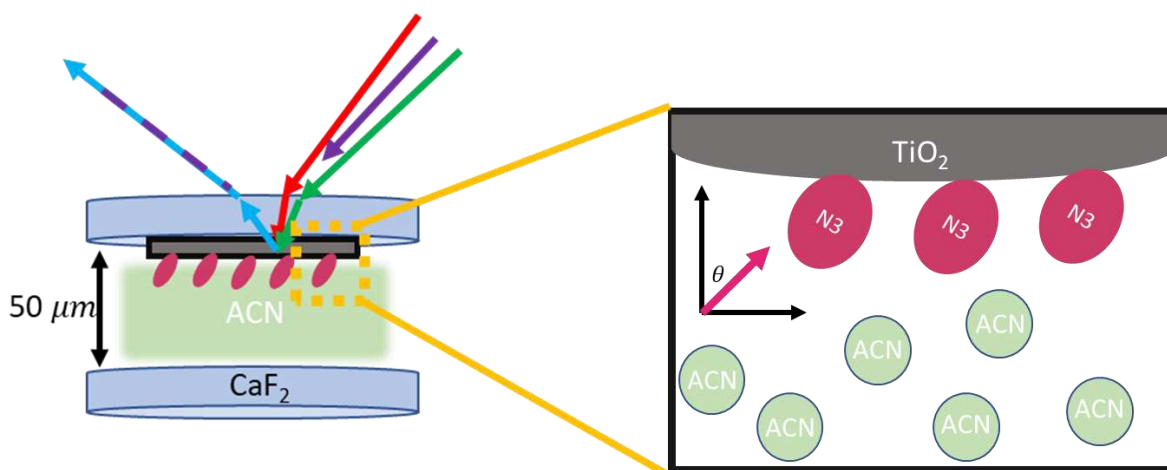


Figure 5.1 Simplified diagram for the sample cell used to study the ACN/N3/TiO₂ interface (left). The IR (red), visible (green), and local oscillator (purple) are overlapped at the ACN/N3/TiO₂ interface buried within the sample cell. The VSGF signal (blue) collinearly travels with the local oscillator. The inset figure (right) shows the transition dipole moment angle of N3 used to determine the structure of N3 in the presence of ACN.

Spectroscopic measurements are done using our home-built heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectrometer described in chapters 2, 3, and 4. The beam path for the HD-VSFG measurements approach the N3/TiO₂ interface from the through the CaF₂ plate, this changes the angle of incidence of the light. Briefly recalling from previous chapters, the Fresnel coefficients are used for the modelling of HD-VSFG data and necessary for determining the orientation of the vibrational mode. Therefore, the calculation of the Fresnel coefficients is done utilizing the refractive index of CaF₂/TiO₂ and the new angles of incidence for each pulse of light, shown in Figure 5.1, when the light pulses travel through the CaF₂ window and TiO₂ film.

5.3 Results and Discussion

The pH conditions during the sensitization of N3 influences the N3 protonation states that exist in solution. During the preparation of the sensitizing solution, dilute HCl is used to titrate the sensitizing solution to desired pH conditions to control the distribution of protonation states

that exist in solution. The pH conditions are chosen to be 3.8, 3.0, and 2.0 in order to primarily form the mono-, di-, and tri-protonated N3 species, respectively. Acid-base protonation stoichiometries are calculated utilizing pK_a values determined for N3-dye from previous studies,²⁰ and the results of the distribution of protonation states versus pH of the sensitizing solution are shown in chapter 4 and in Figure 5.2.

To determine the N3 orientation on within the sample cell, the transition dipole moment of the $\nu(NC)$ of the isothiocyanate (SCN) ligand is probed using HD-VSFG spectroscopic experiments utilizing different polarization setups. Resulting PPP and SSP spectra are shown in Figure 5.2 (solid lines) for each of the pH conditions (3.8, 3.0, and 2.0) explored in this study. The real part (red) reports on the dispersive component of the second order susceptibility, $\chi^{(2)}$, while the imaginary part (blue) reports on the absorptive component.^{21,22} For both polarization setups and all pH conditions, a singular resonant vibrational mode of $\nu(NC)$ is observed at approximately 2120 cm^{-1} . Interestingly, the spectra across all pH conditions look remarkably similar, indicating the possibility that there is no pH-dependent change to the $\nu(NC)$ vibrational mode and/or local chemical environment. To investigate this further, we implement the model for the spectroscopic data developed in previous chapters, as well as the simultaneous fitting procedure to elucidate the structure of N3 within the ACN/N3/TiO₂ interface.^{23,24}

SCN is a linear functional group of N3 and is a useful functional group to use to determine the structure of N3 at the interface due to the symmetry conditions described in chapters 2, 3, and 4. Additionally, the HD-VSFG spectra of the $\nu(NC)$ vibrational mode can be modeled using the equations described previously for the SSP and PPP polarization schemes of the experiment. Calculated spectra in the model are fit using a fitting procedure to simultaneously fit the real and imaginary components of both PPP and SSP experiments to the acquired spectroscopic data for

each pH condition tested. The goal of the model/fitting procedure is to extract the transition dipole moment angle associated with the $\nu(\text{NC})$ vibrational mode. The transition dipole moment angle, θ , can be used to elucidate the structure of N3 on the TiO_2 substrate in the presence of the ACN “electrolyte”. Results of the fitted model are shown in Figure 5.2 with dashed lines.

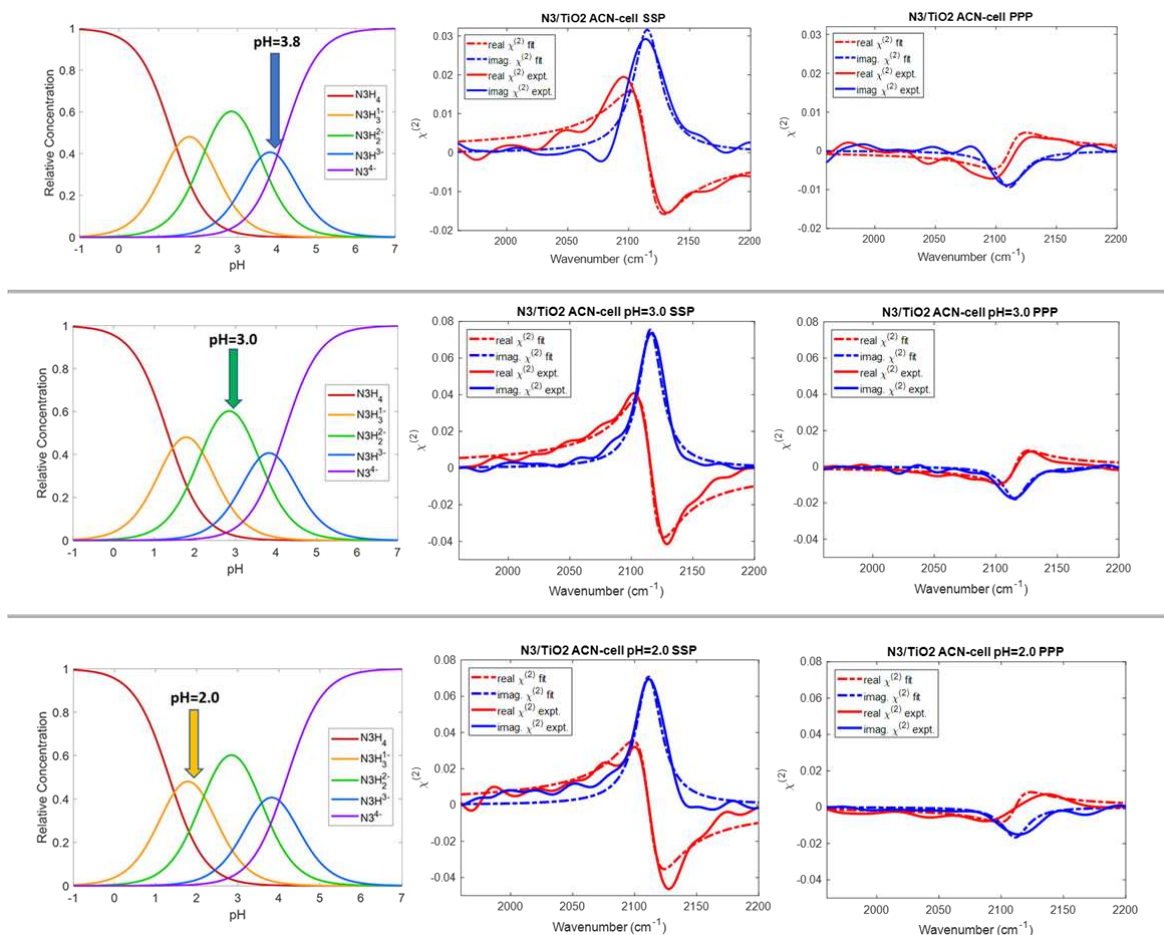


Figure 5.2 Results of the HD-VSFG experiments performed for both polarization conditions, SSP and PPP, on the ACN/N3/ TiO_2 cell fabricated under different pH conditions. Each row represents a different pH condition. The distribution of protonation states as a function of pH are shown on the left side with an arrow corresponding to the specific pH condition used for sensitization.

The resulting $\nu(NC)$ transition dipole moment angles acquired from the fit are 49.7° , 41.1° , and 40.5° for pH conditions 3.8, 3.0, and 2.0, respectively. As previously indicated by the similar HD-VSFG spectra, the change in the transition dipole moment is minimal across the pH sensitization conditions, and here, indicates that there is no pH-dependent structure of N3. Based on the results for θ , the proposed structure of N3 within the ACN/N3/TiO₂ interface would look something like the structure shown in Figure 5.3. In this conformation, three of the four carboxylic acid/carboxylate groups of N3 would be adsorbed to the TiO₂ surface. It could be possible that the three carboxyl groups are participating in a mix of adsorption schemes. For example, chemisorption of the carboxylate groups bonding to TiO₂ surface via Ti-O bonds, or physisorption by a hydrogen bond to an oxygen of the TiO₂ surface and a carboxylic acid group of N3.^{14,20,25,26}

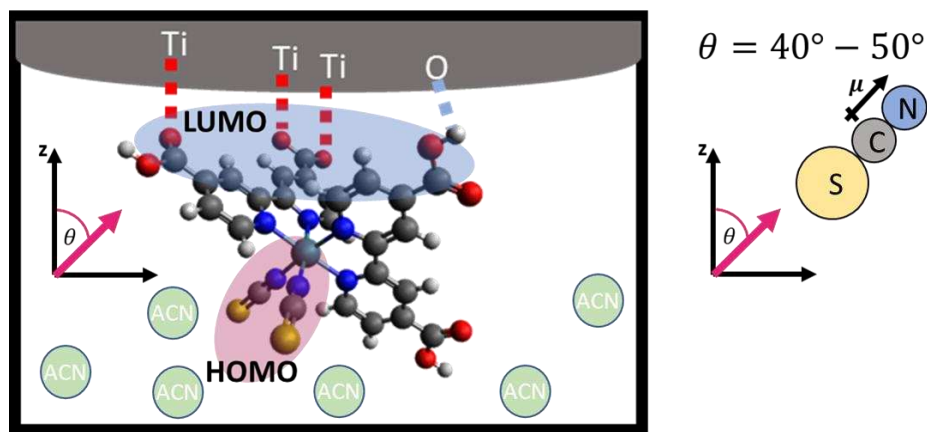


Figure 5.3 Proposed molecular structure of N3 within the ACN/N3/TiO₂ interface. Possible bond formation for the chemisorption (red) and the physisorption (light blue) are indicated by the dashed lines. The HOMO/LUMO orbitals of N3 are visually depicted by the shaded ovals. The transition dipole moment, θ , is given approximate values ranging from 40° - 50° to represent the acquired values for all measured pH sensitization conditions.

The results presented within this chapter are much different than the results of the “dry” N3/TiO₂ pH-dependent study discussed in chapter 4 for two reasons. First, there does not appear to be any reorientation of the dye due to changes in the protonation state and pH conditions during

the sensitization process. Second, proposed structure here is significantly different from the binding moieties of the “dry” N3/TiO₂ structures in that there are three of the four carboxyl groups participating in binding, whereas there are only two or one carboxyl groups in the dry conditions. The explanation for both of these observations can be explained by the interaction between N3 dye and ACN. Specifically, in the presence of the ACN “electrolyte” system, N3 has a preferential interfacial structure due to the solvation of the specific ligand groups of N3.

N3 has four carboxylic acid groups on two bipyridyl rings that are coordinated to the ruthenium center. These four carboxylic acid groups are polar and protic ligands which are not readily solvated by the acetonitrile that is slightly polar and aprotic. On the other hand, the isothiocyanate (SCN) ligands of N3 are slightly polar and aprotic, much like the acetonitrile solvent system; therefore, a preferential solvation shell of ACN could be forming around the SCN ligands of N3, depicted in the chemical cartoon within Figure 5.3. Following this train of thought, the carboxyl groups of N3 would preferentially be adsorbed to the TiO₂ than to be solvated by ACN. This “preferential partial solvation” hypothesis could explain why N3 undergoes one specific adsorption geometry within the ACN/N3/TiO₂ interface and explain why the adsorption geometry is invariant to the N3 protonation states/pH conditions during the sensitization.

Another observation of the spectra shown in Figure 5.2 are the relatively narrow linewidths compared to the linewidths shown in the HD-VSFG spectra of chapter 4. The narrow linewidths could indicate the mitigation of heterogeneous broadening contributions in the measured spectra due to a smaller distribution of chemical environments.²⁷ If, indeed, the ACN is facilitating a specific binding geometry of N3 within the interface, then this would be reflected as a narrow lineshape within the acquired spectrum.

Finally, a last key aspect to note, the positioning of the HOMO and LUMO orbitals of N3 in the proposed structure of Figure 5.3 are in ideal spatial positioning for optimizing DSSC performance.⁹ The LUMO on the carboxyl groups are spatially close to TiO₂ and the HOMO on the SCN groups are oriented away from the surface to encourage favorable interaction with the electrolyte. The results shown by this brief study indicate that one reason that the combination of N3-dye, TiO₂, and the iodide/triiodide acetonitrile electrolyte is effective within DSSCs is due to the ideal interfacial structure that is created within the DSSC device.

5.4 Conclusion and Future Outlooks

The electrolyte/dye/semiconductor interfacial structure is important for the performance and efficiency of dye-sensitized solar cells. N3-dye structural orientation within this interface has been investigated using acetonitrile as the electrolyte and TiO₂ as the semiconductor. It is found that the N3-dye adsorbs to the TiO₂ substrate with three carboxyl groups, and that the isothiocyanate groups of N3 are positioned away from the TiO₂. Additionally, it was found that the pH conditions during sensitization had no effect on the N3 interfacial structure. ACN solvation of the SCN groups could explain the preferred orientation of N3. The result of this study indicates that the role of the solvent/electrolyte chemical system plays a significant role in the structure of the electrolyte/dye/semiconductor system within DSSC architectures. If the opportunity should arise, this study could be expanded upon by introducing the iodide/triiodide redox couple in the acetonitrile to further capture the chemical environment that N3-dye experiences in a DSSC device.

More broadly, this study has shown that HD-VSFG is a powerful spectroscopic technique that can be performed *in-situ* to probe the buried interfacial structure of chemical species within photoelectrochemical cells. For this study, TiO₂ and CaF₂ are both IR and visible transparent and

non-SFG active, allowing for the “backside” approach to study the buried interface. Future studies on different PEC devices are not limited to these materials and can be performed for substrates and optical windows that have similar properties. Using HD-VSFG to probe buried liquid-solid interfaces for *in-situ* characterization of device architectures has been a fairly new push within the field.^{16,17,28–31} With the recent developments of emerging photoelectrochemical cells, HD-VSFG should be regarded as an incredible and insightful spectroscopic techniques for investigating the chemistry and physical properties of buried interfaces.

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CHAPTER 6 – EXTRACTING HOT CARRIERS IN MONOLAYER MoS₂ PHOTOELECTROCHEMICAL CELLS

The work presented in this chapter is being prepared for submission into *Science* magazine and is the resulting manuscript from the collaborative efforts of the Krummel and Sambur, of Colorado State University (Chemistry Department) and the Montoya-Castillo group of University of Colorado, Boulder (Chemistry Department). First authorship of the manuscript is shared between Yusef R. Farah and Rachelle Austin. In this work, spectroscopic and computational techniques work to elucidate the photophysical and excitonic properties of monolayer MoS₂ photoanodes within an operational photoelectrochemical cell. Acknowledgements for the computational work are attributed Thomas Sayer in the Montoya-Castillo group.

6.1 Introduction

Loss of absorbed solar energy above the semiconducting active-material bandgap due to thermalization is the largest limiting factor of efficiency in solar energy conversion devices.¹ Extraction of charge carriers with energy greater than the bandgap (hot carriers) before thermalization can improve device efficiency by up to 33% and has been shown electrochemically in bulk semiconductors.²⁻⁴ However, as bulk carriers migrate to extraction interfaces they still lose a large fraction of the absorbed solar energy, preventing these systems from achieving the theoretical maximum efficiency of 66%.^{2,5}

Single layer transition metal dichalcogenides (2D TMDs) such as MoS₂ are promising materials for hot carrier extraction due to their atomically thin structure,⁶ broad visible light absorption,⁷ direct optical bandgap,⁸ and slow hot carrier cooling⁹ that is an order of magnitude slower in the single layers versus bulk material. The unique optical and electronic properties of monolayer MoS₂ make it a candidate for a broad range of device applications, including

electrodes, transistors, sensors, and spintronics.^{10–13} Monolayer MoS₂ possesses multiple energetically distinct excitons - coulombically bound electron-hole pairs that are bound at room temperature due to strong exciton binding energies.^{12,14–16} The band-edge A- and B-excitons have energies of 1.88 eV and 2.01 eV respectively and are split due to spin-orbit coupling in the valence band. The higher energy C-exciton has an energy of 2.98 eV and arises due to band nesting of the valence and conduction bands.¹⁷ Previous research has shown that hot C-excitons can have lifetimes of up to hundreds of picoseconds,^{9,18} which is longer than reported ultrafast photocurrent responses in 2D TMDs.¹⁹ The long lifetime of hot carriers combined with short charge-transfer distances should facilitate extraction of C-excitons before they cool to the band-edge. The atomically thin structure of MoS₂ facilitates charge transfer because photogenerated charge carriers need only travel the three-atom thickness of the material to reach perpendicular charge extraction interfaces of supporting substrates and electrolyte. This is supported by the recent observation of hot carrier transfer from MoS₂ into graphene and gold.^{9,20} However, extraction of hot carriers to produce photocurrent has not previously been observed in any 2D TMD solar energy conversion device, nor have the effects of in-operando device conditions on exciton dynamics been quantified to date. In this work, we make a crucial step towards understanding how operational device conditions affect hot carrier dynamics by determining whether hot carriers can be extracted to generate photocurrent before cooling to the band-edge and what is the mechanism of photocurrent generation in monolayer MoS₂.

6.2 Electrochemical Characterization of 2D MoS₂ Photoanodes

We studied hot carrier processes of monolayer (ML)-MoS₂ in a photoelectrochemical cell (Figure 6.1a) because electron and hole transport occurs perpendicular to the layer across three atoms, maximizing the possibility of charge separation and extraction. A ML-MoS₂-coated indium

tin oxide (ITO) electrode served as the working electrode in a three-electrode microfluidic electrochemical cell containing 1 M NaI electrolyte. Upon illumination and applied positive bias, photogenerated holes oxidize I^- to I_2 and photogenerated electrons transfer to the ITO substrate, generating net anodic current flow through the cell. We chose to study the iodide oxidation reaction because the quantum yield is nearly 100% and TMDs are photochemically stable in this electrolyte under long-term irradiation.^{21,22}

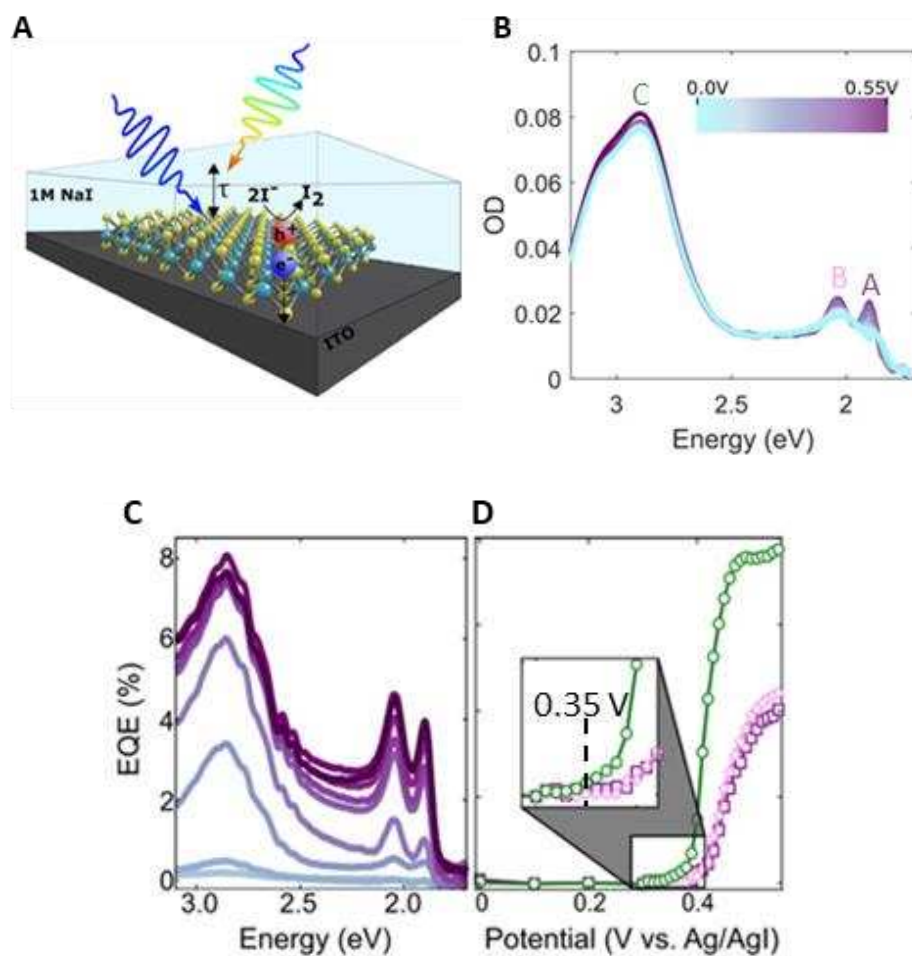


Figure 6.1 **a)** Cartoon illustration of the three-electrode electrochemical cell. The solid blue and rainbow arrows indicate pump and probe pulses for TA measurements. Pt counter and Ag/AgI reference electrodes are omitted for clarity. **b)** Absorbance spectra in 0.25 V increments from 0.0 V to 0.55 V. **c)** EQE spectra versus applied potential from 0.35 V to 0.55 V. **d).** Monochromatic current-EQE measurements for resonant A-, B-, and C-exciton excitation 1.9 eV (purple), 2.2 eV (pink), and 2.9 eV (green), respectively.

To disentangle the mechanism of charge separation upon photo-exciting distinct electron transitions in ML-MoS₂, we simultaneously measured optical absorbance and photocurrent signals under working photoelectrochemical conditions. Figure 6.1b shows absorbance spectra of ML-MoS₂ as a function of applied potential. All spectra feature three peaks because MoS₂ possesses energetically distinct excitons. The band-edge A- and B-excitons occur at 1.88 eV and 2.01 eV, respectively, and differ in energy due to spin-orbit coupling in the valence band.^{16,23} The higher energy C-exciton at 2.98 eV arises from band nesting of the valence and conduction bands.^{16,17} The A- and B-exciton peak intensities increase and blue shift with increasing positive potential. In contrast, the C-exciton, which has a much larger absorption magnitude than the A- and B-excitons, only increases slightly with positive bias. The peak shifts and intensity changes are due to the bandgap renormalization effect, where the electronic bandgap changes with carrier concentration, causing the electronic bandgap of ML-MoS₂ at open circuit conditions (0.3 V) to decrease by 250 meV at 0.0 V, in agreement with literature.¹⁵ Importantly, the magnitude of the band gap renormalization effect is much smaller than the fundamental driving force for hole transfer to [I]⁻ and, therefore, such effects do not complicate interpretation of our photocurrent and TA data in the positive potential regime.

The photocurrent responses induced by photo-excitation of each excitonic feature show striking potential-dependent behavior. At positive bias (e.g., >0.5 V), the photocurrent spectrum mimics the absorbance spectrum (solid purple line in Figure 6.1c), indicating the applied potential generates a sufficiently strong interfacial electric field that effectively dissociates all excitons. Close examination of the potential-dependent spectra reveals subtle differences between the magnitude and photocurrent onset potential for the A, B, and C-excitons that could be further distinguished in monochromatic current-voltage curve measurements (Figure 6.1d). Interestingly,

photocurrent generation onsets first (i.e., more negative potentials) for the C-exciton and the slope of the C-exciton current-EQE (external quantum efficiency – see supplementary information) curve is significantly steeper than the A/B excitons. The lower onset potential means that, under conditions of equivalent interfacial electric field strength, photo-excited C excitons require less driving force to dissociate and contribute to current flow in the cell compared to the lower energy A/B excitons. Our monochromatic current-EQE data strongly suggests that the mechanism of photocurrent generation upon exciting hot C-excitons does not involve C-exciton cooling to the band edge, forming low energy A/B-excitons, because we would have also expected to observe photocurrent upon directly exciting the A/B excitons at the same applied potential (specifically 0.35 V in Figure 6.1d). Hence, the current-EQE data suggests hot C-excitons dissociate and contribute to current flow in the external circuit before cooling to the band edge.

6.3 Ultrafast Pump-Probe *in-operando* Transient Absorption

To assess the feasibility and elucidate the mechanism of hot-carrier extraction in ML-MoS₂ photoelectrodes, we leverage ultrafast pump-probe transient absorption (TA) spectroscopy because this technique measures relative changes in exciton populations under working photoelectrochemical conditions.^{24–28} In a typical experiment, a 50 fs, 3.1 eV pump pulse generates hot, free carriers in continuum states of the ML-MoS₂ photoelectrode at a fixed applied potential condition.²⁹ A white light continuum probe pulse measures the absorbance changes of the sample as a function of pump-probe delay time (τ). Note, a potential-dependent anodic current flows through the cell upon photo-excitation of the sample with the pump pulse (Figure C.5 in Appendix C), further confirming the TA experiment reports on exciton populations under working photoelectrochemical conditions. Figure 6.2a shows TA spectra at $\tau = 1$ ps and as a function of applied potential. The $\tau = 1$ ps condition corresponds to a temporal region that sufficiently allows

the free carriers in continuum states to thermalize after pump excitation.^{29,30} Figure 6.2a shows intense bleach features (i.e., negative $\Delta A(\tau)$ features) at the exciton peak positions and some positive $\Delta A(\tau)$ features due to pump induced lineshape narrowing.^{31,32} The exciton bleach magnitudes are proportional to the exciton populations. The bleach intensities of the A/B excitons are distinct from the C-exciton in that the A- and B-excitons significantly increase as the potential bias is swept to more positive, cathodic potentials, while the C-exciton signal decreases. The decrease of signal corresponds to a depopulation of the C-exciton as the voltage is swept to more cathodic potentials, which indicates that the exciton formation and/or depletion is potential dependent.

To discuss exciton formation and depletion processes in the ML-MoS₂ photoelectrode, we show A- and C-exciton TA decay dynamics at positive and negative potentials in Figure 6.2b, corresponding to conditions of significant anodic photocurrent and no photocurrent, respectively. The B-exciton behavior closely follows that of the A-exciton (supplementary information in Appendix C Figure C.10) and is omitted from Figure 6.2b for visual clarity. The temporal behavior of the hot C-exciton and the band edge A/B-excitons display three key differences. First, the C-exciton bleach intensity reaches a maximum value almost instantaneously (i.e., $\tau = 0$ ps), indicating C-excitons form on a faster timescale than our instrument response (<50 fs), which is expected due to the pump being near resonance with the C-exciton energy. Second, the A-exciton bleach reaches a maximum value at approximately $\tau = 200$ fs. The disparity between the C- and A-exciton rise and decay times at short times (in <200 fs) indicates C-excitons do not cool to A-excitons because we would have expected to observe a fast C-exciton decay component commensurate with the A-exciton rise time. Instead, after C-exciton formation, the fast TA decay rates are approximately 10 ps, consistent with carrier-phonon and carrier-carrier cooling

mechanisms.^{18,33} Third, the magnitude of the C-exciton bleach at $\tau = 0$ ps is smaller (i.e., less negative) at +0.5 V than 0.0 V whereas the opposite trend occurs for the A-exciton. This third observation has important consequences for hot-carrier extraction and will be discussed in greater detail below. Ultimately, if the increase/decrease of band-edge exciton population was solely related to a potential dependent C-exciton cooling mechanism, this would be reflected within the temporal traces; however, we observe no evidence of this within the temporal traces.

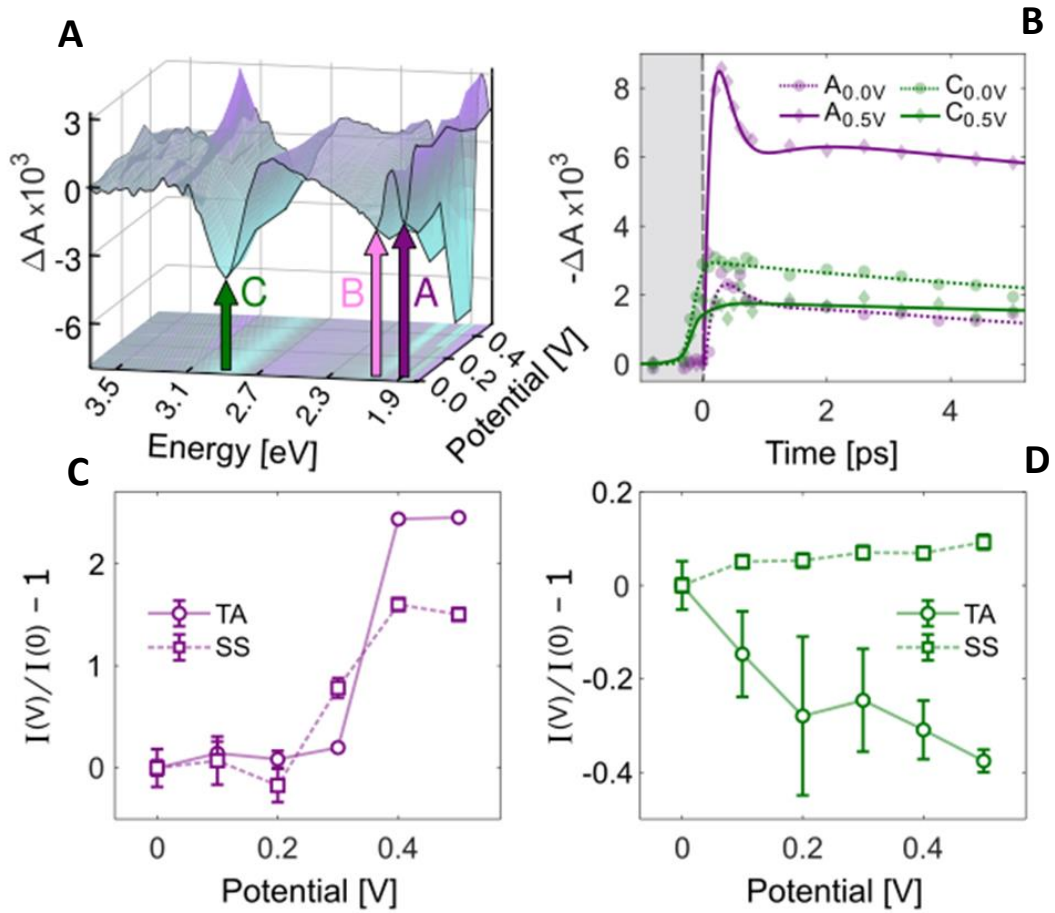


Figure 6.2 a) Transient absorption of MoS₂ photoanodes taken at 1ps over the experimental potential window. b) Temporal trace of the A-exciton (purple) and C-exciton (green) bleach intensity for potentials of 0.0V and 0.5V. Lines through data points are fitted decay curves. B-exciton temporal traces are provided in the Supp Info. c) A-exciton intensity of TA bleach taken at 1ps (solid) and steady state absorption (dashed) for the potential window reported as a ratio compared to the intensity at 0.0V for the respective spectroscopic technique. d) Same analysis as panel (c) but for the C-exciton.

The increase of the band-edge exciton bleach features is not due to C-excitons cooling to the band-edge, but instead attributed to the increase of the ground state absorption of the MoS₂ photoanode system. Recalling the form of the TA signal ($\Delta A = A_{\text{pump}} - A_{\text{unpump}}$), it is clear that an increase in the A-exciton bleach feature can arise when A_{unpump} increases while A_{pump} remains comparatively similar. An increase of ground state absorption is observed in Figure 6.1b and manifests itself in the TA results by the observed increase in the bleach feature caused by the increase of A_{unpump} . Comparison of potential dependent TA and steady state (SS) experiments highlights a compelling relationship between the relative intensity changes and sheds light on the origin of exciton population. The A-exciton potential dependent change of intensity of TA and SS experiments closely follow one another, shown in Figure 6.2c. Therefore, we ascertain that the band-edge exciton bleach features observed in the potential dependent TA experiments rise and fall due to the potential dependent generation of photo-excited carriers.

The C-exciton potential dependent change of intensity for TA and SS experiments do not follow the similar trends observed for band-edge excitons, indicating a different process accounts for the C-exciton intensity (Figure 6.2d). SS experiments show a slight increase in the C exciton intensity when sweeping the potential to more positive potentials. However, the observed decrease of C-exciton intensity for TA measurements indicates a population decrease that is not influenced by the potential dependent ground state absorption. Additionally, temporal traces of exciton intensities reveal that the reduction of C-exciton population is not due to cooling and the formation of band-edge excitons. Instead, the reduced C-exciton bleach feature indicates that after the formation of hot carriers from the pump pulse, an ultrafast (<50 fs) hot carrier extraction occurs at cathodic potentials and competes with the initial formation of C-excitons.

6.4 Calculations of MoS₂ Excitonic States

Given the striking findings of these experiments, it is clearly desirable to understand the underlying differences in the photophysical properties of the band-nested C-excitons, in contrast to those at the band-edge. Previous reports suggest that C-excitons are degenerate with continuum states elsewhere in the Brillouin zone.^{24,34} If this is true, then the explanation seemingly follows readily from an elementary argument comparing activation barriers. Since electron transfer to bulk necessarily separates the electron-hole pair, band-edge excitons would have to overcome their mutual attraction during transfer, whereas C-excitons could have already achieved this in a pre-equilibration step within the material. This would be significant because the band-edge binding energy is known to be several hundred millielectron volts in MoS₂.^{12,16,23}

To investigate the photophysical properties, we obtained the excitonic wavefunctions by solving the Bethe-Salpeter equation (BSE) for pristine, monolayer MoS₂.^{16,34–36} This approach considers two-particle interactions on top of an independent quasiparticle (DFT+GW) picture. States at different k-points are mixed in the BSE, so the resulting eigenfunctions are linear combinations of conduction and valence band states across the Brillouin zone. These calculations predicted that the lowest energy solutions mix states around the K point which correspond to the optical bandgap of MoS₂, i.e. the lowest energy states are the A-exciton and its screened, 2D hydrogenic series (Figure 6.3, purple). To find the first C-exciton state (Figure 6.3, green), we analyzed each solution to find the lowest energy eigenvector that was not centered on the K point, and instead had a majority contribution in the band nesting region (between K and Gamma).

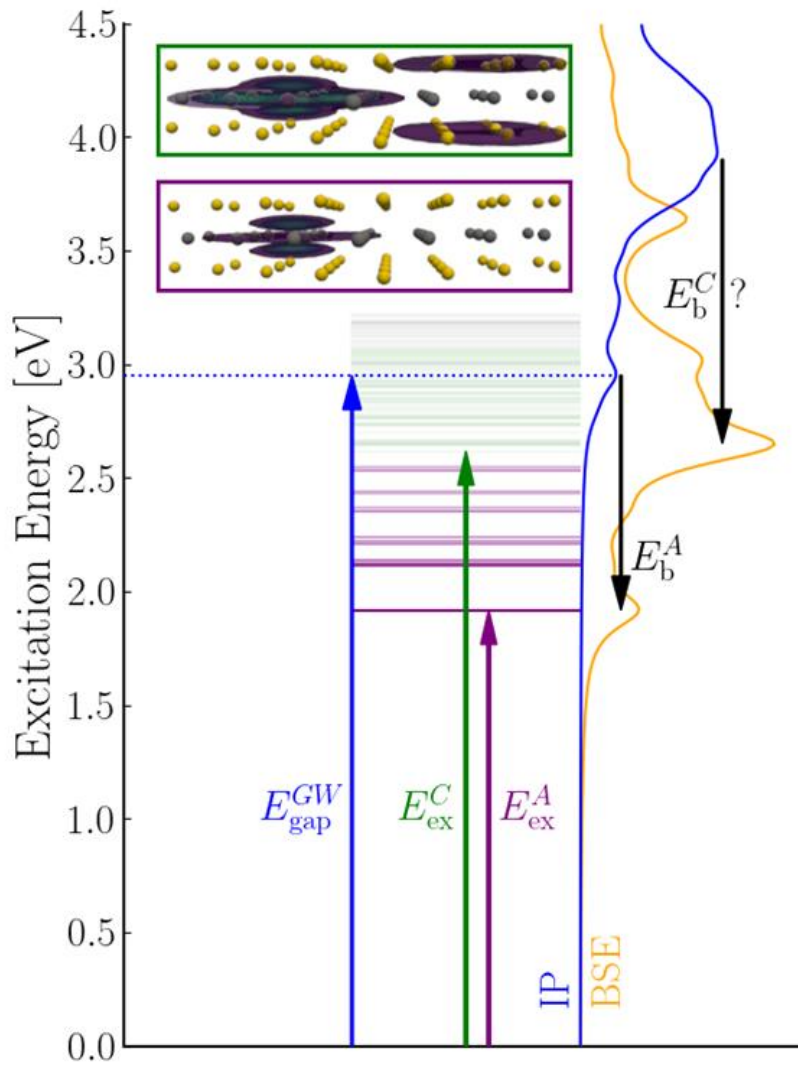


Figure 6.3 Center: Eigenspectrum resulting from the BSE calculation. Spin orbit coupling is neglected to remove B-exciton peaks. The fundamental electronic band gap from the underlying single particle states is shown as a blue dotted line at 2.9 eV. Lowest lying excitations mix states at and around the K-point and are assigned to the A-exciton 'hydrogenic series' (purple). Higher lying states mix states around the Gamma point, the first of these is labeled with E_{ex}^{C} and is considered the first C-exciton state. It and all subsequent states are coloured green. The transparency of each energy level is set to the oscillator strength of the transition, normalized by the A-1s transition (labeled E_{ex}^{A}), which is the strongest. **Top:** The hole-averaged isosurface plots for the electron density in the aforementioned A (below, purple box) and C (above, green box) exciton states. **Right:** The absorption spectra as calculated for the BSE states pictured (orange) and the underlying single particle states (blue). The shift in a peak from blue to orange represents the binding energy. Here, the calculation on freestanding MoS_2 predicts a binding energy of 1.0 eV given the optical excitation energy of 1.9 eV.

How then to define the binding energy? If the difference is taken between the excitation energy of a BSE state and the weighted average difference in energy of the independent-particle states which compose it, then the binding energy of both A and C excitons is not hugely different. Visually, this is equivalent to comparing peak-shifts in the optical spectra computed at the BSE and independent particle levels—see Figure 6.3, right. This result is simply due to the fact that C-excitons appear in a region with a larger gap, whose increase in size is comparable to their increase in excitation energy. Indeed, comparison of the independent particle results and the experimentally known resonances already allows one to deduce the similar binding energy of A- and C-excitons.

However, this does not preclude C-exciton states in the mid-gap region from overlapping the conduction band elsewhere in k-space (namely, near the K point, where it is lowest in energy). In our calculations, the majority of the C peak is below this fundamental gap (Figure 6.3, blue dotted line); yet, additional considerations in the experimental setup of substrate and superstrate screening, as well as the field-induced doping, have the potential to change the relative positions of these peaks. If the C-excitons energy does cut the Fermi surface, then we would expect scattering events to set up an equilibrium between bound species and free carriers, as argued by previous studies.^{24,34} However not the case, and the C-exciton does not have a degeneracy with the continuum, can we still explain its unique behavior within our photoelectrochemical system?

Firstly, while the A-excitons' absorption profile is dominated by the lowest energy resonance, the C-excitons have many states of similar intensity owing to the band-nesting effect. It is therefore reasonable to presume that excitation near (and in our case, above) the C-exciton resonance can easily populate higher lying states which may overlap the continuum, even if the most stable states do not. The argument from activation energies may then still be applied. Indeed, this would explain why C-excitons formed from, say, exciton-exciton annihilation do not transfer

to ITO at low potential, since they are created firstly in the most stable states, with the highest binding energies.

Secondly, because the C-exciton is composed of states in a different region of K space to its band-edge counterparts, it has a different spatial distribution. As a result of the MoS₂ symmetry, A excitons are entirely localized on molybdenum. In contrast, C-excitons gain sulfur character from their conduction states nearing the Gamma point. One can see this quantitatively at the top of Figure 6.3, which shows the (hole-averaged) electron density isosurface for both of the lowest energy A- and C-exciton states. Since the rate of electron transfer grows with increasing electronic coupling between donor (MoS₂) and acceptor (ITO), and the electronic coupling decays exponentially with increasing distance between donor and acceptor, the close proximity of the S-localized electron in C-excitons to the ITO (in comparison to the A-exciton) suggests that the C-exciton would display an exponentially higher transfer efficiency than the band-edge exciton counterparts.

We must reiterate that these calculations are only valid for isolated, pristine MoS₂. Indeed it is challenging to treat the full system accurately within the BSE, since one must include: the role of the external substrate and electrolyte screening, the finite carrier population (as a function of potential), phononic coupling, and excitonic band-dispersion (in the nesting region in particular). The majority of the aforementioned factors are areas of current research in the many-body community, and the results presented in this paper amply justify their continued study. This is not to even begin the statistical sampling and electrochemical treatment required external to the electronic structure problem.

Assuming such developments were possible, these results suggest proceeding by a quantitative comparison of the extent to which the two identified C-exciton properties contribute

to the charge transfer. Why is this question important enough to motivate such developments? Consider: If the binding energy argument from the broad distribution of C states is most significant, then it proposes a design principle wherein we search for other band-nested materials with perhaps even smaller direct gaps. Conversely, if the spatial electron distribution is essential, then this places restrictions on the structures of 2D materials which could exhibit this behavior, as the metal-to-ligand character arises from the specifics of the symmetries of 2p and 4d orbitals within the hexagonal lattice.

6.5 Conclusion

For the first time, we have measured photocurrent generation from hot carriers in a monolayer MoS₂ electrochemical cell under applied bias. We demonstrated proof-of-concept *in-operando* transient absorption measurements in conjunction with steady state spectro-electrochemical measurements. With these techniques, we observed ultrafast extraction of hot carriers (< 50 fs) before band-edge exciton formation, which may explain the high photocurrent yields observed in our device. Calculation of excitonic states revealed that the delocalized orbital composition for high energy C-excitons may facilitate efficient and ultrafast carrier extraction within the photoelectrochemical cell. Methods and findings here are promising for the future development of hot-carrier, light-driven devices and motivate the continued improvement of many-body theories in 2D systems and heterostructures more generally.

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CHAPTER 7 – THE EXCITON ENERGY SHIFT OF MONOLAYER MoS₂ PHOTOANODES

The work presented and discussed in this chapter is a preliminary report intended to become a published article in the year 2022. The steady state and ultrafast spectroscopic experiments performed on the monolayer MoS₂ photoelectrochemical flow cell revealed shifts to the band edge exciton energies. These results indicate that the band edge exciton's energy of monolayer MoS₂, and possibly all monolayer TMDs, can be systematically tuned within device architectures. Results of the potential dependent energy shifts are presented and discussed.

7.1 Introduction

Monolayer transition metal dichalcogenides (TMDs) are a specific class of semiconductor with that hold great promise for applications in future optical and electronic devices such as photodetectors, light emitting diodes, and photovoltaics.¹⁻⁵ Monolayer TMDs are atomically thin, 2-dimensional sheets of a transition metal (M) sandwiched between two hexagonal planes of a chalcogen (X), giving the general formula MX₂. Fascinating light-matter interactions arise in this class of semiconductor due to the reduced dimensionality, strong Coulombic effects, and excitonic species. Monolayer TMDs are unique from typical bulk semiconductors because they have specific excitonic species that arise from photoexcitation with reported binding energies of hundreds of millielectronvolts.^{6,7} Additionally, the excitons are long lived with excitation lifetimes spanning up to the nanosecond time regime.^{2,8,9} Lower energy, band edge excitons arise from photoexcitation and transition of an electron from the valence band (VB) maximum to the conduction band (CB) minimum. This exciton is typically termed the A-exciton. Additionally, spin orbit coupling splits the energy in the VB maximum and gives rise to a similar band edge exciton with slightly higher energy and a different spin, called the B-exciton. A higher energy exciton also

exists and is named the C-exciton, which arises from a “band nesting” transition. Details of this are described elsewhere in this dissertation and a visualization of the specific excitonic transitions is provided in the results section of this chapter. Overall, the excitonic properties of the TMD dictate the material’s function within device architectures, and therefore, a fundamental understanding of the excitonic photophysical properties is necessary to integrate monolayer TMDs into next generation devices.

The large binding energy, long excited lifetimes, and unique photophysical properties of the TMD excitons make them particularly useful within light-driven devices. However, a fundamental understanding of the excitonic properties of these materials is still sought after within the field. For example, changes to the material’s bandgap caused by bandgap renormalization effects^{10,11} and local environment effects to the exciton binding energy^{7,12} can drastically change the photophysical properties of the excitonic species. Specifically, these effects can manifest themselves within the material by changing the energy of the excitonic transition. A change to a TMD’s exciton energy can hinder device performance if a set specific energy is necessary for operation; on the other hand, a change in exciton energy could offer dynamic tunability to the operation of a light-driven device. For either case, a fundamental understanding of the photophysical properties that can alter the excitonic transition energy is needed for the integration of these materials in next generation devices.

Here, we investigate the excitonic properties of monolayer MoS₂, with a specific focus on the excitonic transition energy. We have designed an operational photoelectrochemical cell that integrates a monolayer MoS₂ photoanode and performed steady-state UV-vis and ultrafast transient absorption spectroscopy experiments to monitor the exciton resonant energy as a function of applied voltage potential within the operational device. We observe voltage potential dependent

changes to the exciton energies associated with the band edge excitons (A and B) for both steady state and ultrafast spectroscopic techniques. Additionally, we identify time dependent shifts to the exciton energy caused by dynamic changes to the binding energy through screening effects, bandgap renormalization effects, and photocurrent generation within the PEC.

7.2 Methods

7.2.1 MoS₂ Photoelectrochemical Flow Cell

Monolayer MoS₂ (6Carbon Technology) were grown using chemical vapor deposition and mechanically transferred to an indium tin oxide (ITO) coated glass slide. The resulting 1 cm x 1 cm MoS₂ samples on ITO are then integrated into our photoelectrochemical flow cell apparatus described previously in Chapter 2. Briefly, a 50 μ m spacer and a cover slip are attached to the MoS₂/ITO face of the glass slide using Loctite® epoxy to form a chamber for electrolyte to flow through. Two holes are pre-drilled into the glass slide to act as inlet and outlet ports for the 1 M NaI aqueous electrolyte to enter in and out of the cell. The outlet port feeds the electrolyte into a chamber with a platinum and silver wire. An external pump (Kent Scientific) flows electrolyte through the photochemical cell at a rate of 0.5 mL/hr.

The MoS₂/ITO, platinum wire, and silver wire are all attached to a potentiostat (Ivium Compactsat) in order to apply a potential bias to the photochemical cell, as well as measure the generated photocurrent. The MoS₂/ITO acts as the working electrode and photo-oxidizes iodide [I]⁻ in the electrolyte to form triiodide [I₃]⁻. The platinum wire acts as the counter electrode and reduces triiodide back to iodide, and the silver wire is used as a reference electrode, specifically, referencing the applied voltage to the Ag/AgI redox reaction.

7.2.2 Steady-state UV-Vis

UV-Vis measurements using monochromatic, continuous-wave light is performed using a Horiba OBB Tunable PowerArc Illuminator. The MoS₂ flow cell is exposed to monochromatic light from the UV-Vis spectrometer scanning from 755 nm to 405 nm in 1 nm steps. Voltage potentials are applied to the MoS₂ flow cell and held constant for each UV-Vis measurement. Voltage potentials were applied within the range of 0.0 V to 0.55 V.

7.2.3 Transient Absorption

Ultrafast spectroscopic measurements are done utilizing our homebuilt transient absorption spectrometer described in detail within Chapter 2. Briefly, a regenerative amplification system (Wyvern 1000) is used to produce ultrafast (<50 fs) pulses of light centered at ~790 nm, with an energy of 3.2 mJ and a repetition rate of 1 kHz. The amplified light is lowered to an intensity of ~10 μ J and split into two lines utilizing a half-waveplate and polarizer combination. One line is sent focused down in a 2 mL quartz cuvette to produce a white light continuum to be used as the probe pulse. The other line, used as the pump pulse, is sent to a delay stage to control the timing of the pump pulse with respect to the probe pulse, and then sent to a BBO crystal to frequency double the light from 790 to 395 nm. The pump and probe pulses are spatially overlapped at the sample with fluences of approximately 75 μ J/cm² measured using a Thorlabs power meter and Mightex camera. The probe pulse is collected, collimated, and sent to a spectrometer (iHR550) equipped with a 100 lines/mm grating (450 nm blaze) and a single line 2048 element array detector (OctoPlus, Teledyne e2V). A chopper wheel is used to modulate the repetition rate of the pump pulse from 1 kHz to 500 Hz in order to collect “pump” and “unpump” pulse sequences used to calculate the difference spectrum ΔA .

7.3 Results

The three distinct exciton species of monolayer MoS₂ are identified by our steady-state UV-Vis and ultrafast transient absorption (TA) measurements performed on the flow cell. Figure 7.1 shows the A-, B-, and C-exciton resonant energies at approximately 1.88 eV, 2.01 eV, and 2.98 eV, respectively. By applying a voltage bias to the photoelectrochemical cell, two distinct potential dependent trends to the acquired UV-Vis spectrum (top figures) are observed. First, the intensity of the band edge excitons (A- and B-excitons) are shown to increase as the applied potential bias [V] is swept to more cathodic (positive) potentials. Second, as the potential is swept cathodically, the energy of the band edge excitons blueshift and then slightly red shift at potentials ≥ 0.4 V, indicated by the arrows inset in Figure 7.1.

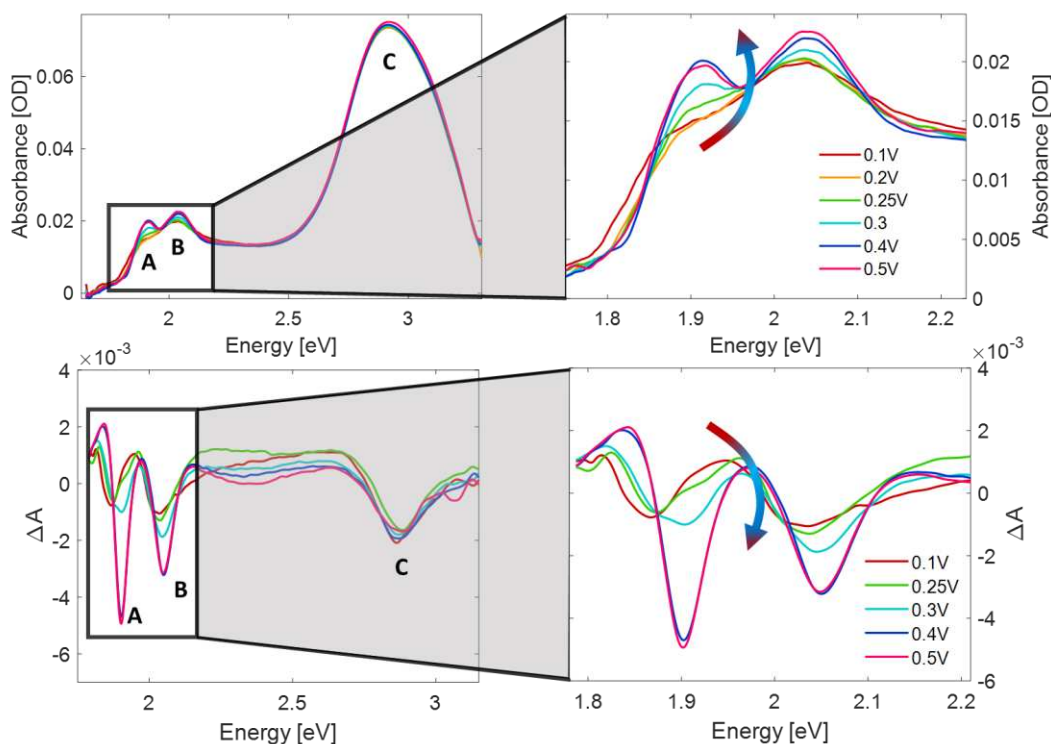


Figure 7.1 Results of the UV-Vis steady state (top) and TA experiments (bottom) of the monolayer MoS₂ photoanode within the PEC flow cell with different applied potentials. The figures to the right are zoomed in band edge excitons of the spectra shown on the left.

The bottom figures of Figure 7.1 show the wavelength resolved transient absorption spectra at 1 ps and reflects identical potential dependent trends seen in the steady state (SS) UV-Vis absorption measurements. TA experiments are done using a pump-probe geometry, with a pump pulse (~50 fs) at 3.1 eV that is used to photoexcite the MoS₂ photoanode and generate photocurrent. Spectra are reported as a difference spectrum, $\Delta A = A_{\text{pump}} - A_{\text{unpump}}$, which reports on the change of intensity of the detected probe pulse as a function of delay time, τ , from the pump pulse. The negative features of the TA spectra are a result of a photo-bleach and indicates the presence of the photo-excited carriers in the system. Therefore, the bleach features at the resonant energies of the exciton species correspond to the presence of the excitonic species within the MoS₂ photoanode at that delay time, which is 1 ps for Figure 7.1.

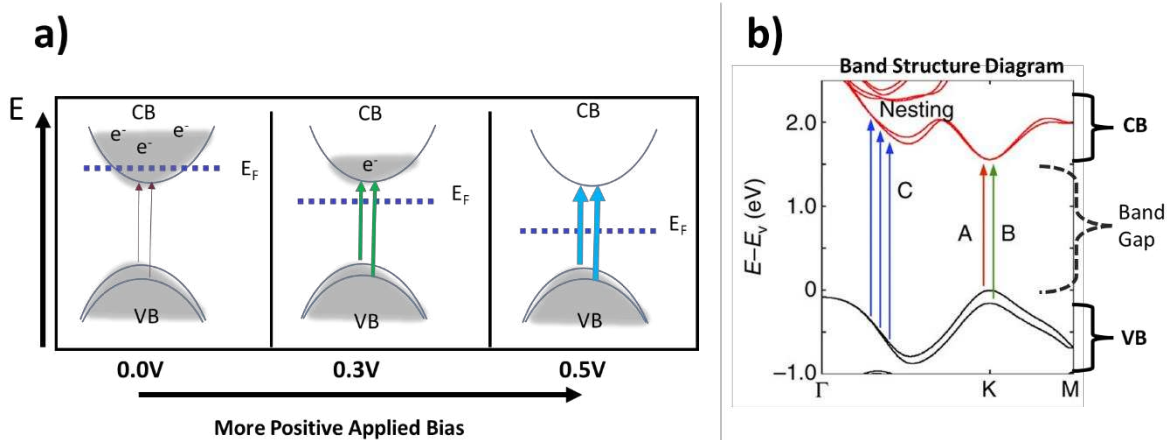


Figure 7.2 (a) A diagram representing the filling/depopulation of electrons within the conduction band of the MoS₂ photoanode as the applied potential is set to more negative/positive biases. (b) a band structure diagram describing the excitonic transitions related to the monolayer MoS₂ material.⁶

Addressed first are the potential dependent changes to the band edge exciton absorption features. The changes to the SS absorption and TA bleach intensity of the band edge excitons is discussed in Chapter 6 and is owed to the filling/depopulation of electrons in the conduction band causing the reduction/increase of photo-excitable carriers. Additionally, a previous study also

observed similar results to the band edge exciton intensities as a function of applied potential.¹³ A more negative applied potential externally “dopes” the system with additional electrons, thus, increasing the Fermi level energy of the electrochemical system, similar to that of an n-doped semiconductor. Shown in the left-most panel in Figure 7.2a, the conduction band (CB) has a large electron density at lower, more negative applied potential biases. Photoexciting electrons from the valence band (VB) to the conduction band is therefore hindered at negative potentials due Pauli blocking because of the increased electron density in the CB. Conversely, at positive applied potential biases, the Fermi level energy is lowered and electron density from the conduction band is depopulated. It follows then, at positive potentials, more electrons can be photoexcited from the VB to the CB due to a reduced Pauli blocking effect.

The band edge excitons (A and B) are specifically focused on in this chapter because the higher energy C-exciton does not have a potential dependent energy shift, seen in Figure 7.1. The A- and B-excitons arise from the same transition, which is associated with the photoexcitation from the VB maximum to the CB minimum, shown in Figure 7.2b. The difference in energy between the A- and B-excitons is due to spin-orbit coupling leading to a splitting of energy levels in the VB. Because both the A- and B-excitons shift and respond similarly to the applied potential, the results presented herein only shows the A-exciton for simplicity but will be discussed to represent both band edge exciton species.

The observed energy shifting of band edge excitons is interesting because it reveals physical changes to the local environment, band gap energy, and exciton binding energies due to the presence of an external applied potential. This has direct implications to device fabrication regarding material photocatalytic activity, thermodynamic barriers, and optical and electronic tunability. To investigate exciton energy shifts, we have fitted the steady state and ultrafast spectra

of Figure 7.1 with a gaussian line function to capture the exciton center energy of the band edge excitons. The fitting procedure utilizes a linear combination of a gaussian lineshape function with amplitude, center position, and FWHM as parameters and a linear polynomial with the slope and y-intercept as parameters to represent a baseline offset. The fitting procedure is identical to the one outlined in Chapter 2 within this dissertation.

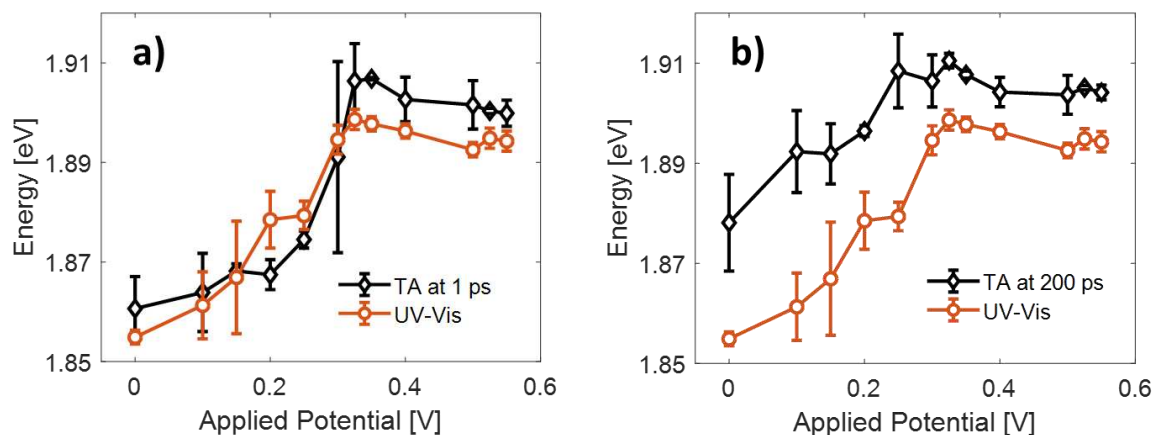


Figure 7.3 (a) The results of the A-exciton energy for UV-Vis (orange) and TA experiments taken at a delay time of 1 ps as a function of applied potential. (b) Similar results as panel (a) but the TA data is taken at a later delay time of 200 ps.

Results of the A exciton energy from the spectral fitting is shown in Figure 7.3 as a function of applied potential. Starting with the results from the steady state (orange), the A-exciton energy changes as a function of applied potential as anticipated by the UV-Vis absorption data shown in the top panel of Figure 7.1. The A-exciton energy is lowest at the most negative applied potential, 0.0 V, with an energy of 1.855 ± 0.001 eV. As the potential is swept to more cathodic (positive) potentials, the A-exciton energy blue shifts, reaching a maximum energy of 1.899 ± 0.002 eV when the applied potential is at approximately 0.325 V. Applying potentials more positive than 0.35V slightly red-shifts the A exciton energy, with a resulting energy of 1.894 ± 0.002 eV at the applied potential of 0.55 V.

Since TA experiments are measured as a function of time, TA spectra at specific delay times are selected to compare to steady state UV-Vis measurements. Using the same time delay used for Figure 7.1 of 1 ps, Figure 7.3a shows the fitted energy of the A-exciton for TA measurements. The A-exciton energies for TA measurements follow the same potential dependent trends as that of the UV-Vis measurements. Moreover, the energies of the A-exciton for the TA spectra at 1 ps are nearly identical to the UV-Vis measurements for the applied potential range of 0.0 V to 0.3 V. At potentials ≥ 0.325 V, the A-exciton energies for the TA spectrum at 1 ps are slightly higher in energy than the UV-Vis energies by approximately 0.01 eV.

Interestingly, shown in Figure 7.3b, the fitted A-exciton energies for the TA spectra of a delay time 200 ps also show potential dependent trends similar to that of the 1 ps time delay and steady state UV-Vis measurements in Figure 7.3a. The UV-Vis data (orange) shown panel (b) of Figure 7.3 is identical to panel (a) and is used to guide the eye to the differences between the time delays of 1ps and 200 ps. However, while the general trends are similar, the energies are all observed to be blue-shifted with respect to both the UV-Vis and TA at 1 ps data. This result is indeed interesting and indicates that there is a time dependent component to the A-exciton energy shift in addition to the potential dependent energy shifts.

Investigating the temporal component of the energy shift can be done by plotting the fitted A-exciton energy as a function of time for each individual applied potential. Shown in Figure 7.4 are the time traces of different applied potentials for the A-exciton energy relative to the initial starting energy of the A-exciton at $\tau = 200$ fs. The A-exciton forms after the initial pump excitation at $\tau = 0$ fs and reaches a maximum at approximately 200 fs, for this reason the starting energy for the A-exciton was chosen to be at 200 fs. By comparing the different data sets with the relative

change to the energy versus time, and by plotting the time axis as a log, the different data sets shown in Figure 7.4 can be more clearly compared to one another.

The data in Figure 7.4 is sectioned into four panels, panel (a) for the potentials ≤ 0.3 V, panel (b) for potentials ≥ 0.3 V, panel (c) for the no applied potential in the flow cell, and panel (d) for glass and ITO samples that are not in a flow cell. Time traces for all applied potentials in Figure 7.4a and 7.4b show that the A-exciton energy has a lower energy within the first few picoseconds compared to times (>100 ps). This observation of the time traces aligns with the data shown in Figure 7.3, where the A-exciton energy at 200 ps was shown to be higher in energy than at 1 ps. Further, the time traces of Figure 7.4 reveal the interesting observation that blue-shift from early to later times (1 ps $\rightarrow$ 200 ps) is not linear nor is it similar for all applied potentials.

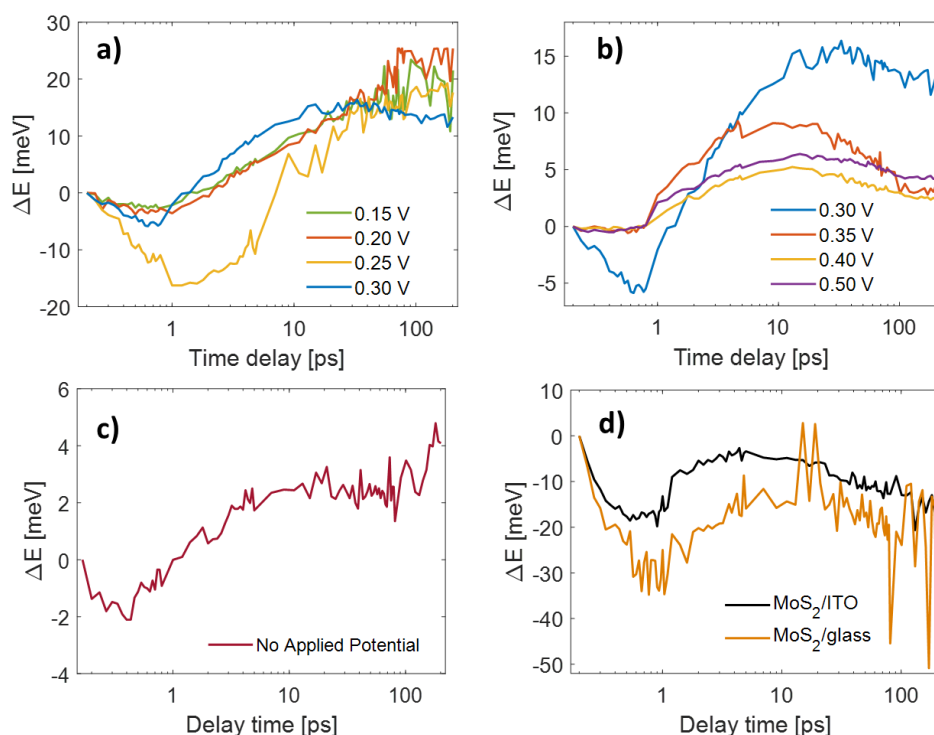


Figure 7.4 The change of the A-exciton energy in time with respect to the initial energy of the A-exciton for each individual applied voltage. (a) The change in energy for applied voltages of 0.15 V – 0.30 V, (b) for voltages 0.30 V – 0.50 V. Panel (c) shows the A-exciton energy shift when there is no applied voltage in the PEC flow cell. Panel (d) shows the results for glass and ITO substrate samples not in the PEC flow cell.

The first observation to note in all the plots shown in Figure 7.4 is the blue shift of the A-exciton between the approximate times of 1→20 ps. The voltage potentials shown in Figure 7.4a are all have a similar trend for the A-exciton energy shift. The most apparent change in A-exciton energy happens between 1-30 picoseconds when the exciton energy blueshifts by approximately 15-20 meV. At later times after ~50 ps, the blueshift is less rapid, eventually reaching an “equilibrium” energy for the A-exciton at around 100 ps. Similar to the traces in Figure 7.4a, traces in Figure 7.4b show that the blue-shift for the A-exciton happens between 1-20 ps. However, very notably, the blue-shift of the A-exciton energy stops, and the energy begins to red-shift at approximately 20 ps. The red-shift does not occur as fast as the initial blue-shift, and eventually the exciton energy equilibrates at around 150 ps.

Figures 7.4c and 7.4d can be thought of as controls for the experiments, as 4c shows the relative A-exciton energy shift of the flow cell sample with no applied potential, and 4d show the results of MoS₂ samples outside of the PEC flow cell. Both plots in 4c and 4d show trends to the voltage potential plots of 7.4a and 7.4b, in that the A-exciton blueshifts from the times of 1→10 ps. However, the sample in the flow cell with no applied potential does not experience a red-shift at times > 20 ps, whereas the energy for the glass and ITO samples does appear to stop blue-shifting and begin to red-shift.

Further, an additional temporal A-exciton energy red-shift is observed within the sub-picosecond timescale ($\tau < 1$ ps). The sub-picosecond red-shift is mostly prominent for potentials ≤ 0.30 V, which are the potentials that do not facilitate the generation of photocurrent, and the red-shift is also observed in the plots for the control samples in panels 7.4c and 7.4d. However, the red shift is not present for the potentials ≥ 0.35 V, which is interesting because these are the potentials that a photocurrent is being generated.

Overall, the A-exciton energy-time traces in Figure 7.4 reveal a sub-picosecond red-shift that is followed by a blue-shift of the energy, which occurs on the approximate time scale of 1-30 ps. For potentials that generate a measurable photocurrent and for glass and ITO samples, an additional red-shift is observed at approximately 15 ps. Eventually, at long times (~150 ps) the A-exciton energy equilibrates and ceases to shift in energy. These results indicate not only that the A-exciton energy is potential dependent and time dependent, but also dependent on if the photoelectrochemical cell is generating photocurrent and if the MoS₂ sample is in the presence of an electrolyte versus “dry” conditions. This finding is important for the future implementation of monolayer TMDs in opto-electronic device architectures with variable electric fields and/or photoelectrochemical environments.

7.4 Discussion

The origin of exciton energy shifts has been extensively studied for monolayer TMDs, and indeed, there are many different physical processes that can induce the observed energy shifts.^{2,6,10,12,14–17} There are two predominant trains of thought to explain the shifting of an exciton’s energy: bandgap renormalization and changes to the exciton binding energy. Shown in Figure 7.5 is the energy of the band edge exciton with respect to the bandgap energy and the binding energy. In panel Figure 7.5a, a theoretical, unperturbed system in equilibrium is shown for a semiconductor. Bandgap renormalization is a change in the bandgap of the semiconductor material due to non-equilibrium effects such as doping the semiconductor or photoexciting an electron from the VB to CB. These non-equilibrium effects cause changes to the electronic structure of the semiconductor and overall alter the energy gap between the VB and CB. Bandgap renormalization typically manifests itself as a redshift in spectroscopic measurements, including TA.^{11,18} An energy level diagram describing how bandgap renormalization effects can redshift the

exciton energy is shown in Figure 7.5b, where E'_{exciton} is the new exciton resonant energy and it is lower in energy than the unperturbed E_{exciton} in panel (a).

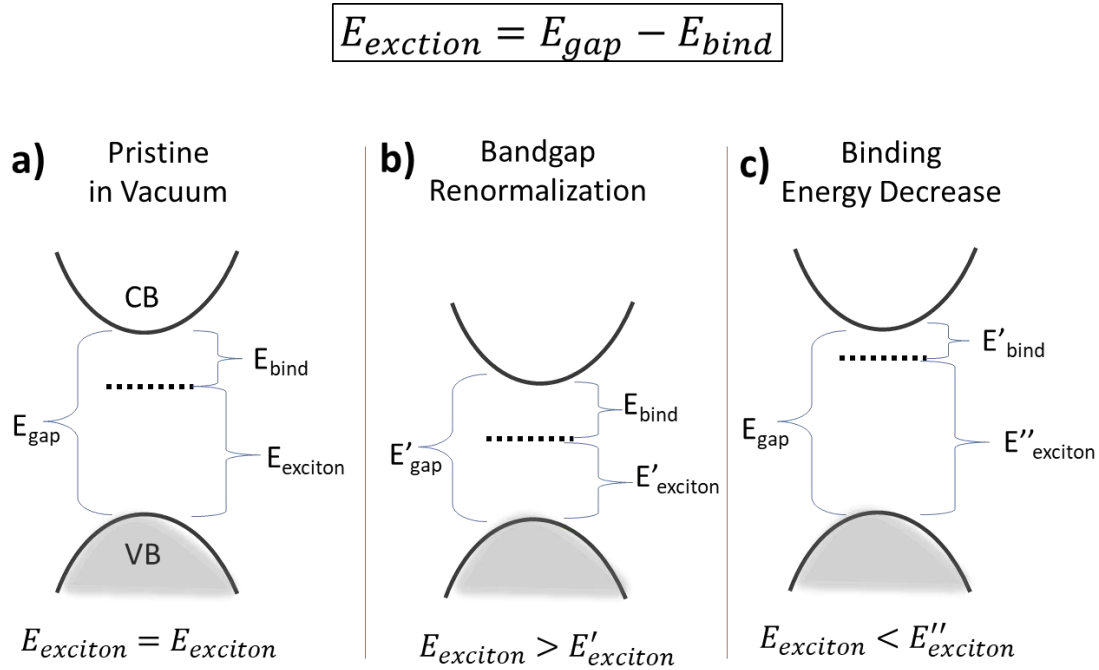


Figure 7.5 An energy diagram representing the valence band (VB) and conduction band (CB) of monolayer MoS₂. Panel (a) represents the energies associated with the bandgap, binding energy, and the exciton resonant transition energy for a MoS₂ in a pristine condition, unperturbed by substrate, doping, or other external factors. Panels (b) and (c) show the changes to the exciton resonant transition energy when external effects cause changes to the bandgap energy and binding energy.

An increase or decrease to the exciton binding energy can lead to a red-shift or blue-shift, respectively, of the resonant exciton energy.^{2,12} The example in Figure 7.5c shows the decrease in the exciton binding energy from the equilibrium binding energy, described as $E'_{\text{bind}} < E_{\text{bind}}$, which results in a blue-shift to the exciton energy compared to the semiconductor conditions in panel (a) such that $E_{\text{exciton}} < E''_{\text{exciton}}$. Screening of the electron and hole pair can reduce the Coulombic interaction between them and subsequently reduce the exciton binding energy. Screening effects can be caused by substrate, charge carriers, and even other excitons.^{19,20} Both the bandgap

renormalization and binding energy effects are present in typical, bulk semiconductor materials; however, these effects tend to be more substantial for monolayer TMDs due to the high density of excitons and the low-dimensionality of the material.

By applying an external potential bias to the photochemical cell, we can effectively “dope” the MoS₂ photoanode. The change in electron density due to the external applied bias can induce a bandgap renormalization effect, which results in the the potential dependent A-exciton energy shifts seen in Figure 7.3. Applying more negative potentials to the system can be thought as doping in electron density to the MoS₂/ITO electrode; similarly, applying more positive potentials can be thought as removing electron density. As the potential is swept to more negative potentials, this increases the electron density and electron population in the CB of MoS₂, which in turn causes a bandgap renormalization effect and red-shifts the A-exciton, following the results presented in Figure 7.3 and diagram in Figure 7.6b. The same logic follows that, when applying a positive bias, electron density is removed from MoS₂ and the A-exciton blue-shifts (Figure 7.3). Similar A-exciton energy shifting and conclusions based on the electrical doping of MoS₂ photoanodes has been shown in previous studies and reflect our results presented here.^{13,14} While the energy shift trends shown in Figure 7.3 are explained via electrical doping by the external potential bias, the temporal shifts of the A-exciton shown in Figures 7.4 cannot be explained with the same logic.

Addressed first is the blue-shift within the first 1-30 ps of the A-exciton seen at all potential biases in Figure 7.4. Following the logic presented in Figure 7.5c, a blue-shift can manifest itself in spectroscopic measurements due to a reduction of the exciton binding energy. The exciton-exciton interactions that occur within the material can screen the Coulombic attraction between an electron-hole pair, leading to a reduction of binding energy and causing a blue-shift seen within the A-exciton time traces of Figure 7.4.^{12,15,20,21} Additionally, screening effects can be brought on

by the electrolyte used within our PEC flow cell. However, what then causes the red-shift seen in the photocurrent-generating potentials of Figure 7.4b?

When photocurrent is generated in our PEC flow cell, this is the direct result of extracting electrons from the MoS₂ photoanode. The extraction of electrons reduces the exciton-exciton interactions. Essentially, when carriers are extracted, this alleviates the effects that would cause the blue-shift seen within the first 10s of picoseconds, and so, the A-exciton red-shifts as shown for Figure 7.4b. It follows, then, that at applied potentials with no photocurrent generation, electrons are not extracted to the PEC system and the blue-shifting effects are not alleviated.

Lastly, the initial red-shift at the sub-picosecond timescale shown in Figure 7.4 is most likely caused by the initial generation of hot free carriers in the system.^{12,15,20,22,23} The initial excitation of the system with a pump pulse well above the bandgap energy generates electrons and holes that are not bound to each other, hence they are termed as “free” carriers. Eventually, at later times, the free carriers relax to form bound excitonic species and cool to the band edge. These free carriers induce bandgap renormalization effects as well as carrier-exciton screening effects within the sub-picosecond time scale, which partially canceling each other out, but overall leads to the slight red-shift seen in Figure 7.4a and Figure 7.4b(0.3V).^{12,20,21} The lack of sub-picosecond shifting for the positive potentials ≥ 0.35 V shown in Figure 4b might be the result of ultrafast hot carrier extraction to the PEC flow cell, and supports the findings and discussion presented in chapter 6.

7.5 Conclusion

We have shown that the band edge excitons of monolayer MoS₂ photoanodes in an operational photoelectrochemical cell (PEC) experience shifts to their energy, which are dependent on applied external voltage, time, and photocurrent generation. The applied voltage effectively

dopes the system with electron density, causing a bandgap renormalization effect and leads to a red-shift of the band edge excitons as electron density is doped into the MoS₂ photoanode system. Temporally, at the sub-picosecond time scale, the generation of free carriers induce a slight red shift to the exciton energy. At positive, photocurrent generating voltages (≥ 0.35 V), free carriers are extracted at the sub-picosecond time scale and mitigates the exciton energy shift within this time scale.

The temporal blue-shift of the band edge exciton energies seen within the time region of 1-30 ps is a direct result of exciton-exciton interactions. When a photocurrent is generated in the PEC, this blue-shift stops and the energy begins to red-shift, possibly due to the extraction of electrons, and mitigates the exciton-exciton interactions that causes the blue-shift. Our work here presents systematic tuning of the bandgap and exciton energies within an operational PEC and will inform the integration and design of optical and electrical devices utilizing monolayer TMDs.

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CHAPTER 8 – CONCLUSION

The research and work presented in this dissertation has focused on studying the structure and dynamics of chemical systems pertaining to photoelectrochemical cells using nonlinear optical spectroscopic methods. Specifically, the two spectroscopic methods of heterodyne-detected vibrational sum frequency generation and ultrafast transient absorption are independently utilized to study two different photoelectrochemical systems. In chapters 3, 4, and 5, HD-VSFG is used to investigate how acidic/basic conditions effect the interfacial structure of N3-dye on different substrates and in the presence of an electrolyte. In chapters 6 and 7, TA explores the ultrafast exciton dynamics and photophysical properties of monolayer MoS₂ photoanodes in an operating photoelectrochemical cell. Expanding our fundamental understanding of these chemical systems presented here will inform on the development of next-generation photoelectrochemical devices; but also, the work here provides the foundation for the application of nonlinear optical spectroscopic methods for the purpose of researching photoelectrochemical systems.

The HD-VSFG research done on the N3-dye chemical system revealed a pH-dependent interfacial structure of N3-dye on both gold and TiO₂ substrates. Both substrates were sensitized with N3 sensitizing solutions that were titrated to different pH's. By titrating the solution to a desired pH, the distribution of N3 protonation states can be altered, and these different protonation states were shown to have different binding structures to gold and TiO₂ substrates. Effectively, this study showed that the molecular structure of N3 can be controlled by simply changing the pH of the solution. Tuning the interfacial structure of N3-dye (or any chromophore/photocatalysts) is a desirable parameter to control during sample preparation and/or during device fabrication because the molecular structure can influence electron transfer kinetics, redox reactions, and

photocatalytic activity. Further, HD-VSFG experiments on the acetonitrile/N3/TiO₂ chemical system highlights the inherent advantages of this spectroscopic method of probing buried interfaces within device relevant chemical environments. While the experiments showed no pH-dependent orientation of N3 within the acetonitrile/N3/TiO₂ interface, this is a significant result and fascinating discovery. The addition of the acetonitrile established a preferential solvent shell around the surface-bound N3 molecules, and consequently, the structure of N3 previously established during the sensitization step was not sustained. This calls to attention the importance of studying the impacts of the electrolyte in photoelectrochemical systems to truly understand the chemistry at the electrolyte/chromophore/semiconductor interface.

Additionally, the use of the multivariate fitting procedure developed for HD-VSFG measurements is a novel application of the real and imaginary parts of the second order susceptibility, $\chi^{(2)}$, and constrains the fitting parameters to give precise molecular orientational information. Overall, the experiments performed on metallic (Au), nanoparticulate semiconductor (TiO₂), and buried interfaces (ACN/N3/TiO₂) showcase the utility of HD-VSFG for studying the molecular interfacial structure across a multitude of substates.

The research performed on the MoS₂ photoanodes utilizes TA measurements to investigate exciton photophysics in an operational photoelectrochemical system. Exciton population dynamics and transition energy are important characteristics of semiconductor materials. The reduced dimensionality, intense Coulombic interactions, and strong light-matter properties of monolayer transition metal dichalcogenide semiconductors create the perfect stage for fascinating exciton photophysical properties. By integrating monolayer MoS₂ into a PEC, we effectively dope the material with an external voltage bias and simultaneously generate an *in-operando* photocurrent during TA measurements. In chapter 6, it was shown that high-energy C-exciton and hot free

carriers contribute to the generation of photocurrent via an ultrafast electron extraction. This was evident due to the hindered formation of C-excitons at time scales < 50 femtoseconds. The result is exciting because it not only reports the extraction of hot carriers in a relevant and operational chemical system, but also encourages the research and development of monolayer TMD technologies for photovoltaic and photochemical purposes to break past the Shockley-Queisser limit. Moreover, the shifts in energy to the band-edge excitons discussed in chapter 7 reveal that the exciton transition energy is far from consistent. In fact, just looking at the material changes the exciton energy, literally! Light from the pump pulse creating free carriers, electronically doping the system via an applied bias, and exciton-exciton interactions (just to name a few) are sources that induce bandgap renormalization effects and/or screening effects, which shift the transition energy of the band edge exciton. These energy shifts can be used advantageously in device fabrication; however, much remains unknown regarding the shifts to exciton energy, and it is currently a pressing topic within the field.

The spectroscopic techniques and chemical systems studied within this dissertation present new information to the fields of nonlinear optical spectroscopy and photoelectrochemical systems. This research will inform the design of next generation solar powered devices and stimulate the implementation of nonlinear spectroscopic techniques to study these chemical systems.

APPENDIX A

A.1 Labview Virtual Instrument and Computer Interface

The first section of this appendix contains images from the computer used to collect the data for HD-VSFG and TA experiments. For Labview virtual instruments (VI's) shown here, only the front panel and specific back panel images are shown. The complete back panel code/sub-VI's can be accessed through the Krummel group's backup memory storage devices, cloud storage, or directly using the computer in the laser lab B207.

First, the monochrometer program used for both HD-VSFG and TA experiments is shown in Figure A.1.

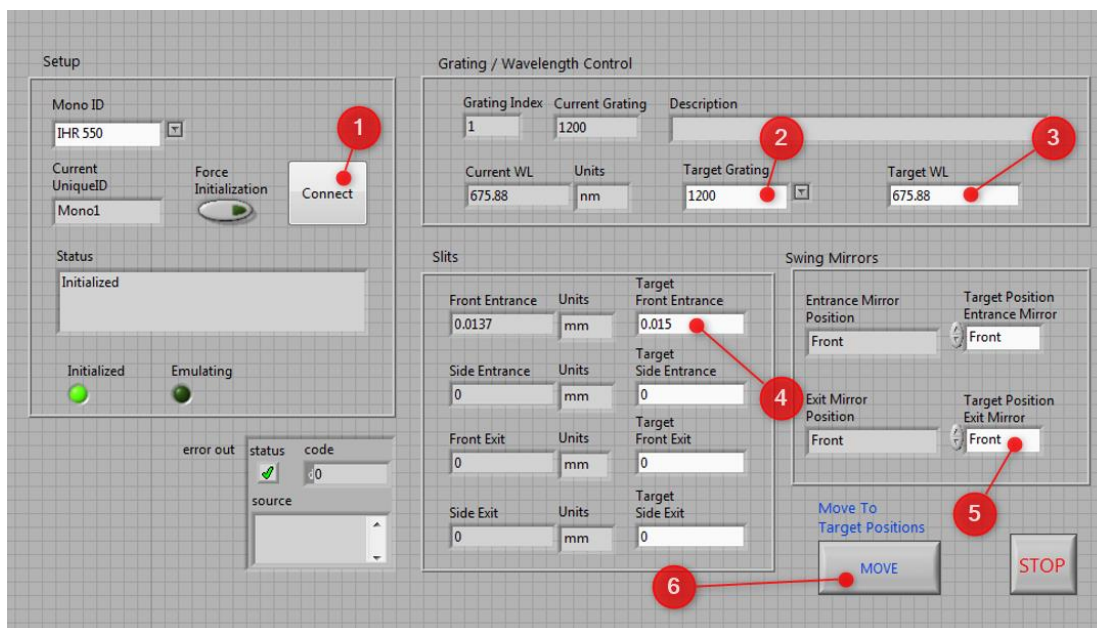


Figure A.1 The front panel of the “JY Mono Example” program used to control the iHR550 monochromator. The description corresponding to the numbers are addressed within the main text of this appendix.

Starting with #1 in Figure A.1, upon loading the program, the connect button is pressed to connect the computer to the iHR550 monochromator. The options to select are shown in numbers 2-5 in Figure A.1. The #2 selects the grating, there are three options, for HD-VSFG experiments

the 1200 option is selected, for the TA experiments the 1800 option is selected. It is noted here that the interface specifies 1800, but as of spring of 2021 the 1800 lines/mm grating was replaced with a 100 lines/mm. Number 3 selects the target wavelength that is desired, number 4 selects the entrance slit width reported in mm, number 5 selects which detector to go to depending on the experiment. For HD-VSFG, the Synapse camera is used, and corresponds to the “front” exit position; while the “side” exit position is for the TA measurements which uses the Ocotoplus detector. Finally, number 6 is moves the monochromator to the desired settings established for numbers 2-5.

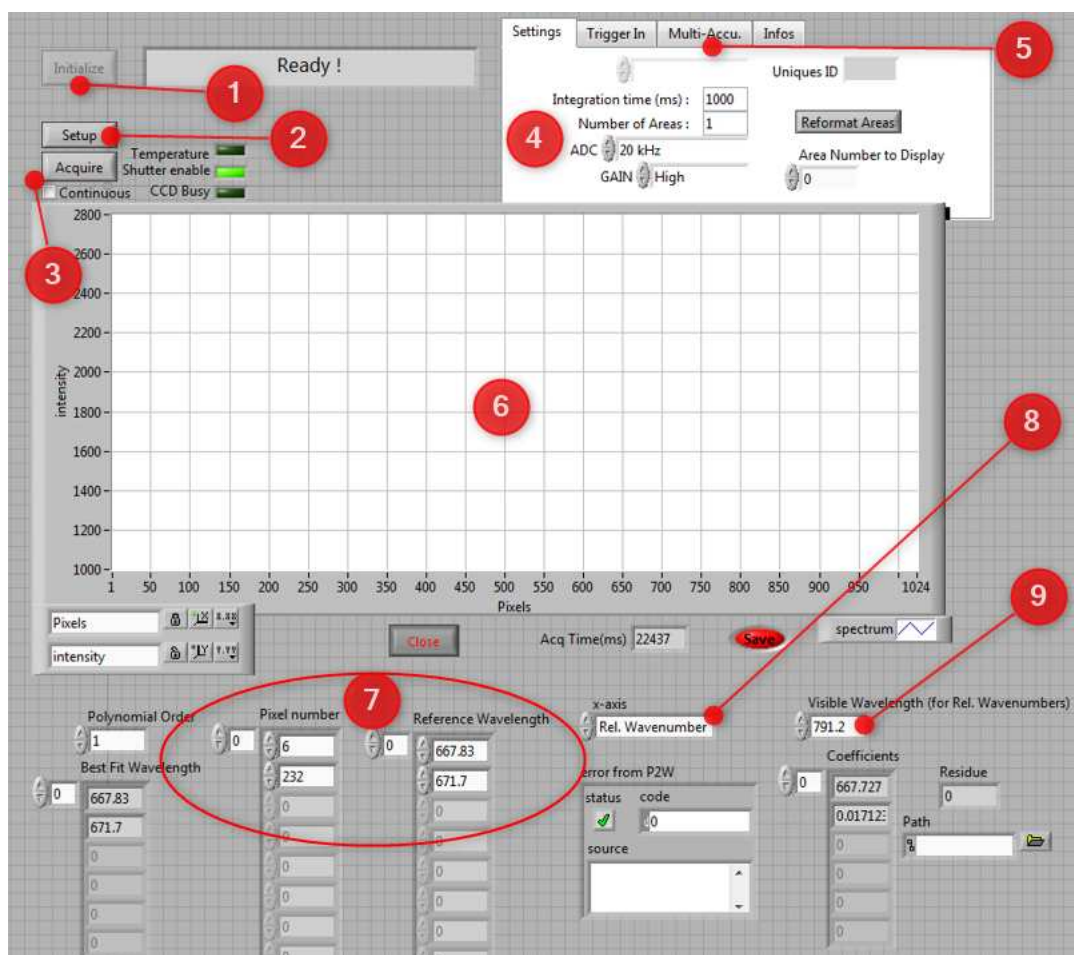
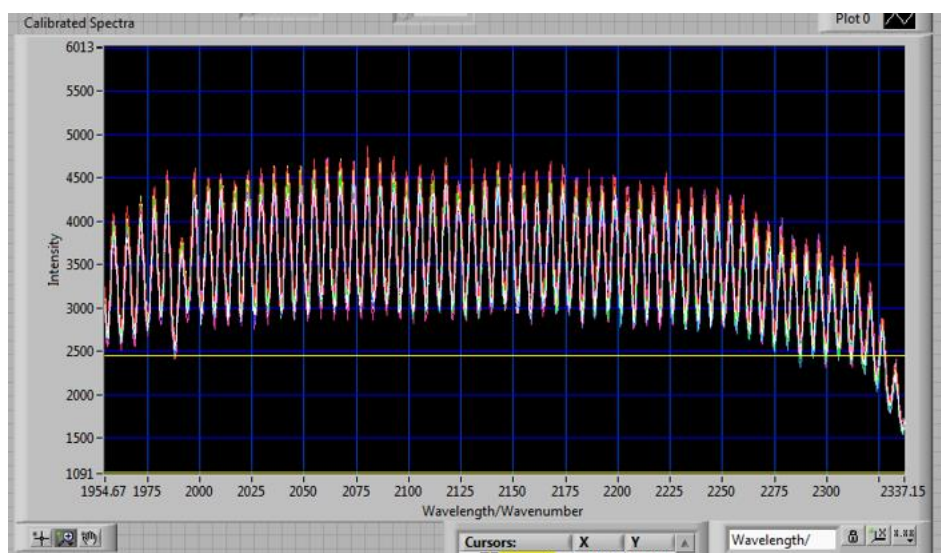


Figure A.2 The front panel of the “Synapse Labview 8-5 Spectral Mode Test” program used to control the Synapse detector. The description corresponding to the numbers are addressed within the main text of this appendix.

Shown in Figure A.2 is the front panel of the Labview program used to collect HD-VSFG data. Upon starting the program, the initialize button (#1) needs to be pressed, followed by setup (#2). Number 3 is how the camera is activated by either a specified shot duration, by clicking “acquire” or in a continuous mode by simply checking the box. Setting up the camera for the specific measurement is done with numbers 4 and 5. In the tab shown by #4 the integration time can be specified in milliseconds. The tab “Multi-Accu.” shown by #5 can be selected and interfaced to collect a specified number of spectra. Number 6 is the displayed intensity of light corresponding to the pixel of the detector. Finally, number 7 shows the calibration of the camera by selecting the wavelength and corresponding pixel number. To save the calibration, click “close” then, re-initialize and setup the camera (#1 and #2), this will re-initialize the program/camera with the new values for the calibration. Number 8 will specify the display of the data, once calibrated, the selection of “Rel. Wavenumber” will display the data with the calibrated x-axis of wavenumber (cm^{-1}) with respect to the incident visible pulse, which is specified in by number 9.

Figure A.3 Resulting calibrated data for HD-VSFG. The multiple colors are the different number



of data acquisitions specified by #5 in Figure A.2

The resulting calibrated spectra for HD-VSFG measurements is shown in Figure A.3 as an example. This data is the data that is saved and stored for further data processing in Matlab.

For TA measurements on of the first steps is to activate the camera using the CommCam program installed in the computer. Images from the CommCam program are shown in Figures A.4 and A.5.

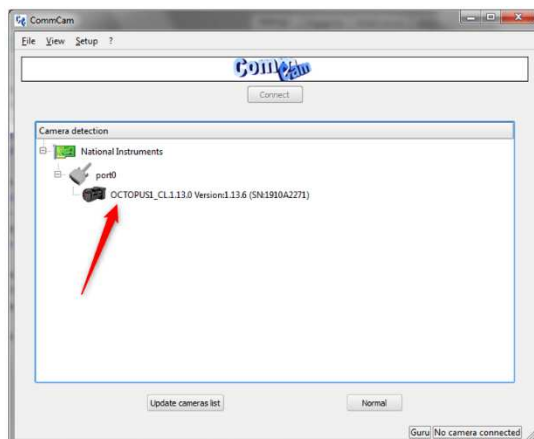


Figure A.4 Start the CommCam program and load in the camera by double clicking the camera shown by the red arrow.

Selecting the camera is shown in Figure A.4 will open up the next window for interfacing with the camera shown in Figure A.5.

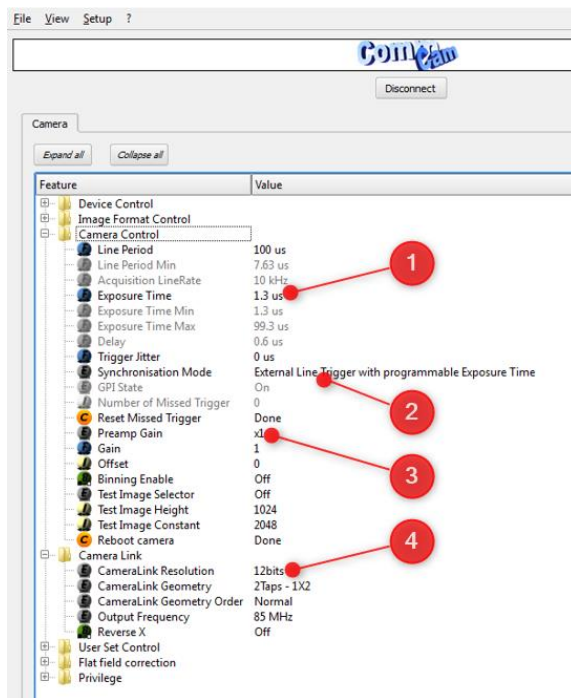


Figure A.5 The main interface to change settings of the Octoplus.

Once the interface is opened, the default programs need to be changed to the ones highlighted in Figure A.5 by numbers 1-4. Number 1 designates the exposure time, and for TA experiments this needs to be changed to the fastest time possible, which is $1.3 \mu\text{s}$. Additionally, the trigger for the camera comes from the internal clock of the laser system (operating at 1 kHz), so the setting needs to be changed to the “External Line Triggered...” mode shown in Figure A.5. The pre-amp gain (#3) can be selected to increase the signal if desired, up to x4. And finally, the last important step for setting up the camera is specifying the cameralink resolution to be 12-bit, shown by number 4.

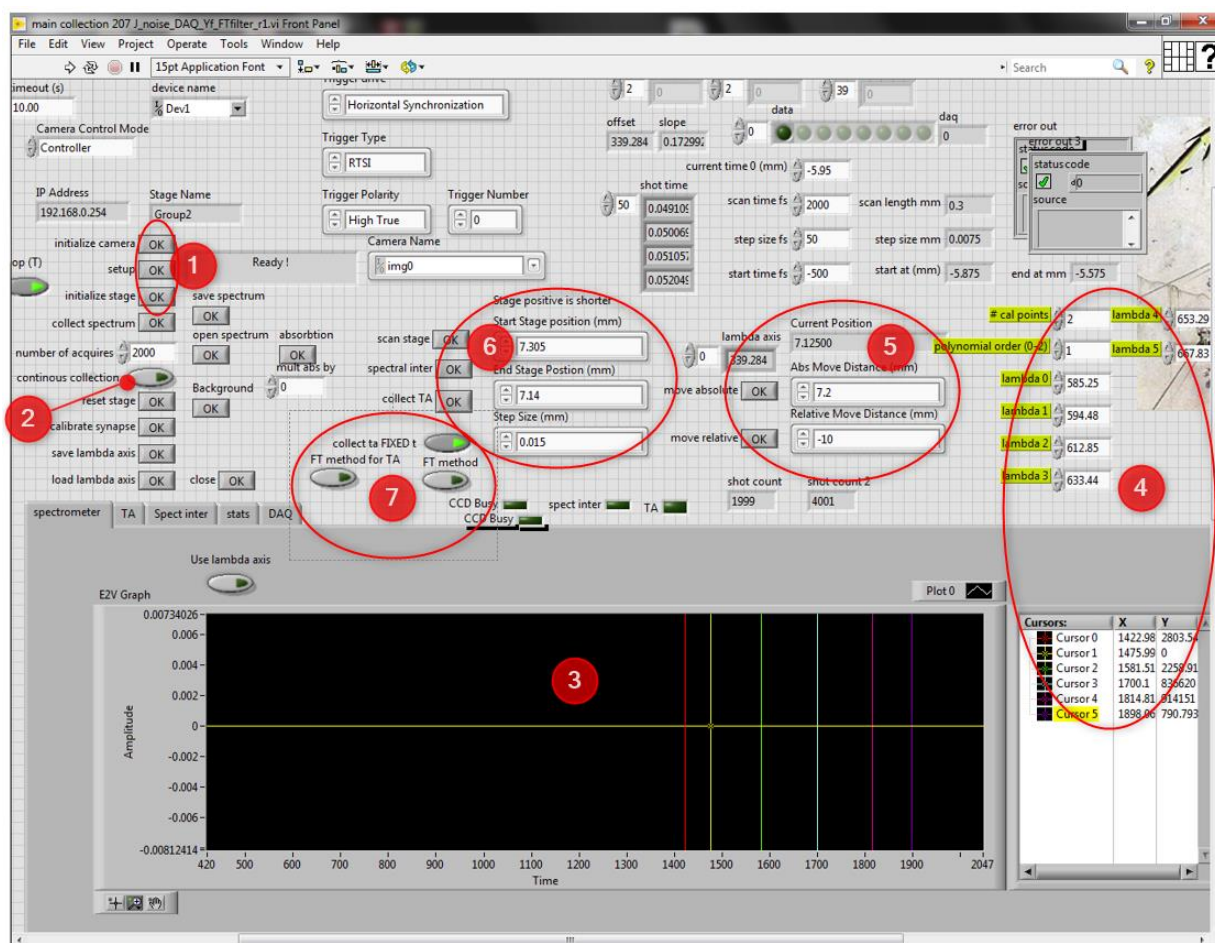


Figure A.6 The front panel of “main_collection_207_J_noise_DAQ_Yf_FTfilter_r1” which is the most update TA collection program in Labview as of May 2022.

The front panel of the program used for the TA experiments is shown in Figure A.6. The first step shown by number 1 in figure A.6 is to initialize the camera, then click “setup”, then initialize the stage. Then, number 2 shows the collection of the light to the detector in continuous mode, and the intensity of light for the pixels is displayed in the plot shown by number 3. To calibrate, use the neon lamp and click on the continuous collection. The cursors in number 4 can be moved to the pixel corresponding to the emission lines of the neon lamp, and the wavelengths entered into the cells shown by number 4. Then, by clicking “calibrate” and “save lambda axis” the program will save the calibration, then “load lambda axis” can be selected and clicking the “use lambda axis” in number 3 will change the horizontal axis in 3 to the calibrated lambda axis.

After calibration, the stage can be manually moved using the cells shown in number 5 of Figure A.6. The range of motion and step sizes of the translation stage are specified in number 6. An interferogram can then be measured by clicking “spectral inter” and by clicking the “spectral inter” tab of the plot will display the measured interferogram within number 3. This way, the $\tau = 0$ can be identified. For TA experiments, the start and ending positions and step size is specified by number 6, and then clicking “collect TA” will acquire the TA for the number of shots specified by the “number of acquires” (above number 2 in Figure A.6) at each time step and will be displayed in the plot (#3). Number 7 in Figure A.6 can be used to toggle a “live” TA spectra at a single time point. Additionally, in number 7, the Fourier filtering method of collection can be specified. Toggling “FT method” will use the Fourier filtering method during the “live” continuous TA if the “collect ta FIXED t” is toggled on. Otherwise, the “FT method for TA” can be toggled on and then clicking the “collect TA” in number 6 will now collect a full TA experiment using the Fourier filter method. The data will be displayed in the plot in number 3, and then right click, and save the data for further processing in Matlab.

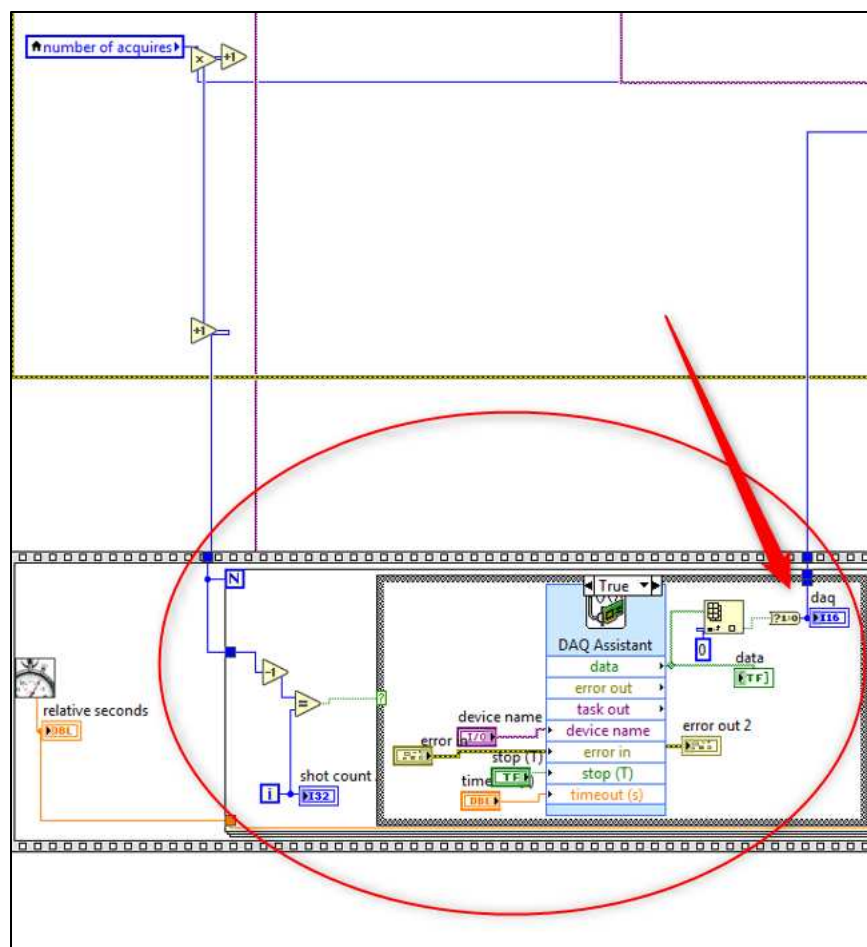


Figure A.7 The back panel of the TA measurements for the DAQ card readings.

The back panel for the DAQ card is shown in Figure A.7. Taking in the “number of acquies”, the DAQ card reads out the last signal from the chopper wheel used in the TA spectrometer which corresponds to the last number for the “number of acquies”. The signal is converted to binary, either 1 or 0, shown by the arrow in Figure A.7. This relates to pump “on” or pump “off” and will arrange the array of collected data to correctly subtract the pump “on” vs pump “off” signals to calculate the difference spectra ΔA . This is described in the main text in Chapter 2 of this dissertation.

The Fourier data collection code used in the TA signal collection, described in the main text of Chapter 2, is shown in Figure A.8. A $\log_{10}$ function is applied to the input array from the

collected data before performing the FFT. Then, the 500 Hz signal is acquired by taking the last value of the array for each 2048 pixel, and only the real component is taken. The step size is the inverse of the number of acquired shots and multiplied to normalize the FFT. The final “500hz Amp” is a 1x2048 array that is plotted versus the calibrated lambda axis and will show up in the plot in number 3 of Figure A.6

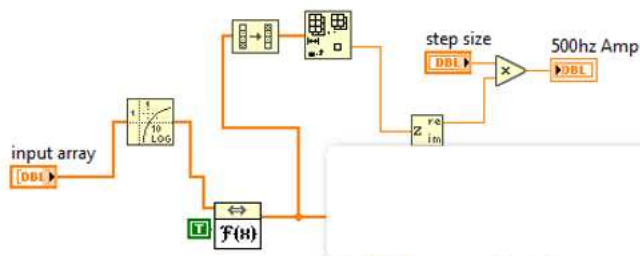


Figure A.7 The back panel of the TA measurements for the Fourier filtering method of data collection.

A.2 Matlab Code for Data Processing and Modelling

A.2.1 Code for HD-VSFG Experimental Data

The Matlab code shown here for the averaging, Fourier filtering, and phase referencing for HD-VSFG measurements was adapted and edited from the original code used by Christopher Rich in the publication “Direct Measurement of the Absolute Orientation of N3 Dye at Gold and Titanium Dioxide Surfaces with Heterodyne-Detected Vibrational SFG Spectroscopy” from the Journal of Physical Chemistry C. The Matlab code is called “fda.m” and can be found in the Krummel group’s backup memory storage devices, cloud storage, or directly using the computer in the laser lab B207.

%% FDA.m is a script which process frequency domain data for HD-SFG.

```
y=mean(data(:,2:31),2); % should convey number of spectra collected
%y=y_cleaned; %the y_cleaned is the original y data that has outliers
%removed
x=data(:,1);
```

```

% yLO=mean(dataLO(:,2:31),2);

%y=data(:,2);

Ndt=1/((x(1)-x(2))*2.998e10);
dt=Ndt/1023; % denominator is number of x-axis points minus one

t=zeros(1024,1); % number of time points equals number of frequency points
for n=1:1024 % same here
    t(n)=(-(1024)/2 + 1).*dt+(n-1)*dt; % if number of points is even (1024) (-N/2+1); if number of
    points is odd (1023) (-(N+1)/2) (see Zanni book)
end

t=t.*10^15;

figure(1); % Raw spectrum
plot(x,y);

A=fftshift(fft(iffshift(y))); % FT into time domain with shift functions
% Aa=fftshift(fft(iffshift(yLO)));
% A=A-Aa;

figure(2); % Temporal Interferogram
plot(t,real(A),'r',t,imag(A),'b');

%% Fourier filtering section

ff=zeros(1024,1);

for n=1:1024
    if t(n)<3800; %this is establishing the filter window
        ff(n)=0;
    elseif t(n)>6900;
        ff(n)=0;
    % elseif t(n)>6000;
    %     ff(n)=0;
    % elseif t(n)>8000 && t(n)<12000;
    %     ff(n)=0;
    % elseif t(n)>29500 && t(n)<31000;
    %     ff(n)=0;
    else
        ff(n)=1;
    end
end

B=ff.*A; % Filtered Temporal Interferogram

```

```

C=fftshift(fftshift(fftshift(B))); % FT back to the frequency domain

figure(3);
plot(x,real(C),'r',x,imag(C),'b'); % Spectral Interferogram of the Sample

figure(4);
plot(x,C.*conj(C)); % The Absolute Square of the Spectral Interferogram

%% Reference

yref=mean(ref(:,2:31),2);
%yref = yref_cleaned;
% yrefLO=mean(refLO(:,2:31),2);

figure(5);
plot(x,yref); % Raw reference spectrum

D=fftshift(fft(fftshift(yref))); % FT to time domain
% Da=fftshift(fft(fftshift(yrefLO)));
% D=D-Da;

figure(6);
plot(t,real(D),'r',t,imag(D),'b'); % Temporal Interferogram

%% Fourier filtering section

E=ff.*D; % Fourier Filtered Temporal Interferogram

F=fftshift(fftshift(fftshift(E))); % FT back to the frequency domain

figure(7);
plot(x,real(F),'r',x,imag(F),'b'); % Spectral Inteferogram of the Reference

figure(8);
plot(x,F.*conj(F)); % Absolute square of spectral interferogram

%% Normalization

G=-1i*Ca./F;

figure(9);
plot(x,real(G),'r',x,imag(G),'b'); % HDVSFG spectrum of the sample

figure(10);
plot(x,G.*conj(G)); % Abs square off HDVSFG spectrum

```

```
R=smoothn(real(G),2000); % smoothn is a smoothing function found on the MATLAB file
exchange.
```

```
I=smoothn(imag(G),2000); % The 'ROBUST' input can be replaced with a number
corresponding to the number of iterations the smoothing function uses.
```

```
figure(11);
plot(x,R,'r',x,I,'b','linewidth',3); % Smoothed HDVSFG spectrum
title('N3/TiO2 - ACN wash SSP pH=2.0');xlabel('Wavenumber (cm-1'));ylabel('\chi(2)
Intensity')
set(gca,'FontSize',16);
xlim([2000 2250])
```

```
H=(R+ 1i.*I).*(R - 1i.*I); % Abs square
```

```
figure(12);
plot(x,H,'linewidth',3)
title('N3/TiO2 SSP pH=2.0');xlabel('Wavenumber (cm-1'));ylabel('|\chi(2)|2 Intensity')
set(gca,'FontSize',16);
xlim([2000 2200])
```

A1.2.2 Code for HD-VSFG Fitting and Modelling

The first section of this code titled “Chi2_play_TiO2_dry” and is an example of one of the Matlab scripts used to calculate the Fresnel coefficients for the HD-VSFG experiments. Then the calculated Fresnel coefficients feed into the simultaneous fitting, of which the code for the example presented here is named “multifit_sfg_multiple_TiO2_dry_real_and_imag_Jan2022_pH_3_8_b”. The simultaneous fitting uses the results from the imaginary and real spectra of the experiment, which is done using the code presented in the previous section. And then the values from the simultaneous fitting are used to reproduce a spectrum for the imaginary and real components, and then the calculated and experimental data are plotted with each other. Again, all code can be found in the Krummel group archives.

```

% refractive index of Air & TiO2
nIR1 = 1; %4.7 micron
nVis1 = 1; % 790 nm
nIR2 = 2.1403 + 0; %not really zero for extincin coefficient, but e-7, so approx as zero
nVis2 = 2.3432 + 0;
nSF1 = 1; %676 nm
nSF2 = 2.3729 + 0;

% refractive index of adsorbate, average of two interfaces
nIRint = 1.2;%nIR2; %sqrt((nIR1^2 + nIR2^2 + 4)/(2*(nIR1^-2 + nIR2^-2 +
1))) %(nIR1+nIR2)./2;
nVisint = 1.2;%nVis2; %sqrt((nVis1^2 + nVis2^2 + 4)/(2*(nVis1^-2 + nVis2^-2 +
1)))%(nVis1+nVis2)./2;
nSFint = 1.2;%nSF2; %sqrt((nSF1^2 + nSF2^2 + 4)/(2*(nSF1^-2 + nSF2^-2 +
1)))%(nSF1+nSF2)./2;

thetaIR1 = 60.7;
thetaVis1 = 66.2;
thetaSF1 = 65.6; %phase matching

%refracted angles using snell's law
thetaIR2 = asind(nIR1.*sind(thetaIR1)./nIR2);
thetaVis2 = (asind(nVis1.*sind(thetaVis1)./nVis2));
thetaSF2 = (asind(nSF1.*sind(thetaSF1)./nSF2));

%in equals out angle,
%thetaIR2 = thetaIR1;
%thetaVis2 = thetaVis1;
%thetaSF2 = thetaSF1;

% L factors from Zhuang Miranda Kim & Shen (1999) fresnel factors
LxxIR = 2.*nIR1.*cosd(thetaIR2)/(nIR1.*cosd(thetaIR2)+nIR2.*cosd(thetaIR1));
LyyIR = 2.*nIR1.*cosd(thetaIR1)/(nIR1.*cosd(thetaIR1)+nIR2.*cosd(thetaIR2));
LzzIR =
(2.*nIR2.*cosd(thetaIR1)/(nIR1.*cosd(thetaIR2)+nIR2.*cosd(thetaIR1))).*(nIR1./nIRint).^2;

LxxVis = 2.*nVis1.*cosd(thetaVis2)/(nVis1.*cosd(thetaVis2)+nVis2.*cosd(thetaVis1));
LyyVis = 2.*nVis1.*cosd(thetaVis1)/(nVis1.*cosd(thetaVis1)+nVis2.*cosd(thetaVis2));
LzzVis =
(2.*nVis2.*cosd(thetaVis1)/(nVis1.*cosd(thetaVis2)+nVis2.*cosd(thetaVis1))).*(nVis1./nVisint).^2;

LxxSF = 2.*nSF1.*cosd(thetaSF2)/(nSF1.*cosd(thetaSF2)+nSF2.*cosd(thetaSF1));
LyySF = 2.*nSF1.*cosd(thetaSF1)/(nSF1.*cosd(thetaSF1)+nSF2.*cosd(thetaSF2));
LzzSF =
(2.*nSF2.*cosd(thetaSF1)/(nSF1.*cosd(thetaSF2)+nSF2.*cosd(thetaSF1))).*(nSF1./nSFint).^2;

```

```

%LxxSF = cosd(thetaSF2)./((nSF1*cosd(thetaSF2)+ nSF1*nSF2*cosd(thetaSF1)));
%LyySF = 1/(nSF1*cosd(thetaSF1)+ nSF2*cosd(thetaSF2));
%LzzSF = sind(thetaSF1)./(nSF1*nSF2*cosd(thetaSF2) + (nSF2^2)*cosd(thetaSF1));

% A factors include Fresnel Coefficients (L), and input & output angles
AxxIR = cosd(0).*cosd(thetaIR1).*LxxIR;
AyyIR = sind(90).*LyyIR;
AzzIR = cosd(0).*sind(thetaIR1).*LzzIR;

AxxVis = cosd(0).*cosd(thetaVis1).*LxxVis;
AyyVis = sind(90).*LyyVis;
AzzVis = cosd(0).*sind(thetaVis1).*LzzVis;

AxxSF = cosd(0).*cosd(thetaSF1).*LxxSF;
AyySF = sind(90).*LyySF;
AzzSF = cosd(0).*sind(thetaSF1).*LzzSF; %question here about the sign of angle of sf

%this is to monitor what the above calulated values are
Lzzz = abs(LzzIR*LzzVis*LzzSF)*sind(thetaSF1)*sind(thetaVis1)*sind(thetaIR1)
Lyyz = abs(LzzIR*LyyVis*LyySF)*sind(thetaIR1)
Lxxz = abs(AxxSF.*AxxVis.*AzzIR)
Lxxz = abs(AxxSF.*AzzVis.*AxxIR)
Lzxx = abs(AzzSF.*AxxVis.*AxxIR)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%% Simultaneous Fit with input data and Fresnel coefficients

% Generate X vectors for each data set
x9 = x(301:944);
x10 = x(301:944);
x11 = x(301:944);
x12 = x(301:944);

% Generate Y data
y9 = I_zero_dry_3_8_ppp(301:944);
y10 = I_zero_dry_3_8_ssp(301:944);
y11 = R_zero_dry_3_8_ppp(301:944);
y12 = R_zero_dry_3_8_ssp(301:944);

% Define fitting functions and parameters, with identical
% exponential decay for both data sets
mdl1 = @(beta,x) imag(((Lzzz*(beta(1)*(cosd(beta(2))*beta(3) + (cosd(beta(2))^3)*(1 -
beta(3)))))) + (-Lxxz.*((1/2).*beta(1)*(cosd(beta(2)).*(1+beta(3)) + (cosd(beta(2)).^3).*(beta(3)-

```

```

1)))) + (-Lxxz.*((1/2).*beta(1)*(cosd(beta(2)) - (cosd(beta(2)).^3))*(1 - beta(3)))) +
Lzxx.*((1/2).*beta(1)*(cosd(beta(2)) - (cosd(beta(2)).^3))*(1 - beta(3)))/.(2103 - x - 1i*12.69))
+ imag(((Lzzz*(beta(4)*(cosd(beta(5))*beta(6) + (cosd(beta(5)).^3)*(1 - beta(6)))) + (-
Lxxz.*((1/2).*beta(4)*(cosd(beta(5)).*(1+beta(6)) + (cosd(beta(5)).^3).*(beta(6)-1)))) + (-
Lxxz.*((1/2).*beta(4)*(cosd(beta(5)) - (cosd(beta(5)).^3))*(1 - beta(6)))) +
Lzxx.*((1/2).*beta(4)*(cosd(beta(5)) - (cosd(beta(5)).^3))*(1 - beta(6)))/.(2134 - x - 1i*12));
mdl2 = @(beta,x) imag(((Lyyz*((1/2).*beta(1)*(cosd(beta(2)).*(1+beta(3)) +
(cosd(beta(2)).^3).*(beta(3)-1))))/.(2101 - x - 1i*19.25)) +
imag((Lyyz*((1/2).*beta(4)*(cosd(beta(5)).*(1+beta(6)) + (cosd(beta(5)).^3).*(beta(6)-
1))))/.(2121 - x - 1i*13.81));
mdl3 = @(beta,x) real(((Lzzz*(beta(1)*(cosd(beta(2))*beta(3) + (cosd(beta(2)).^3)*(1 -
beta(3)))) + (-Lxxz.*((1/2).*beta(1)*(cosd(beta(2)).*(1+beta(3)) + (cosd(beta(2)).^3).*(beta(3)-
1)))) + (-Lxxz.*((1/2).*beta(1)*(cosd(beta(2)) - (cosd(beta(2)).^3))*(1 - beta(3)))) +
Lzxx.*((1/2).*beta(1)*(cosd(beta(2)) - (cosd(beta(2)).^3))*(1 - beta(3)))/.(2103 - x - 1i*12.69))
+ real(((Lzzz*(beta(4)*(cosd(beta(5))*beta(6) + (cosd(beta(5)).^3)*(1 - beta(6)))) + (-
Lxxz.*((1/2).*beta(4)*(cosd(beta(5)).*(1+beta(6)) + (cosd(beta(5)).^3).*(beta(6)-1)))) + (-
Lxxz.*((1/2).*beta(4)*(cosd(beta(5)) - (cosd(beta(5)).^3))*(1 - beta(6)))) +
Lzxx.*((1/2).*beta(4)*(cosd(beta(5)) - (cosd(beta(5)).^3))*(1 - beta(6)))/.(2134 - x - 1i*12));
mdl4 = @(beta,x) real(((Lyyz*((1/2).*beta(1)*(cosd(beta(2)).*(1+beta(3)) +
(cosd(beta(2)).^3).*(beta(3)-1))))/.(2101 - x - 1i*19.25)) +
real((Lyyz*((1/2).*beta(4)*(cosd(beta(5)).*(1+beta(6)) + (cosd(beta(5)).^3).*(beta(6)-
1))))/.(2121 - x - 1i*13.81));

```

```

% Prepare input for NLINMULTIFIT and perform fitting
x_cell = {x9, x10, x11, x12};%, x3, x4, x5, x6};
y_cell = {y9, y10, y11, y12};%, y3, y4, y5, y6};
mdl_cell = {mdl1, mdl2, mdl3, mdl4};%, mdl3, mdl4, mdl5, mdl6};
%beta0 = [134.1, 0, -1.0436, 0, 0, 0, 0, 0, 129.6, 2110, 15];
%beta0 = [20, 175, 0.6, 20, 175, 0.6, 2096, 8, 2140, 8, 2100, 8, 2150, 8];
beta0 = [20, 170, 0.6, 30, 170, 0.6];
options = statset('nlinfit'); options.DerivStep = 1e-15; options.MaxFunEvals = 20000;
options.MaxIter = 20000; options.TolFun = 1e-15; options.TolX = 1e-15;
[beta,r,J,Sigma,mse,errorparam,robustw] = ...
    nlinmultifit(x_cell, y_cell, mdl_cell, beta0,options);
%6.0555e-06
%options = statset('nlinfit'); options.MaxIter = 20000; options.Tolfun = 1e-150; options.TolX =
1e-15;
%
% opts = statset('nlinfit');
%
% opts = statset('TolFun',1e-15);
%
% opts = statset('Display','iter','TolFun',1e-10);
%
% opts.MaxIter = 15000;
%
% opts.TolFun = 1e-11;
%
% opts.TolX = 1e-11;
%
% opts.RobustWgtFun = 'bisquare';
% Calculate model predictions and confidence intervals
[ypred9,delta9] = nlpredci(mdl1,x9,beta,r,'covar',Sigma);

```

```
[ypred10,delta10] = nlpredci(mdl2,x10,beta,r,'covar',Sigma);
[ypred11,delta11] = nlpredci(mdl3,x11,beta,r,'covar',Sigma);
[ypred12,delta12] = nlpredci(mdl4,x12,beta,r,'covar',Sigma);
```

% Calculate parameter confidence intervals

```
ci = nlparci(beta,r,'Jacobian',J);
```

% Plot results

```
figure();
hold all;
box on;
scatter(x9,y9);
scatter(x10,y10);
scatter(x11,y11);
scatter(x12,y12);
plot(x9,ypred9);
plot(x9,ypred9+delta9,'Color',[0 0.5 0],'LineStyle',':');
plot(x9,ypred9-delta9,'Color',[0 0.5 0],'LineStyle',':');
plot(x10,ypred10);
plot(x10,ypred10+delta10,'Color',[0 0.5 0],'LineStyle',':');
plot(x10,ypred10-delta10,'Color',[0 0.5 0],'LineStyle',':');
plot(x11,ypred11);
plot(x11,ypred11+delta11,'Color',[0 0.5 0],'LineStyle',':');
plot(x11,ypred11-delta11,'Color',[0 0.5 0],'LineStyle',':');
plot(x12,ypred12);
plot(x12,ypred12+delta12,'Color',[0 0.5 0],'LineStyle',':');
plot(x12,ypred12-delta12,'Color',[0 0.5 0],'LineStyle',':');
```

beta

%%%

%% Take results from the “beta” variable and generate a computed spectra that is plotted on top of the experimental data. “beta” above is the result of the simultaneous fit, “beta” below refers to the hyperpolarizability β

```
beta_zzz_1 = [beta(1)];%34.6*(0.05);
beta_xxz_1 = [beta(1)]*[beta(3)];%0.42212;
r_1 = beta_xxz_1/beta_zzz_1;
trans_theta_1 = beta(2);%[127.5];
gamma_1 = 12.69; %damping constant
vib_1 = 2103;
om = [1918:0.3725:2299.4];
```

```
Chi_XXZ_1 = (1/2).*(beta_zzz_1*(cosd(trans_theta_1).*(1+r_1) +
(cosd(trans_theta_1)^3).*(r_1-1));
```

```
Chi_ZZZ_1 = beta_zzz_1*(cosd(trans_theta_1).*r_1 + (cosd(trans_theta_1)^3).*(1 - r_1));
Chi_XZX_1 = (1/2).*beta_zzz_1*(cosd(trans_theta_1) - (cosd(trans_theta_1)^3)).*(1 - r_1);
```

```
Chi_SSP_1 = abs(AyySF.*AyyVis.*AzzIR).*Chi_XXZ_1;
Chi_PPP_1 = -abs(AxxSF.*AxxVis.*AzzIR).*Chi_XXZ_1...
- abs(AxxSF.*AzzVis.*AxxIR).*Chi_XZX_1 +...
abs(AzzSF.*AxxVis.*AxxIR).*Chi_XZX_1...
+ abs(AzzSF.*AzzVis.*AzzIR).*Chi_ZZZ_1;
```

```
% high frequency mode
```

```
beta_zzz_2 = [beta(4)];%11.95*(0.05);
beta_xxz_2 = [beta(4)]*[beta(6)];%-1.03965;
r_2 = beta_xxz_2/beta_zzz_2;
trans_theta_2 = beta(5)-.8; %135.587584100440;
gamma_2 = 12; %damping constant
vib_2 = 2134;
```

```
Chi_XXZ_2 = (1/2).*beta_zzz_2*(cosd(trans_theta_2).*(1+r_2) +
(cosd(trans_theta_2)^3).*(r_2-1));
Chi_ZZZ_2 = beta_zzz_2*(cosd(trans_theta_2).*r_2 + (cosd(trans_theta_2)^3).*(1 - r_2));
Chi_XZX_2 = (1/2).*beta_zzz_2*(cosd(trans_theta_2) - (cosd(trans_theta_2)^3)).*(1 - r_2);
```

```
Chi_SSP_2 = abs(AyySF.*AyyVis.*AzzIR).*Chi_XXZ_2;
Chi_PPP_2 = -abs(AxxSF.*AxxVis.*AzzIR).*Chi_XXZ_2 -
abs(AxxSF.*AzzVis.*AxxIR).*Chi_XZX_2 +...
abs(AzzSF.*AxxVis.*AxxIR).*Chi_XZX_2 + abs(AzzSF.*AzzVis.*AzzIR).*Chi_ZZZ_2;
```

```
SSP_spec = (Chi_SSP_1./(2101 - om - (1i).*19.25) + Chi_SSP_2./(2121 - om - (1i).*13.81)) ;
PPP_spec = (Chi_PPP_1./(vib_1 - om - (1i).*gamma_1) + Chi_PPP_2./(vib_2 - om -
(1i).*gamma_2));
%SSP_spec = Chi_SSP.*((vib - om)./((vib - om).^2 + gamma^2) + 1i.*(gamma)./((vib - om).^2
+ gamma^2));
%PPP_spec = Chi_PPP.*((vib - om)./((vib - om).^2 + gamma^2) + 1i.*(gamma)./((vib - om).^2
+ gamma^2));
```

```
%figure();
%plot(om,real(SSP_spec),'r',om,imag(SSP_spec),'b',om,real(PPP_spec),'r --
',om,imag(PPP_spec),'b --');
%figure(); plot(om,imag(SSP_spec),'b',om,imag(PPP_spec),'b --');
%axis ([1800 2500 -.6 .6])
%figure();plot(om,real(SSP_spec),'r',om,imag(SSP_spec),'b',om,real(PPP_spec),'r
-','om,imag(PPP_spec),'b -','x,I_zero_ppp_4_9','g -','x,I_zero_ssp_4_9','g','x,R_zero_ppp_4_9','k
-','x,R_zero_ssp_4_9','k','linewidth',2);
%axis ([1975 2250 -.4 .6])
figure();plot(om,real(SSP_spec),'r -','om,imag(SSP_spec),'b
-','x,R_zero_dry_3_8_ssp','r',x,I_zero_dry_3_8_ssp,'b','linewidth',3);
```

```

axis ([1960 2200 -0.08 0.045])
xlabel('Wavenumber (cm-1);ylabel('\chi(^2^)')
set(gca,'FontSize',16)
title('N3/TiO2 pH=3.8 SSP')
figure();plot(om,real(PPP_spec),'r-.',om,imag(PPP_spec),'b
-','x,R_zero_dry_3_8_ppp','r',x,I_zero_dry_3_8_ppp,'b','linewidth',3);
axis ([1960 2200 -0.08 0.045])
xlabel('Wavenumber (cm-1);ylabel('\chi(^2^)')
set(gca,'FontSize',16)
title('N3/TiO2 pH=3.8 PPP')

```

A1.2.3 Code for TA Data Processing and Fitting

The following code is used for loading in the TA data, then stitching together different temporal sections, averaging, smoothing, creating contour plots, and then dividing up the spectrum at each time point to individually fit each exciton peak to a gaussian function and a linear polynomial. This is described and visualized within the main text in Chapter 2. The code can be accessed through the Krummel archives and the Sambur group archives. The first Matlab script is the main one that is used titled “Automated_Fitting_Code_Yusef.m” and has other functions buried in this code, which are shown as well below. Acknowledgement to Rachelle Austin, a joint PhD graduate student of the Krummel/Sambur group, who helped polish, make functions, and clean up the code.

%% Import Round 1 data using the import_TA_data function. Change the file paths for each new round of data to import.

```

data_R_r1_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.0V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.0V_r',34);
data_A_r1_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.0V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.0V_r',31);
data_B_r1_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.0V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.0V_r',39);
data_C_r1_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.0V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.0V_r',13);

```

```

data_R_r1_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.1V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.1V_r',34);
data_A_r1_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.1V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.1V_r',31);
data_B_r1_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.1V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.1V_r',39);
data_C_r1_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.1V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.1V_r',13);

```

```

data_R_r1_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.15V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.15_r',34);
data_A_r1_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.15V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.15V_r',31);
data_B_r1_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.15V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.15V_r',39);
data_C_r1_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.15V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.15_r',13);

```

```

data_R_r1_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.2V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.2V_r',34);
data_A_r1_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.2V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.2V_r',31);
data_B_r1_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.2V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.2V_r',39);
data_C_r1_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.2V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.2V_r',13);

```

```

data_R_r1_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.25V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.25_r',34);
data_A_r1_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.25V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.25V_r',31);

```

```
data_B_r1_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.25V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.250_r',39);
```

```
data_C_r1_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.25V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.25_r',13);
```

```
data_R_r1_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.3V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.3V_r',34);
```

```
data_A_r1_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.3V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.3V_r',31);
```

```
data_B_r1_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.3V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.3V_r',39);
```

```
data_C_r1_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.3V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.3V_r',13);
```

```
data_R_r1_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.325V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.325V_r',34);
```

```
data_A_r1_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.325V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.325V_r',31);
```

```
data_B_r1_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.325V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.325V_r',39);
```

```
data_C_r1_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.325V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.325V_r',13);
```

```
data_R_r1_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.35V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.35_r',34);
```

```
data_A_r1_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.35V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.35V_r',31);
```

```
data_B_r1_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.35V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.350_r',39);
```

```
data_C_r1_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
1\0.35V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.35V_r',13);
```

```

data_R_r1_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.4V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.4V_r',34);
data_A_r1_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.4V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.4V_r',31);
data_B_r1_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.4V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.4V_r',39);
data_C_r1_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.4V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.4V_r',13);

```

```

data_R_r1_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.5V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.5V_r',34);
data_A_r1_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.5V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.5V_r',31);
data_B_r1_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.5V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.5V_r',39);
data_C_r1_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.5V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.5V_r',13);

```

```

data_R_r1_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.525V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.525V_r',34);
data_A_r1_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.525V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.525V_r',31);
data_B_r1_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.525V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.525V_r',39);
data_C_r1_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.525V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.525V_r',13);

```

```

data_R_r1_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.55V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.55V_r',34);
data_A_r1_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.55V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.55V_r',31);

```

```
data_B_r1_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.55V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.55V_r',39);
data_C_r1_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
1\0.55V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.55V_r',13);
```

%% Import Round 2 Data

```
data_R_r2_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.0V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.0Vrepeat_r',34);
data_A_r2_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.0V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.0Vrepeat_r',31);
data_B_r2_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.0V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.0Vrepeat_r',39);
data_C_r2_00V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.0V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.0Vrepeat_r',13);
```

```
data_R_r2_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.1V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.1Vrepeat_r',34);
data_A_r2_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.1V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.1Vrepeat_r',31);
data_B_r2_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.1V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.1Vrepeat_r',39);
data_C_r2_01V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.1V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.1Vrepeat_r',13);
```

```
data_R_r2_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.15V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.15Vrepeat_r',34);
data_A_r2_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.15V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.15Vrepeat_r',31);
data_B_r2_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.15V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.15Vrepeat_r',39);
```

```
data_C_r2_015V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.15V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.15Vrepeat_r',13);
```

```
data_R_r2_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.2V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.20Vrepeat_r',34);  
data_A_r2_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.2V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.20Vrepeat_r',31);  
data_B_r2_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.2V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.20Vrepeat_r',39);  
data_C_r2_02V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.2V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.20Vrepeat_r',13);
```

```
data_R_r2_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.25V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.25Vrepeat_r',34);  
data_A_r2_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.25V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.25Vrepeat_r',31);  
data_B_r2_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.25V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.25Vrepeat_r',39);  
data_C_r2_025V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.25V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.25Vrepeat_r',13);
```

```
data_R_r2_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.3V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.30Vrepeat_r',34);  
data_A_r2_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.3V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.30Vrepeat_r',31);  
data_B_r2_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.3V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.30Vrepeat_r',39);  
data_C_r2_03V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.3V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.30Vrepeat_r',13);
```

```
data_R_r2_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient  
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round  
2\0.325V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.325Vrepeat_r',34);
```

```

data_A_r2_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.325V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.325Vrepeat_r',31);
data_B_r2_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.325V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.325Vrepeat_r',39);
data_C_r2_0325V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.325V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.325Vrepeat_r',13);

```

```

data_R_r2_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.35V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.35Vrepeat_r',34);
data_A_r2_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.35V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.35Vrepeat_r',31);
data_B_r2_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.35V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.35Vrepeat_r',39);
data_C_r2_035V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.35V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.35Vrepeat_r',13);

```

```

data_R_r2_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.4V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.40Vrepeat_r',34);
data_A_r2_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.4V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.40Vrepeat_r',31);
data_B_r2_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.4V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.40Vrepeat_r',39);
data_C_r2_04V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.4V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.40Vrepeat_r',13);

```

```

data_R_r2_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.5V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.5V_r',34);
data_A_r2_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.5V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.5V_r',31);
data_B_r2_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.5V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.5V_r',39);

```

```
data_C_r2_05V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.5V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.5V_r',13);
```

```
data_R_r2_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.525V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.525Vrepeat_r',34);
data_A_r2_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.525V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.525Vrepeat_r',31);
data_B_r2_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.525V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.525Vrepeat_r',39);
data_C_r2_0525V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.525V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.525Vrepeat_r',13);
```

```
data_R_r2_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.55V\1L_MoS2_Flow_7.305_to_7.14_0.005mmsteps_7.26tzero_0.55Vrepeat_r',34);
data_A_r2_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.55V\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_0.55Vrepeat_r',31);
data_B_r2_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.55V\1L_MoS2_Flow_6.51_to_-4.89_0.3mmsteps_7.26tzero_0.55Vrepeat_r',39);
data_C_r2_055V = func_import_TA_data('C:\Users\Yusef\Documents\DATA\Transient
Absorption\MoS2\Paper1\Transient_absorption_data\Flow Cell\Round
2\0.55V\1L_MoS2_Flow_-4.89_to_-22.89_1.5mmsteps_7.26tzero_0.55Vrepeat_r',13);
```

%% Concatenate data along the time axis

```
r_1_00V = vertcat(data_R_r1_00V, data_A_r1_00V, data_B_r1_00V, data_C_r1_00V);
r_1_01V = vertcat(data_R_r1_01V, data_A_r1_01V, data_B_r1_01V, data_C_r1_01V);
r_1_015V = vertcat(data_R_r1_015V, data_A_r1_015V, data_B_r1_015V, data_C_r1_015V);
r_1_02V = vertcat(data_R_r1_02V, data_A_r1_02V, data_B_r1_02V, data_C_r1_02V);
r_1_025V = vertcat(data_R_r1_025V, data_A_r1_025V, data_B_r1_025V, data_C_r1_025V);
r_1_03V = vertcat(data_R_r1_03V, data_A_r1_03V, data_B_r1_03V, data_C_r1_03V);
r_1_0325V = vertcat(data_R_r1_0325V, data_A_r1_0325V, data_B_r1_0325V,
data_C_r1_0325V);
r_1_035V = vertcat(data_R_r1_035V, data_A_r1_035V, data_B_r1_035V, data_C_r1_035V);
r_1_04V = vertcat(data_R_r1_04V, data_A_r1_04V, data_B_r1_04V, data_C_r1_04V);
r_1_05V = vertcat(data_R_r1_05V, data_A_r1_05V, data_B_r1_05V, data_C_r1_05V);
r_1_0525V = vertcat(data_R_r1_0525V, data_A_r1_0525V, data_B_r1_0525V,
data_C_r1_0525V);
r_1_055V = vertcat(data_R_r1_055V, data_A_r1_055V, data_B_r1_055V, data_C_r1_055V);
```

```

r_2_00V = vertcat(data_R_r2_00V, data_A_r2_00V, data_B_r2_00V, data_C_r2_00V);
r_2_01V = vertcat(data_R_r2_01V, data_A_r2_01V, data_B_r2_01V, data_C_r2_01V);
r_2_015V = vertcat(data_R_r2_015V, data_A_r2_015V, data_B_r2_015V, data_C_r2_015V);
r_2_02V = vertcat(data_R_r2_02V, data_A_r2_02V, data_B_r2_02V, data_C_r2_02V);
r_2_025V = vertcat(data_R_r2_025V, data_A_r2_025V, data_B_r2_025V, data_C_r2_025V);
r_2_03V = vertcat(data_R_r2_03V, data_A_r2_03V, data_B_r2_03V, data_C_r2_03V);
r_2_0325V = vertcat(data_R_r2_0325V, data_A_r2_0325V, data_B_r2_0325V,
data_C_r2_0325V);
r_2_035V = vertcat(data_R_r2_035V, data_A_r2_035V, data_B_r2_035V, data_C_r2_035V);
r_2_04V = vertcat(data_R_r2_04V, data_A_r2_04V, data_B_r2_04V, data_C_r2_04V);
r_2_05V = vertcat(data_R_r2_05V, data_A_r2_05V, data_B_r2_05V, data_C_r2_05V);
r_2_0525V = vertcat(data_R_r2_0525V, data_A_r2_0525V, data_B_r2_0525V,
data_C_r2_0525V);
r_2_055V = vertcat(data_R_r2_055V, data_A_r2_055V, data_B_r2_055V, data_C_r2_055V);
%% use the optimizeTA function to ensure each spectra is flipped the correct way, smooth the
data using smoothn, and average the 5 trials of each data using trimmean

```

```

opt_r1_00V = func_optimizeTA(r_1_00V);
opt_r1_01V = func_optimizeTA_for_01V_r1(r_1_01V);
opt_r1_015V = func_optimizeTA(r_1_015V);
opt_r1_02V = func_optimizeTA(r_1_02V);
opt_r1_025V = func_optimizeTA(r_1_025V);
opt_r1_03V = func_optimizeTA(r_1_03V);
opt_r1_0325V = func_optimizeTA(r_1_0325V);
opt_r1_035V = func_optimizeTA(r_1_035V);
opt_r1_04V = func_optimizeTA(r_1_04V);
opt_r1_05V = func_optimizeTA(r_1_05V);
opt_r1_0525V = func_optimizeTA(r_1_0525V);
opt_r1_055V = func_optimizeTA(r_1_055V);

```

```

opt_r2_00V = func_optimizeTA(r_2_00V);
opt_r2_01V = func_optimizeTA(r_2_01V);
opt_r2_015V = func_optimizeTA(r_2_015V);
opt_r2_02V = func_optimizeTA(r_2_02V);
opt_r2_025V = func_optimizeTA(r_2_025V);
opt_r2_03V = func_optimizeTA(r_2_03V);
opt_r2_0325V = func_optimizeTA(r_2_0325V);
opt_r2_035V = func_optimizeTA(r_2_035V);
opt_r2_04V = func_optimizeTA(r_2_04V);
opt_r2_05V = func_optimizeTA(r_2_05V);
opt_r2_0525V = func_optimizeTA(r_2_0525V);
opt_r2_055V = func_optimizeTA(r_2_055V);

```

%% Create axis for data set R, once you have the time axis set up you dont need to repeat this section for data sets of same time steps.

```

% Units in micrometers for positions
t_zero_positionR = 7260; %input zero position here
start_positionR = 7305; %input starting position here
step_sizeR = 5; %input step sizes here
zero_adjusted_start_positionR = (start_positionR - t_zero_positionR)./step_sizeR + 1;

total_stepR = 34;
stepsR = 1:total_stepR;
total_step_correctedR = stepsR - zero_adjusted_start_positionR;
% time_zeros_accountedA = total_step_correctedA - 2;
timeR_1 = (total_step_correctedR.*step_sizeR.*2*3.336);

% Create axis for data set A

t_zero_positionA = 7260; %input zero position here
start_positionA = 7440; %input starting position here
step_sizeA = 30; %input step sizes here
zero_adjusted_start_positionA = (start_positionA - t_zero_positionA)./step_sizeA + 1;

total_stepA = 31;
stepsA = 1:total_stepA;
total_step_correctedA = stepsA - zero_adjusted_start_positionA;
% time_zeros_accountedA = total_step_correctedA - 2;
timeA_1 = (total_step_correctedA.*step_sizeA.*2*3.336);

% create time axis for B

t_zero_positionB = 7260; %input zero position here
start_positionB = 6510; %input starting position here
step_sizeB = 300; %input step sizes here
zero_adjusted_start_positionB = (start_positionB - t_zero_positionB)./step_sizeB + 1;

total_stepB = 39;
stepsB = 1:total_stepB;
total_step_correctedB = stepsB - zero_adjusted_start_positionB;
% time_zeros_accountedB = total_step_correctedB - 2;
timeB_1 = (total_step_correctedB.*step_sizeB.*2*3.336);

% create C time axis

t_zero_positionC = 7260; %input zero position here
start_positionC = -4890; %input starting position here
step_sizeC = 1500; %input step sizes here
zero_adjusted_start_positionC = (start_positionC - t_zero_positionC)./step_sizeC + 1;

total_stepC = 13;

```

```

stepsC = 1:total_stepC;
total_step_correctedC = stepsC - zero_adjusted_start_positionC;
% time_zeros_accountedC = total_step_correctedC - 2;
timeC_1 = (total_step_correctedC.*step_sizeC.*2*3.336);

time = [timeR_1 timeA_1 timeB_1 timeC_1]; %full time axis
time = time./1000;
%% Create Wavelength axis
x = 0:2047;
nm = x*((693.892-337.509)/2047) + (337.509);%(601.049);%Bounds determined from
calibration
%nm_B = x*(57.0/2047) + (600 - 6.01);
%nm_C = x*(57.9/2047) + (415 - 6.36);
%for spline
%xx = 0:500;
%nmnm = xx*((694.57-337.61)/500) + (337.61);

%% Resort the time array, resort the data matrices in temporal order, and transpose the data so
the rows are pixels and the columns are time delays
[time_sorted, I, ~] = unique(time, 'sorted'); %removes the repeated values

%[time_sorted,I] = sort(time);
sorted_opt_r1_00V = opt_r1_00V(I,:).';
sorted_opt_r1_01V = opt_r1_01V(I,:).';
sorted_opt_r1_015V = opt_r1_015V(I,:).';
sorted_opt_r1_02V = opt_r1_02V(I,:).';
sorted_opt_r1_025V = opt_r1_025V(I,:).';
sorted_opt_r1_03V = opt_r1_03V(I,:).';
sorted_opt_r1_0325V = opt_r1_0325V(I,:).';
sorted_opt_r1_035V = opt_r1_035V(I,:).';
sorted_opt_r1_04V = opt_r1_04V(I,:).';
sorted_opt_r1_05V = opt_r1_05V(I,:).';
sorted_opt_r1_0525V = opt_r1_0525V(I,:).';
sorted_opt_r1_055V = opt_r1_055V(I,:).';

sorted_opt_r2_00V = opt_r2_00V(I,:).';
sorted_opt_r2_01V = opt_r2_01V(I,:).';
sorted_opt_r2_015V = opt_r2_015V(I,:).';
sorted_opt_r2_02V = opt_r2_02V(I,:).';
sorted_opt_r2_025V = opt_r2_025V(I,:).';
sorted_opt_r2_03V = opt_r2_03V(I,:).';
sorted_opt_r2_0325V = opt_r2_0325V(I,:).';
sorted_opt_r2_035V = opt_r2_035V(I,:).';
sorted_opt_r2_04V = opt_r2_04V(I,:).';
sorted_opt_r2_05V = opt_r2_05V(I,:).';
sorted_opt_r2_0525V = opt_r2_0525V(I,:).';

```

```

sorted_opt_r2_055V = opt_r2_055V(I,:).';

%% Plot contour figures of the sorted and optimized data
f = 4; %%number of colors to "fill" contour plot
f = 4; %%number of colors to "fill" contour plot

figure();contourf(nm, time_sorted, sorted_opt_r1_00V,f)
title('r1 00V smooth');xlabel('Wavelength (nm)');ylabel('Time (ps)')

figure();contourf(nm, time_sorted,sorted_opt_r1_015V,f)
title('r1 015V smooth');xlabel('Wavelength (nm)');ylabel('Time (ps)')

figure();contourf(nm, time_sorted,sorted_opt_r1_03V,f)
title('r1 03V smooth smooth');xlabel('Wavelength (nm)');ylabel('Time (ps)')

figure();contourf(nm, time_sorted,sorted_opt_r1_05V,f)
title('r1 05V smooth smooth');xlabel('Wavelength (nm)');ylabel('Time (ps)')

figure();contourf(nm, time_sorted,sorted_opt_r1_055V,f)
title('r1 055V smooth smooth');xlabel('Wavelength (nm)');ylabel('Time (ps)')

%% Plotting frequency resolved at different time points

i = 31; %%choose which temporal slice you want
figure();
hold on
plot(nm,sorted_opt_r1_00V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_01V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_015V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_02V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_025V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_03V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_0325V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_035V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_04V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_05V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_0525V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r1_055V(:,i),'linewidth',3.5);
legend('0.0V','0.1V','0.15V','0.2V','0.25V','0.3V','0.325V','0.35V','0.4V','0.5V','0.525V','0.55V')
title('r1 timestep 39');xlabel('Wavelength (nm)');ylabel('DeltaA');
set(gca,'FontSize',16)
hold off

figure();
hold on
plot(nm,sorted_opt_r2_00V(:,i),'linewidth',3.5);

```

```

plot(nm,sorted_opt_r2_01V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_015V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_02V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_025V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_03V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_0325V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_035V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_04V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_05V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_0525V(:,i),'linewidth',3.5);
plot(nm,sorted_opt_r2_055V(:,i),'linewidth',3.5);
legend('0.0V','0.1V','0.15V','0.2V','0.25V','0.3V','0.325V','0.35V','0.4V','0.5V','0.525V','0.55V')
title('r2 timestep 40');xlabel('Wavelength (nm)');ylabel('\DeltaA');
set(gca,'FontSize',16)
hold off
%% Fit exciton bleach peaks with a gaussian + line to get the peak amplitude at every time point

%[nm_cut_B, B_amp, B_cent_freq, B_fwhm, B_slope] = func_fitBexciton(TAdata, nm)

% Round 1
[nm_cut_A_r1_00V, A_amp_r1_00V, A_cent_freq_r1_00V, A_fwhm_r1_00V,
A_slope_r1_00V] = func_fitAexciton(sorted_opt_r1_00V, nm);
[nm_cut_B_r1_00V, B_amp_r1_00V, B_cent_freq_r1_00V, B_fwhm_r1_00V,
B_slope_r1_00V] = func_fitBexciton(sorted_opt_r1_00V, nm);
[nm_cut_C_r1_00V, C_amp_r1_00V, C_cent_freq_r1_00V, C_fwhm_r1_00V,
C_slope_r1_00V] = func_fitCexciton(sorted_opt_r1_00V, nm);

[nm_cut_A_r1_01V, A_amp_r1_01V, A_cent_freq_r1_01V, A_fwhm_r1_01V,
A_slope_r1_01V] = func_fitAexciton(sorted_opt_r1_01V, nm);
[nm_cut_B_r1_01V, B_amp_r1_01V, B_cent_freq_r1_01V, B_fwhm_r1_01V,
B_slope_r1_01V] = func_fitBexciton(sorted_opt_r1_01V, nm);
[nm_cut_C_r1_01V, C_amp_r1_01V, C_cent_freq_r1_01V, C_fwhm_r1_01V,
C_slope_r1_01V] = func_fitCexciton(sorted_opt_r1_01V, nm);

[nm_cut_A_r1_015V, A_amp_r1_015V, A_cent_freq_r1_015V, A_fwhm_r1_015V,
A_slope_r1_015V] = func_fitAexciton(sorted_opt_r1_015V, nm);
[nm_cut_B_r1_015V, B_amp_r1_015V, B_cent_freq_r1_015V, B_fwhm_r1_015V,
B_slope_r1_015V] = func_fitBexciton(sorted_opt_r1_015V, nm);
[nm_cut_C_r1_015V, C_amp_r1_015V, C_cent_freq_r1_015V, C_fwhm_r1_015V,
C_slope_r1_015V] = func_fitCexciton(sorted_opt_r1_015V, nm);

[nm_cut_A_r1_02V, A_amp_r1_02V, A_cent_freq_r1_02V, A_fwhm_r1_02V,
A_slope_r1_02V] = func_fitAexciton(sorted_opt_r1_02V, nm);
[nm_cut_B_r1_02V, B_amp_r1_02V, B_cent_freq_r1_02V, B_fwhm_r1_02V,
B_slope_r1_02V] = func_fitBexciton(sorted_opt_r1_02V, nm);

```

```
[nm_cut_C_r1_02V, C_amp_r1_02V, C_cent_freq_r1_02V, C_fwhm_r1_02V,  
C_slope_r1_02V] = func_fitCexciton(sorted_opt_r1_02V, nm);
```

```
[nm_cut_A_r1_025V, A_amp_r1_025V, A_cent_freq_r1_025V, A_fwhm_r1_025V,  
A_slope_r1_025V] = func_fitAexciton(sorted_opt_r1_025V, nm);  
[nm_cut_B_r1_025V, B_amp_r1_025V, B_cent_freq_r1_025V, B_fwhm_r1_025V,  
B_slope_r1_025V] = func_fitBexciton(sorted_opt_r1_025V, nm);  
[nm_cut_C_r1_025V, C_amp_r1_025V, C_cent_freq_r1_025V, C_fwhm_r1_025V,  
C_slope_r1_025V] = func_fitCexciton(sorted_opt_r1_025V, nm);
```

```
[nm_cut_A_r1_03V, A_amp_r1_03V, A_cent_freq_r1_03V, A_fwhm_r1_03V,  
A_slope_r1_03V] = func_fitAexciton(sorted_opt_r1_03V, nm);  
[nm_cut_B_r1_03V, B_amp_r1_03V, B_cent_freq_r1_03V, B_fwhm_r1_03V,  
B_slope_r1_03V] = func_fitBexciton(sorted_opt_r1_03V, nm);  
[nm_cut_C_r1_03V, C_amp_r1_03V, C_cent_freq_r1_03V, C_fwhm_r1_03V,  
C_slope_r1_03V] = func_fitCexciton(sorted_opt_r1_03V, nm);
```

```
[nm_cut_A_r1_0325V, A_amp_r1_0325V, A_cent_freq_r1_0325V, A_fwhm_r1_0325V,  
A_slope_r1_0325V] = func_fitAexciton(sorted_opt_r1_0325V, nm);  
[nm_cut_B_r1_0325V, B_amp_r1_0325V, B_cent_freq_r1_0325V, B_fwhm_r1_0325V,  
B_slope_r1_0325V] = func_fitBexciton(sorted_opt_r1_0325V, nm);  
[nm_cut_C_r1_0325V, C_amp_r1_0325V, C_cent_freq_r1_0325V, C_fwhm_r1_0325V,  
C_slope_r1_0325V] = func_fitCexciton(sorted_opt_r1_0325V, nm);
```

```
[nm_cut_A_r1_035V, A_amp_r1_035V, A_cent_freq_r1_035V, A_fwhm_r1_035V,  
A_slope_r1_035V] = func_fitAexciton(sorted_opt_r1_035V, nm);  
[nm_cut_B_r1_035V, B_amp_r1_035V, B_cent_freq_r1_035V, B_fwhm_r1_035V,  
B_slope_r1_035V] = func_fitBexciton(sorted_opt_r1_035V, nm);  
[nm_cut_C_r1_035V, C_amp_r1_035V, C_cent_freq_r1_035V, C_fwhm_r1_035V,  
C_slope_r1_035V] = func_fitCexciton(sorted_opt_r1_035V, nm);
```

```
[nm_cut_A_r1_04V, A_amp_r1_04V, A_cent_freq_r1_04V, A_fwhm_r1_04V,  
A_slope_r1_04V] = func_fitAexciton(sorted_opt_r1_04V, nm);  
[nm_cut_B_r1_04V, B_amp_r1_04V, B_cent_freq_r1_04V, B_fwhm_r1_04V,  
B_slope_r1_04V] = func_fitBexciton(sorted_opt_r1_04V, nm);  
[nm_cut_C_r1_04V, C_amp_r1_04V, C_cent_freq_r1_04V, C_fwhm_r1_04V,  
C_slope_r1_04V] = func_fitCexciton(sorted_opt_r1_04V, nm);
```

```
[nm_cut_A_r1_05V, A_amp_r1_05V, A_cent_freq_r1_05V, A_fwhm_r1_05V,  
A_slope_r1_05V] = func_fitAexciton(sorted_opt_r1_05V, nm);  
[nm_cut_B_r1_05V, B_amp_r1_05V, B_cent_freq_r1_05V, B_fwhm_r1_05V,  
B_slope_r1_05V] = func_fitBexciton(sorted_opt_r1_05V, nm);  
[nm_cut_C_r1_05V, C_amp_r1_05V, C_cent_freq_r1_05V, C_fwhm_r1_05V,  
C_slope_r1_05V] = func_fitCexciton(sorted_opt_r1_05V, nm);
```

```
[nm_cut_A_r1_0525V, A_amp_r1_0525V, A_cent_freq_r1_0525V, A_fwhm_r1_0525V,
A_slope_r1_0525V] = func_fitAexciton(sorted_opt_r1_0525V, nm);
[nm_cut_B_r1_0525V, B_amp_r1_0525V, B_cent_freq_r1_0525V, B_fwhm_r1_0525V,
B_slope_r1_0525V] = func_fitBexciton(sorted_opt_r1_0525V, nm);
[nm_cut_C_r1_0525V, C_amp_r1_0525V, C_cent_freq_r1_0525V, C_fwhm_r1_0525V,
C_slope_r1_0525V] = func_fitCexciton(sorted_opt_r1_0525V, nm);
```

```
[nm_cut_A_r1_055V, A_amp_r1_055V, A_cent_freq_r1_055V, A_fwhm_r1_055V,
A_slope_r1_055V] = func_fitAexciton(sorted_opt_r1_055V, nm);
[nm_cut_B_r1_055V, B_amp_r1_055V, B_cent_freq_r1_055V, B_fwhm_r1_055V,
B_slope_r1_055V] = func_fitBexciton(sorted_opt_r1_055V, nm);
[nm_cut_C_r1_055V, C_amp_r1_055V, C_cent_freq_r1_055V, C_fwhm_r1_055V,
C_slope_r1_055V] = func_fitCexciton(sorted_opt_r1_055V, nm);
```

%% Round 2

```
[nm_cut_A_r2_00V, A_amp_r2_00V, A_cent_freq_r2_00V, A_fwhm_r2_00V,
A_slope_r2_00V] = func_fitAexciton(sorted_opt_r2_00V, nm);
[nm_cut_B_r2_00V, B_amp_r2_00V, B_cent_freq_r2_00V, B_fwhm_r2_00V,
B_slope_r2_00V] = func_fitBexciton(sorted_opt_r2_00V, nm);
[nm_cut_C_r2_00V, C_amp_r2_00V, C_cent_freq_r2_00V, C_fwhm_r2_00V,
C_slope_r2_00V] = func_fitCexciton(sorted_opt_r2_00V, nm);
```

```
[nm_cut_A_r2_01V, A_amp_r2_01V, A_cent_freq_r2_01V, A_fwhm_r2_01V,
A_slope_r2_01V] = func_fitAexciton(sorted_opt_r2_01V, nm);
[nm_cut_B_r2_01V, B_amp_r2_01V, B_cent_freq_r2_01V, B_fwhm_r2_01V,
B_slope_r2_01V] = func_fitBexciton(sorted_opt_r2_01V, nm);
[nm_cut_C_r2_01V, C_amp_r2_01V, C_cent_freq_r2_01V, C_fwhm_r2_01V,
C_slope_r2_01V] = func_fitCexciton(sorted_opt_r2_01V, nm);
```

```
[nm_cut_A_r2_015V, A_amp_r2_015V, A_cent_freq_r2_015V, A_fwhm_r2_015V,
A_slope_r2_015V] = func_fitAexciton(sorted_opt_r2_015V, nm);
[nm_cut_B_r2_015V, B_amp_r2_015V, B_cent_freq_r2_015V, B_fwhm_r2_015V,
B_slope_r2_015V] = func_fitBexciton(sorted_opt_r2_015V, nm);
[nm_cut_C_r2_015V, C_amp_r2_015V, C_cent_freq_r2_015V, C_fwhm_r2_015V,
C_slope_r2_015V] = func_fitCexciton(sorted_opt_r2_015V, nm);
```

```
[nm_cut_A_r2_02V, A_amp_r2_02V, A_cent_freq_r2_02V, A_fwhm_r2_02V,
A_slope_r2_02V] = func_fitAexciton(sorted_opt_r2_02V, nm);
[nm_cut_B_r2_02V, B_amp_r2_02V, B_cent_freq_r2_02V, B_fwhm_r2_02V,
B_slope_r2_02V] = func_fitBexciton(sorted_opt_r2_02V, nm);
[nm_cut_C_r2_02V, C_amp_r2_02V, C_cent_freq_r2_02V, C_fwhm_r2_02V,
C_slope_r2_02V] = func_fitCexciton(sorted_opt_r2_02V, nm);
```

```
[nm_cut_A_r2_025V, A_amp_r2_025V, A_cent_freq_r2_025V, A_fwhm_r2_025V,
A_slope_r2_025V] = func_fitAexciton(sorted_opt_r2_025V, nm);
```

```
[nm_cut_B_r2_025V, B_amp_r2_025V, B_cent_freq_r2_025V, B_fwhm_r2_025V,  
B_slope_r2_025V] = func_fitBexciton(sorted_opt_r2_025V, nm);  
[nm_cut_C_r2_025V, C_amp_r2_025V, C_cent_freq_r2_025V, C_fwhm_r2_025V,  
C_slope_r2_025V] = func_fitCexciton(sorted_opt_r2_025V, nm);
```

```
[nm_cut_A_r2_03V, A_amp_r2_03V, A_cent_freq_r2_03V, A_fwhm_r2_03V,  
A_slope_r2_03V] = func_fitAexciton(sorted_opt_r2_03V, nm);  
[nm_cut_B_r2_03V, B_amp_r2_03V, B_cent_freq_r2_03V, B_fwhm_r2_03V,  
B_slope_r2_03V] = func_fitBexciton(sorted_opt_r2_03V, nm);  
[nm_cut_C_r2_03V, C_amp_r2_03V, C_cent_freq_r2_03V, C_fwhm_r2_03V,  
C_slope_r2_03V] = func_fitCexciton(sorted_opt_r2_03V, nm);
```

```
[nm_cut_A_r2_0325V, A_amp_r2_0325V, A_cent_freq_r2_0325V, A_fwhm_r2_0325V,  
A_slope_r2_0325V] = func_fitAexciton(sorted_opt_r2_0325V, nm);  
[nm_cut_B_r2_0325V, B_amp_r2_0325V, B_cent_freq_r2_0325V, B_fwhm_r2_0325V,  
B_slope_r2_0325V] = func_fitBexciton(sorted_opt_r2_0325V, nm);  
[nm_cut_C_r2_0325V, C_amp_r2_0325V, C_cent_freq_r2_0325V, C_fwhm_r2_0325V,  
C_slope_r2_0325V] = func_fitCexciton(sorted_opt_r2_0325V, nm);
```

```
[nm_cut_A_r2_035V, A_amp_r2_035V, A_cent_freq_r2_035V, A_fwhm_r2_035V,  
A_slope_r2_035V] = func_fitAexciton(sorted_opt_r2_035V, nm);  
[nm_cut_B_r2_035V, B_amp_r2_035V, B_cent_freq_r2_035V, B_fwhm_r2_035V,  
B_slope_r2_035V] = func_fitBexciton(sorted_opt_r2_035V, nm);  
[nm_cut_C_r2_035V, C_amp_r2_035V, C_cent_freq_r2_035V, C_fwhm_r2_035V,  
C_slope_r2_035V] = func_fitCexciton(sorted_opt_r2_035V, nm);
```

```
[nm_cut_A_r2_04V, A_amp_r2_04V, A_cent_freq_r2_04V, A_fwhm_r2_04V,  
A_slope_r2_04V] = func_fitAexciton(sorted_opt_r2_04V, nm);  
[nm_cut_B_r2_04V, B_amp_r2_04V, B_cent_freq_r2_04V, B_fwhm_r2_04V,  
B_slope_r2_04V] = func_fitBexciton(sorted_opt_r2_04V, nm);  
[nm_cut_C_r2_04V, C_amp_r2_04V, C_cent_freq_r2_04V, C_fwhm_r2_04V,  
C_slope_r2_04V] = func_fitCexciton(sorted_opt_r2_04V, nm);
```

```
[nm_cut_A_r2_05V, A_amp_r2_05V, A_cent_freq_r2_05V, A_fwhm_r2_05V,  
A_slope_r2_05V] = func_fitAexciton(sorted_opt_r2_05V, nm);  
[nm_cut_B_r2_05V, B_amp_r2_05V, B_cent_freq_r2_05V, B_fwhm_r2_05V,  
B_slope_r2_05V] = func_fitBexciton(sorted_opt_r2_05V, nm);  
[nm_cut_C_r2_05V, C_amp_r2_05V, C_cent_freq_r2_05V, C_fwhm_r2_05V,  
C_slope_r2_05V] = func_fitCexciton(sorted_opt_r2_05V, nm);
```

```
[nm_cut_A_r2_0525V, A_amp_r2_0525V, A_cent_freq_r2_0525V, A_fwhm_r2_0525V,  
A_slope_r2_0525V] = func_fitAexciton(sorted_opt_r2_0525V, nm);  
[nm_cut_B_r2_0525V, B_amp_r2_0525V, B_cent_freq_r2_0525V, B_fwhm_r2_0525V,  
B_slope_r2_0525V] = func_fitBexciton(sorted_opt_r2_0525V, nm);  
[nm_cut_C_r2_0525V, C_amp_r2_0525V, C_cent_freq_r2_0525V, C_fwhm_r2_0525V,  
C_slope_r2_0525V] = func_fitCexciton(sorted_opt_r2_0525V, nm);
```

```
[nm_cut_A_r2_055V, A_amp_r2_055V, A_cent_freq_r2_055V, A_fwhm_r2_055V,
A_slope_r2_055V] = func_fitAexciton(sorted_opt_r2_055V, nm);
[nm_cut_B_r2_055V, B_amp_r2_055V, B_cent_freq_r2_055V, B_fwhm_r2_055V,
B_slope_r2_055V] = func_fitBexciton(sorted_opt_r2_055V, nm);
[nm_cut_C_r2_055V, C_amp_r2_055V, C_cent_freq_r2_055V, C_fwhm_r2_055V,
C_slope_r2_055V] = func_fitCexciton(sorted_opt_r2_055V, nm);
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
func_import_TA_data
```

```
function [TA_data] = func_import_TA_data(file_path, num_timesteps)
```

```
% rise time = 34 steps
% time window 1 = 32 steps
% time window 2 = 39 steps
% time window 3 = 13 steps
```

```
final_index = num_timesteps +2;
TA_data = zeros(num_timesteps, 2048, 5);
```

```
for i = 1:5
    filename1= file_path; % should have name like 'C:\Users\raraa\OneDrive\Desktop\New
Data\Spring 2021\2021-3-
3\OCP\1L_MoS2_Flow_7.44_to_6.51_0.03mmsteps_7.26tzero_Pristine_r';
    filename2=num2str(i);
    filename=strcat(filename1,filename2);
    filename3='.txt';
    filename=strcat(filename,filename3);
    data = importdata(filename);
    data_corrected = data(3:final_index,:); %remove extra 2 timesteps at beginning of data and
possible extra timestep at end
    TA_data(:, :,i) = data_corrected;
```

```
end
end
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
func_optimizeTA
```

```
%% Flip spectra so they are all facing the same way
%flip is done by taking value at pixel 298 (scatter from pump pulse) and flipping based on if this
is
```

```

%negative or positive
%datasets are set up as timedelay:pixel:trial
dataset_flipped = zeros(size(dataset,1),size(dataset,2),size(dataset,3));

for m = 1:size(dataset,3); % cycle through each trial
    for n = 1:size(dataset,1); % cycle through each row(timestep)
        if dataset(n,298,m) > 0; % check that pixel 298 is negative
            dataset_flipped(n,:,m) = dataset(n,:,m).*-1;

            else dataset_flipped(n,:,m) = dataset(n,:,m);
        end
    end
end

%% smooth data of frequency/wavelength axis

dataset_smooth = zeros(size(dataset_flipped,1),size(dataset_flipped,2),size(dataset_flipped,3));
ss = 1500; %how much to smooth with smoothn function

for m = 1:size(dataset_flipped,3);
    for n = 1:size(dataset_flipped,1);
        dataset_smooth(n,:,m) = smoothn(dataset_flipped(n,:,m),ss);
    end
end
%% average the trials (3rd dimension) using trimmean function and subtract background
fulldata = trimmean(dataset_smooth,30,3);

% % Subtract negative spectrum

neg_spectrum = trimmean(fulldata((36:39),:),33,1);
data_subtract_neg_spectrum = zeros(size(fulldata,1),size(fulldata,2));
for n = 1:size(fulldata,1)
    data_subtract_neg_spectrum(n,:) = smoothn((fulldata(n,:) - neg_spectrum),1000);
end

fullTA = data_subtract_neg_spectrum;
end

```

%%%

Only the fitting function for the A-exciton bleach feature is shown here, as the fitting procedure for the other two excitons are essentially identical. The only difference is in the selection of the truncated window that the automated fitting code operates on.

```
func_fitAexciton
```

```
function [nm_cut_A, A_amp, A_cent_freq, A_fwhm, A_slope] = func_fitAexciton(TAdata, nm)  
%% truncate data for A exciton for automated fitting
```

```
nm_window_A = nm(1682:1997); %630nm-685nm initial window to find min
```

```
A_min_40 = min(TAdata(1682:1997,40)); % find the intensity of the minimum (bleach peak) at  
1ps (timestep 40)
```

```
A_min_39 = min(TAdata(1682:1997,39)); % find the intensity of the minimum (bleach peak) at  
1ps (timestep 40)
```

```
A_min_41 = min(TAdata(1682:1997,41)); % find the intensity of the minimum (bleach peak) at  
1ps (timestep 40)
```

```
A_index_40 = find(TAdata(1682:1997,40) == A_min_40); % find the pixel where the intensity  
of the min is
```

```
A_index_39 = find(TAdata(1682:1997,39) == A_min_39); % find the pixel where the intensity  
of the min is
```

```
A_index_41 = find(TAdata(1682:1997,41) == A_min_41); % find the pixel where the intensity  
of the min is
```

```
diff_A_min_1 = abs(A_index_40 - A_index_39);
```

```
diff_A_min_2 = abs(A_index_40 - A_index_41);
```

```
if diff_A_min_1 > 28 || diff_A_min_2 > 28 % 28 pixels is 5 nm, so the max can't have changed  
more than 5 nm
```

```
    A_min = A_min_41;
```

```
    A_index = A_index_41;
```

```
else A_min = A_min_40; A_index = A_index_40;
```

```
end
```

```
A_min = min(TAdata(1682:1997,31));
```

```
A_index = find(TAdata(1682:1997,31) == A_min);
```

```
A_min_nm = nm_window_A(A_index);
```

```
A_index_nm = find(nm == A_min_nm);
```

```
nm_cut_A = nm((A_index_nm-144):(A_index_nm+132)); %132 b/c upper limit (2048) for  
negative run for redshifted A exciton
```

```
A_sub_cut = TAdata((A_index_nm-144):(A_index_nm+132),:);
```

```
%% FFit: 'Gauss and line B exciton'.
```

```
A_amp = zeros(1,110);
```

```
A_cent_freq = zeros(1,110);
```

```
A_fwhm = zeros(1,110);
```

```

A_slope = zeros(1,110);

for n = 1:110
    [xData, yData] = prepareCurveData( nm_cut_A, -A_sub_cut(:,n) );

    % Set up fittype and options.
    ft = fittype( 'a1*exp(-((x-b1)/c1)^2) + d1*x + f1', 'independent', 'x', 'dependent', 'y' );
    opts = fitoptions( 'Method', 'NonlinearLeastSquares' );
    opts.Display = 'Off';
    opts.Lower = [0 A_min_nm-10 5 -Inf -Inf];
    opts.MaxFunEvals = 2000;
    opts.MaxIter = 2000;
    opts.StartPoint = [0.001 A_min_nm 15 0.620958643935308 0.573709764841198];
    opts.TolFun = 1e-08;
    opts.TolX = 1e-08;
    opts.Upper = [Inf A_min_nm+10 40 Inf Inf];

    % Fit model to data.
    [fitresult, gof] = fit( xData, yData, ft, opts );

    % %Plot fit with data.
    % figure( 'Name', 'untitled fit 3' );
    % h = plot( fitresult, xData, yData );
    % legend( h, 'A_gauss_test_32 vs. nm_cut_A', 'untitled fit 3', 'Location', 'NorthEast' );
    % % Label axes
    % xlabel nm_cut_A
    % ylabel A_gauss_test_32
    % grid on

    fit_values = coeffvalues(fitresult);
    A_amp(n) = fit_values(1);
    A_cent_freq(n) = fit_values(2);
    A_fwhm(n) = 1.175*fit_values(3);
    A_slope(n) = fit_values(4);
end

%%
A_amp = A_amp - trimmean(A_amp(3:12),30);

end

```

APPENDIX B

The following figures and text are the supplementary material referenced in chapters 3 and 4 for the published article “The pH-Dependent Orientation of N3 Dye on a Gold Substrate is Revealed Using Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy” and the submitted manuscript “The N3/TiO₂ Interfacial Structure is Dependent on the pH Conditions During Sensitization”.

B.1 Ultraviolet – visible (UV-Vis) Spectroscopy

UV-Vis absorption spectra of N3 solutions were collected over a pH range of 12 to 1 to identify the spectral changes due to different N3 dye protonation states present in solution at a given pH. A 140 mL, 42 μ M solution of N3 in 1:1 volume ratio of ethanol to water was made with 0.1M NaNO₃. Using NaOH, the N3 solution was initially brought to a pH of 12. Titration with HNO₃ was performed to decrease the solution pH to 1. Small amounts (15 – 50 μ L) of 75.0 mM HNO₃ were added in order to mitigate dilution of the N3 solution. After the addition of HNO₃, the N3 solution was allowed 5 minutes to equilibrate before recording the pH. Aliquots were taken at various pH points (33 points in total), and UV-Vis measurements of the aliquots were performed. UV-Vis measurements (Thermo Scientific Evolution 300) were collected using a single scan with a 1 nm resolution. Figure S1 shows the UV-Vis measurements of aliquots taken during the titration between pH range 7-1.8. We have not included the spectra of the aliquots above a pH of 7 because no changes to the N3 acid-base equilibria occur at pH conditions above 7, and similarly, no changes were observed in the UV-Vis spectrum. Our resulting spectra of the N3 solution as a function of pH produced similar results to what was reported previous works.^{1,2} Therefore, we are confident

in our determination of the protonation state(s) of N3 existing in a sensitizing solution according to the pH of the sensitizing solution.

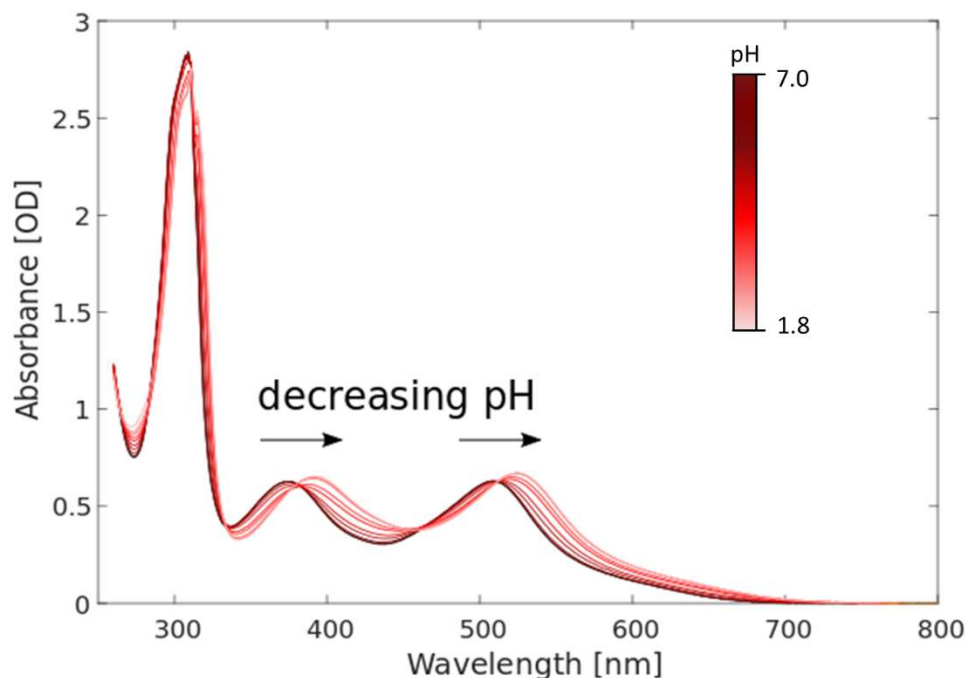


Figure B.1 UV-Vis absorbance spectrum of N3 dye. Dark red indicates the higher pH values, starting at a pH of 7.4. Lighter red moves toward more acidic solutions with the lowest pH being 1.8.

Relative concentrations of each N3 protonation species are calculated using pK_a values determined by previous DFT and UV-Vis spectroscopic studies.^{1,3} The calculated concentrations allow us to quantify the protonation species that exist in solution at a given pH; and therefore, determine the N3 protonation states available to adsorb to the gold surface during the sensitization process. Figure S2 reveals the convolved nature of the acid-base equilibria of N3; specifically, that many protonation species can exist at a single pH condition.

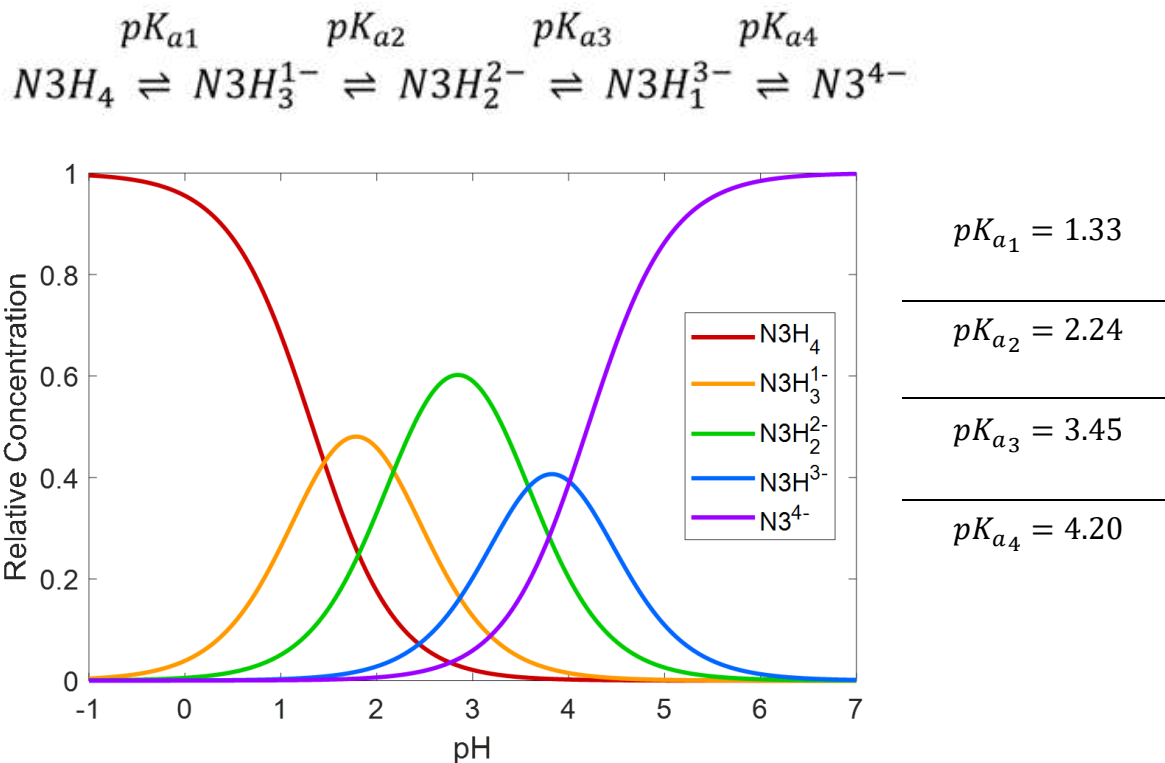


Figure B.2 Calculated relative concentration of N3 protonation species that exist in the sensitization solution at a given pH (left). pK_a values shown on the right correspond to the pK_a values shown in the equilibria equation (top).

B.2 Linear Combination Model for pH conditions of 2.0

Presented here are the separate components used to model the pH conditions of 2.0 for the N3/TiO₂ HD-VSFG spectra. Described within the main text, when the sensitizing solution is titrated to a pH of 2.0, the triprotonated N3 ($N3H_3^-$) is the most abundant protonation state in solution. However, from the acid/base stoichiometric calculations, there is a significant amount of diprotonated species existing in solution at this pH condition. The fitted parameters of the pH conditions of 3.0 from the HD-VSFG polarization simultaneous fitting procedure are used to

model the diprotonated contribution to the HD-VSFG spectra for pH conditions of 2.0. Figure S1 shows the experimental and fitted results of the pH conditions of 2.0.

HD-VSFG measurements report on the macroscopic average dipole moment angle of the molecular oscillator. With prior knowledge of the acid/base stoichiometry, we can assume that at least two components (the di- and tri-protonated species) contribute to the macroscopic average. Therefore, by fixing parameters for the diprotonated contribution, the tri-protonated contribution to the HD-VSFG spectra can be extracted.

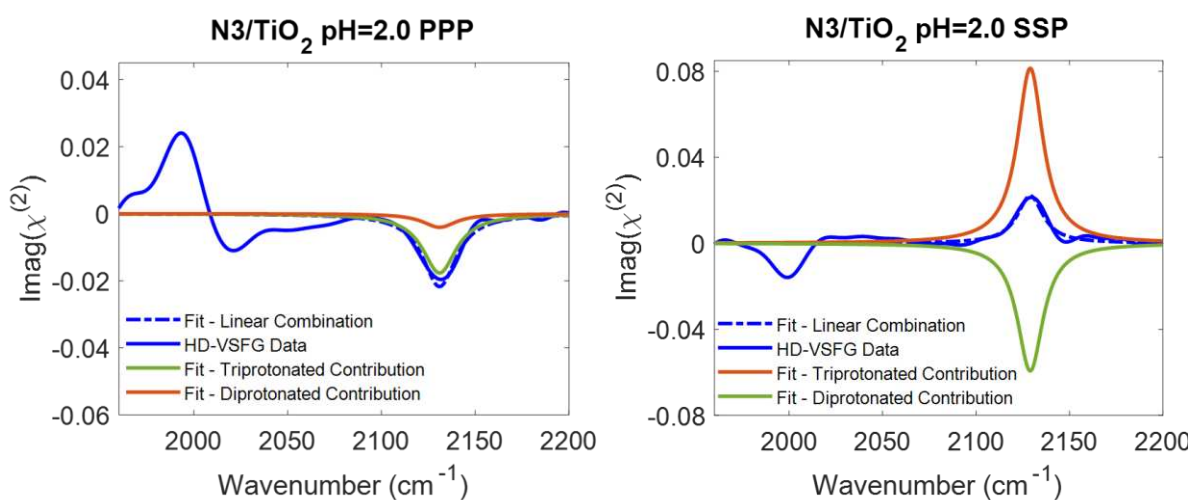


Figure B.3 The linear combination, HD-VSFG data, and individual di- and tri-protonated components used within the linear combination for both polarization conditions.

References

- ¹ G. Pizzoli, M.G. Lobello, B. Carlotti, F. Elisei, M.K. Nazeeruddin, G. Vitillaro, and F.D. Angelis, *Dalton Trans.* **41**, 11841 (2012).
- ² Md.K. Nazeeruddin, S.M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, and M. Grätzel, *Inorg. Chem.* **38**, 6298 (1999).
- ³ J.M. Cole, Y. Gong, J. McCree-Grey, P.J. Evans, and S.A. Holt, *ACS Appl. Energy Mater.* **1**, 2821 (2018).

APPENDIX C

The following figures and text are the supplementary material referenced in chapters 6 and 7. Chapter 6 is the manuscript draft which is being prepared for submission in *Science*, and this appendix contains the supplementary information for that manuscript. Additionally, since the experimental procedures are identical, the information presented in this appendix overlaps both studies presented in Chapters 6 and 7. This appendix includes methods and results regarding the spectroscopic setup, characterization methods, controls, and additional information for the studies performed on the MoS₂ photoanode flow cell experiments.

C.1 Methods for Chapter 6 and 7

C.1.1 Sample Characterization

Monolayer MoS₂ films (1 cm x 1 cm, 6Carbon Technology, Shenzhen, China) were synthesized via chemical vapor deposition on sapphire substrates and mechanically transferred to ITO-coated glass slides using a polymethyl methacrylate stamp and stored in nitrogen-purged glovebox until use. Raman spectra were taken to confirm samples were monolayer. The Raman spectra were recorded via an inverted Olympus IX73 optical microscope with 532 nm laser excitation source directed through a 100× NA0.95 air objective (Olympus PlanFL N100X) onto the sample. The signals were collected and filtered by an Ondax 532 nm THz Raman system, passed through a Horiba iHR 550 spectrometer, and then detected by a Synapse charge-coupled device detector. For UV-Vis measurements, the sample was excited via monochromatic light from a Horiba OBB Tunable PowerArc Illuminator. A 20× microscope objective was used to collect the light transmitted through the sample (I) and the ITO substrate (I₀) and send it to a Photometrics Prime 95B back illuminated complementary metal–oxide–semiconductor camera.

C.1.2 Electrochemical Flow Cell Construction

After characterization, MoS₂ samples were constructed into three-electrode microfluidic flow cells as shown in Figure 8. Holes were predrilled in the ITO slides to serve as inlet and outlet ports for electrolyte through the cell. Two pieces of approximately 50 μm thick polytetrafluorethylene (PTFE) spacers were placed between the ITO and a glass cover slip (Thermo Scientific) to form the microfluidic channel. An electrode chamber containing an Ag/AgI reference electrode and Pt counter electrode was attached to the outlet port. All components were attached/sealed with Loctite epoxy. Electrolyte solution (1M NaI, Fisher Scientific) was pulled through the cell at a constant rate of 0.5 mL/hr using a Kent Scientific syringe pump.

C.1.3 Electrochemical Measurements

To characterize the electrochemistry of the constructed monolayer MoS₂ flow cells, the open circuit potential, potential-dependent UV-Vis spectra, photocurrent spectra, and potential dependent current were measured. An Ivium Compactstat Potentiostat was used for all measurements. Positive current designated anodic (oxidation) reactions occurring at the working electrode (the MoS₂ sample) while negative current designated cathodic (reduction) events occurring at the working electrode. Open circuit for constructed flow cells was approximately 0.27 V vs. Ag/AgI. Thus, “high potential” refers to applied potential above 0.27 V vs. Ag/AgI and “low potential” refers to applied potential below 0.27 V vs. Ag/AgI. For potential-dependent absorbance measurements, a potential range was scanned stepwise from 0.0 V vs. Ag/AgI to 0.55 V vs. Ag/AgI in steps of 0.025 V while the light absorbance of the sample was recorded via the method detailed in section 2.1. Photocurrent measurements were performed by applying a constant voltage to the cell and measuring the resulting current while monochromatic light (Horiba OBB Tunable PowerArc Illuminator) was scanned from 750 nm to 375 nm in 1 nm steps. The measured current

and monochromator output were synced with a data acquisition card (DATAQ Instruments). For potential-dependent photocurrent measurements, potentials ranging from 0.0V to 0.55V vs. Ag/AgI were applied to the MoS₂ cell while monochromatic light resonant to the A, B, or C exciton (650 nm, 605 nm, and 432 nm, respectively) was chopped at 10 Hz and detected via a Stanford Research Systems SR830 lock-in amplifier. The lock-in signal was converted from arbitrary units to amperes via a proportionality constant (include section below?). Photocurrent was converted from amperes to EQE by dividing the current-per-second at each wavelength by the photons-per-second of the excitation source at each wavelength.

C.1.4 Transient Absorption (TA) Measurements

Transient absorption measurements are done with a home-built, femtosecond, pump-probe spectrometer setup. Light from a Ti:sapphire regenerative amplifier (Wyvern 1000, KM Laboratories) produces 3.3 mJ, <50 fs pulses centered at 790 nm with a repetition rate of 1kHz. Front reflections off a beam splitter and wedged CaF₂ plate are used to drop the light intensity before splitting the light with a half-wave plate and polarizer. A fraction of the light is sent through a delay stage controlled by a Newport motion controller driver (XPS model) to control timing and a 1mm BBO crystal to frequency double the light by SHG to 395 nm to create the pump pulse. The probe is created by taking the remaining portion of light that was split and focusing it down in a 2 mm quartz cuvette filled with 18 M Ω water to create a white-light continuum. The pump and probe are then non-collinearly focused and overlapped on the sample. The probe is collected, collimated, and focused into a spectrometer (iHR550, Horiba) with a 200 mm slit opening, equipped with a 100 line/mm grating (450 blaze), and detected by a single line 2048 element array detector (OctoPlus, Teledyne e2V). Resulting spectral and temporal resolution are 0.6nm and ~50fs, respectively. The pump pulse is modulated by a triggered, optical chopper (Thorlabs)

operating at 500 Hz to acquire “pumped” and “unpumped” pulse sequences used to calculate ΔA . Both the pump and probe pulse have a spatial FWHM of ~ 100 μm and fluence of 75 uJ/cm^2 .

C.2 Supplementary Results

C.2.1 Results: Steady State and Characterization

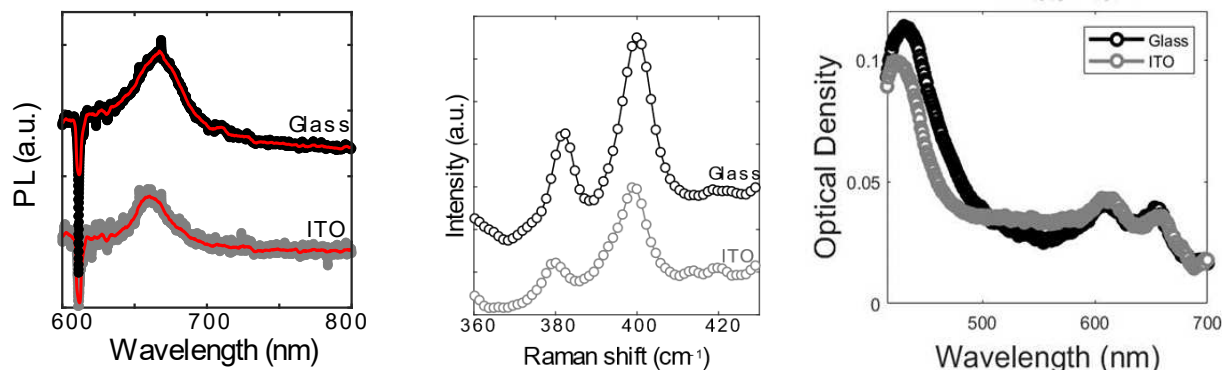


Figure C.1 a) Photoluminescence spectra of monolayer MoS_2 on glass (black data points) and ITO (grey data points). The red lines overlaying the data are 5-point smooths. The energy of the PL peaks is consistent with literature (citation). The PL intensity is quenched on conducting ITO substrate relative to insulating glass substrate, indicating additional recombination pathways or charge transfer on ITO. **b)** Raman spectra of monolayer MoS_2 on glass (black data points) and ITO (grey data points). The lower energy peak is attributed to the E_{2g}^1 mode and the higher energy peak is assigned to the A_{1g} mode (citation). The peak-splitting of 20 cm^{-1} is consistent with previous literature for monolayer MoS_2 (citation). **c)** Visible Optical Density (OD) spectra for the monolayer MoS_2 samples on conductive ITO and on glass.

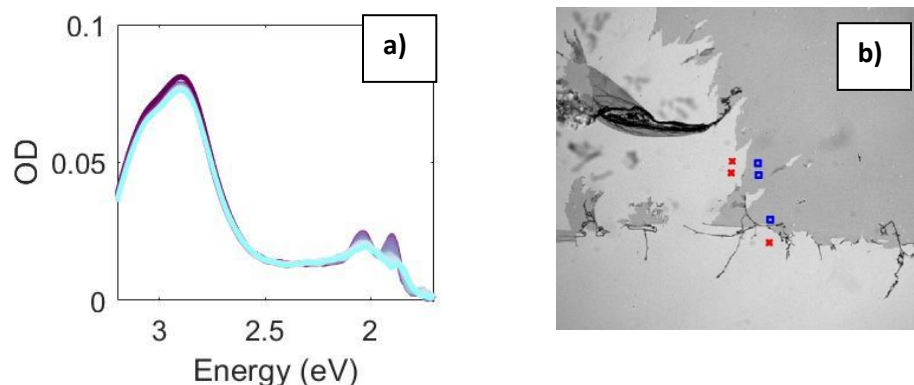


Figure C.2 a) Visible optical density spectra for monolayer MoS_2 in electrochemical cell as a function of applied potential. The image of the sample used for the OD calculations is shown in **b)**. Blue squares are the pixels averaged for intensity of light through the sample and substrate (I) and red squares are the pixels averaged for intensity of light through only the substrate (I_0).

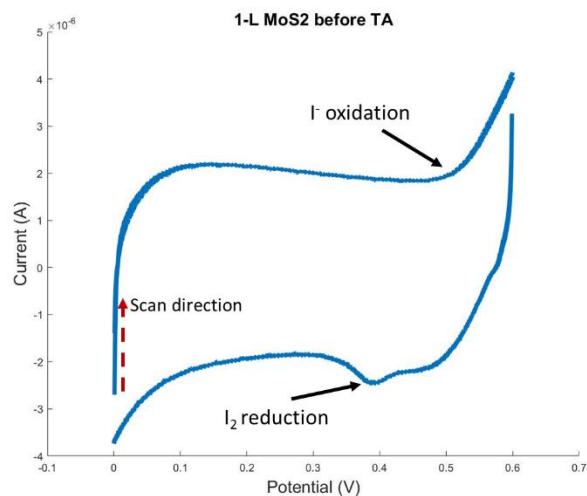


Figure C.3 Cyclic voltammogram of monolayer MoS₂/ITO|1 M NaI|Pt electrochemical cell under white light illumination. Oxidative current from the oxidation of I⁻ to I₂ onsets at approximately 0.5 V vs. Ag/AgI and reduction of I₂ occurs at approximately 0.39 V vs. Ag/AgI.

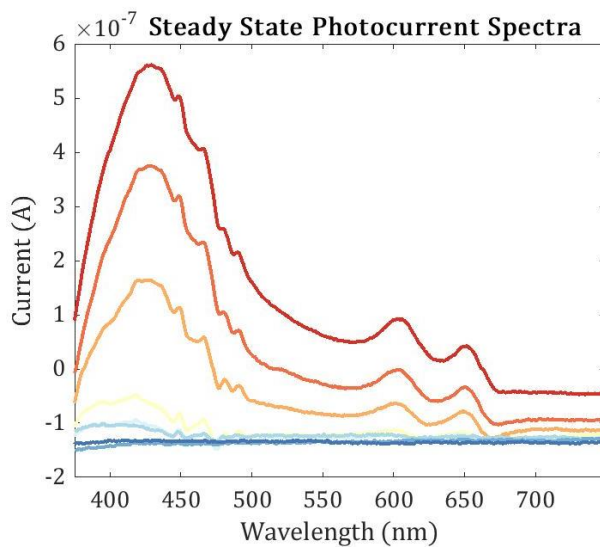


Figure C.4 Photocurrent as a function of energy for a range of applied potentials.

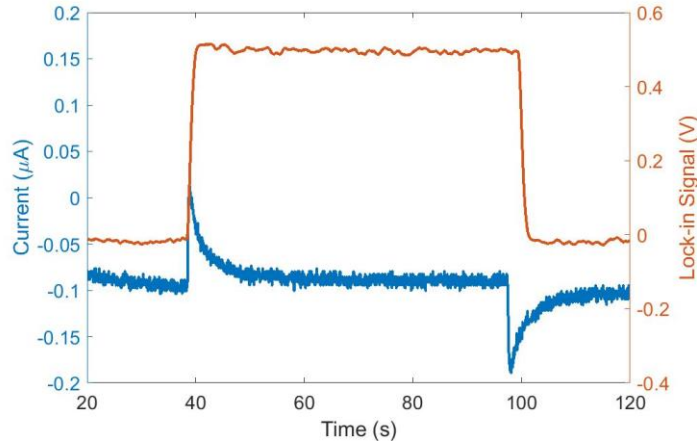


Figure C.5 Conversion of lock in signal (in volts) to current (in amps) via proportionality constant between chopped lock-in signal and un-chopped photocurrent. This proportionality constant measurement is replicated from Wang *et al* 2019.

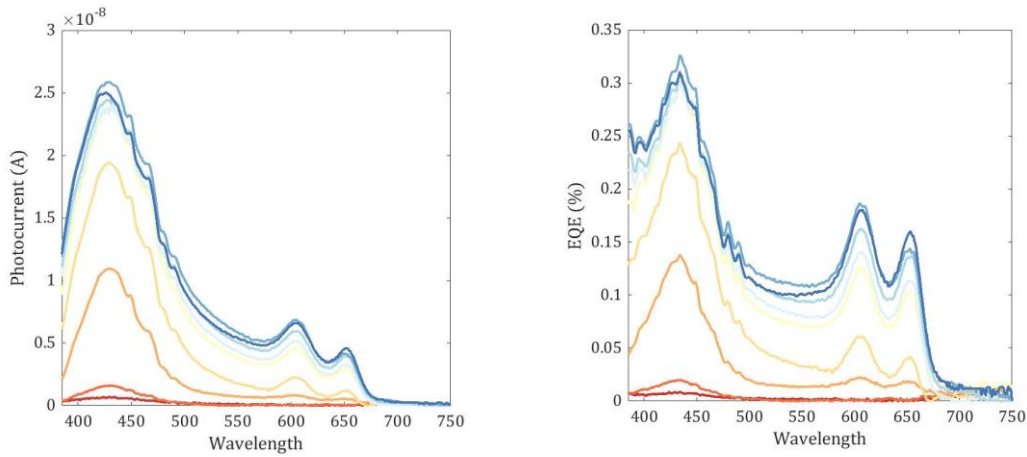


Figure C.6 Photocurrent as a function of energy for a range of applied potentials measured with a lock-in amplifier.

Lock-in signal is converted to amps via the lock-in proportionality constant, then converted to EQE using the equation

$$EQE (\%) = \frac{Current * Energy}{q * Power}$$

where q is fundamental charge and Power is the measured power of the excitation source as a function of wavelength.

C.2.2 Results: Transient Absorption

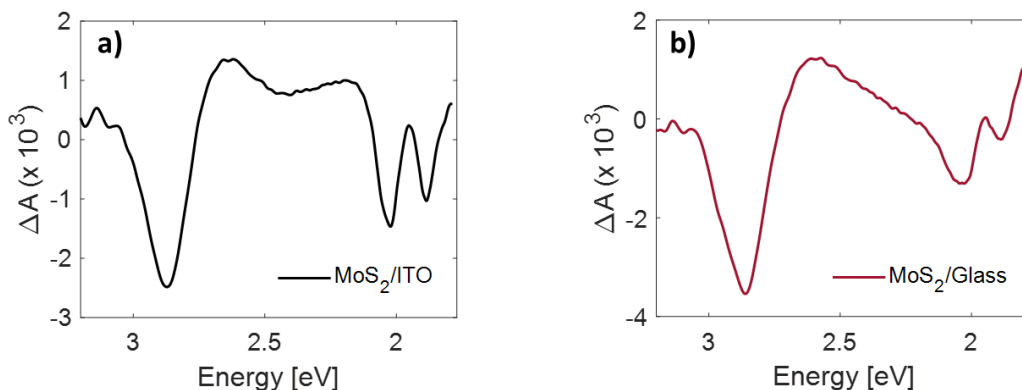


Figure C.7. Energy resolved TA spectra for MoS₂ on ITO (a) and glass (b) substrates taken at a delay time of 1 ps.

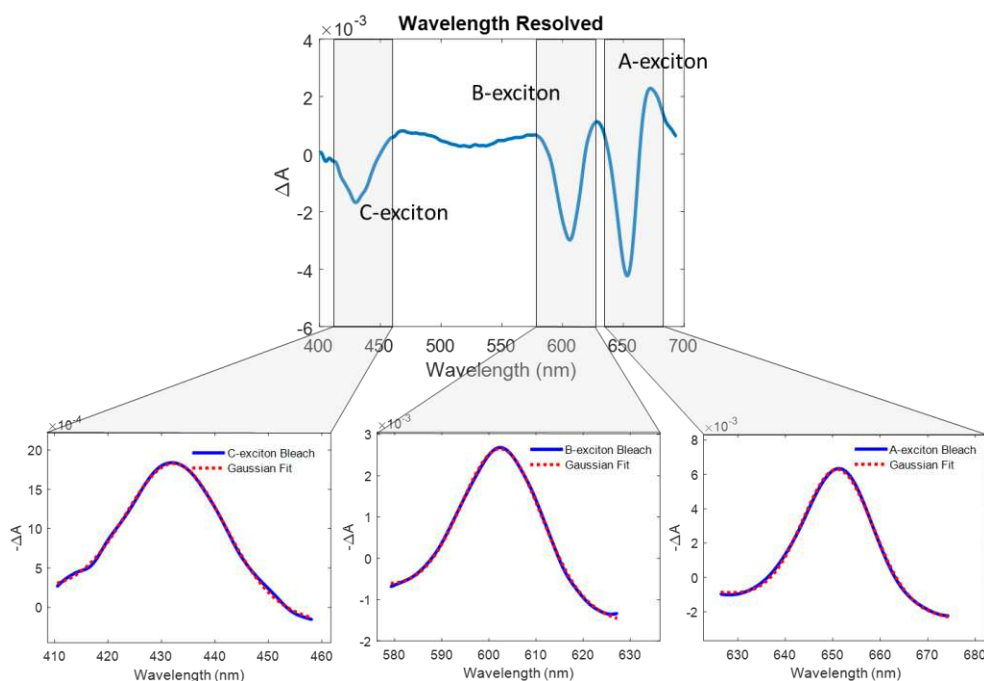


Figure C.8 An example of the spectral fitting procedure done at every time step of the TA experiment to C-, B-, and A-exciton features. The wavelength resolved spectra is shown on top, and each exciton region is truncated and fit with a gaussian and linear polynomial. The plots on the bottom show the data (blue) with the fit (red). Plots on the bottom are flipped from the original spectrum, but the fitted results are the same except that the amplitude is positive instead of negative.

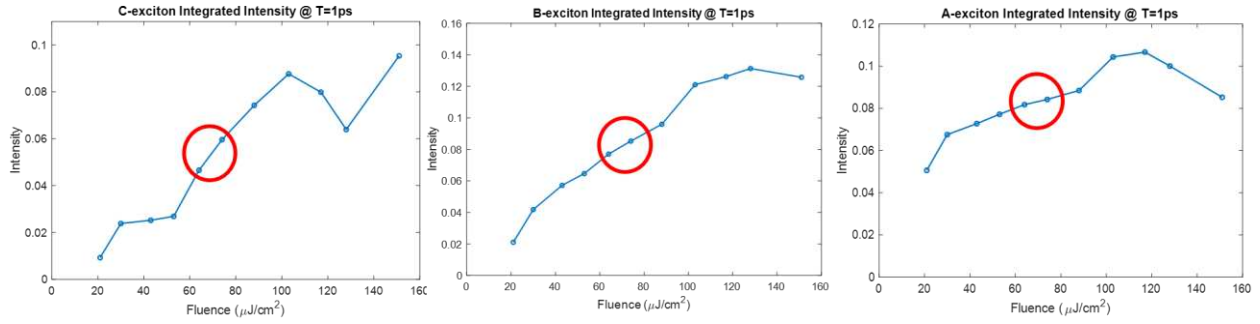


Figure C.9 Integrated TA bleach intensity of the C-, B-, and A-excitons of MoS₂ as a function of pump fluence. The red circle highlights the pump fluence of 75 $\mu\text{J}/\text{cm}^2$ that was chosen and can be seen to be within the linear regime of the excitonic bleach signal. Notice, at fluences $>100 \mu\text{J}/\text{cm}^2$, the exciton bleach signal deviates from the linearity.

$$\Delta A(\lambda, t) = A_0 + \left(\sum_{i=1}^3 A_i(\lambda) * \exp\left(-\frac{t}{\tau_i}\right) \right) * \left(A_4 - \exp\left(-\frac{t}{\tau_4}\right) \right)$$

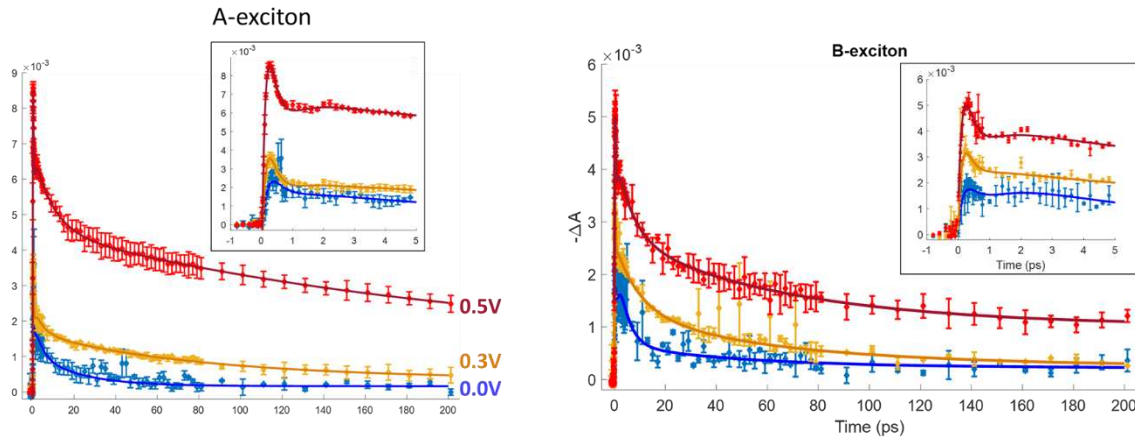


Figure C.10 Fitted bleach decay curves for the A- and B-excitons at applied potentials of 0.5 V (red), 0.3 V (yellow), and 0.0 V (blue). The full temporal window spanning up to 200 ps is shown, with the inset in the plots showing the first 5 ps. The time traces of the bleach intensity are fitted using a tri-exponential function to capture the decay of the bleach, and a rising exponential function to capture the exciton formation, shown in the equation above the plots. Additionally, a static offset (A_0) is used in the functional form.