

Time-Resolved Mid-Infrared Modes at the Surface of Hydrated Titanium

Oxides: The Titanium Oxyl and Phonon Polaritons

by

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B.A., Saint Anselm College, 2020

A thesis submitted to the Faculty of the Graduate School of the University of

Colorado in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

2026

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Abstract

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Time-Resolved Mid-Infrared Modes at the Surface of Hydrated Titanium Oxides: The Titanium Oxyl and Phonon Polaritons

Thesis directed by Associate Professor Tanja Cuk

Hydrogen fuel is an energy dense and carbon neutral source of energy when combusted, with water as the only biproduct. Photo-electrochemical water splitting is a promising and environmentally clean method to produce hydrogen. However, the efficiency of this process is limited by the significant energetic demands of the oxygen evolution half-reaction (OER) of the water splitting process, which involves four distinct proton and electron transfer steps. Optimizing OER on a catalyst surface requires an understanding of the intermediate species formed during each mechanistic step. Thus, it is essential to isolate and observe the intermediates of OER through spectroscopic techniques on a model catalyst surface under different reaction conditions to better understand how to improve OER efficiency. This work will make use of time-resolved vibrational studies of SrTiO_3 and TiO_2 surfaces to observe the formation of the first intermediate species of OER, the titanium oxyl (Ti-O^*), and better understand the vibrational modes on these catalyst surfaces.

A new vibration that arises from the motion of the sub-surface oxygen beneath the titanium oxyl when a photoexcited hole traps on a hydroxylated surface site has been previously detected with mid-infrared attenuated total reflection (ATR) spectroscopy. The spectral shape of the interfacial mode exhibited a distinctive Fano resonance, characterized by the coupling of the

vibrational mode to nearby continuum excitations. Here, that Fano resonance is used to define the formation kinetics of the oxyl radical at the n-doped SrTiO₃ interface with air through three frequency regimes: the anti-resonance to obtain the kinetics of the coupling factor $\Gamma(t)$, the resonance to obtain the kinetics of the coupled continuum excitations $A(t)$, and the frequency integrated spectrum to obtain the kinetics of the bare vibrational cross-section $S(t)$. All three regimes yield the same logistic growth that characterizes the growth of the oxyl to be exponential at early times ($t \sim 0$) before a surface saturation is reached.

The question remains whether the energetics of the formation of the titanium radical depends solely on the reorganization associated with the crystal lattice or whether the reorganization of solvent molecules at the interface needs to be included. Introducing electrolyte to the n-STO interface allows for coupling of the water librational continua to the subsurface vibrational mode through the Fano resonance, tuning the observed vibrational lineshape. The kinetics of the bare and coupled vibrational mode at four different interfaces (air, pD 13, pH 7, and pH 13) are modelled by the logistic function with a half rise of 1.76 ± 0.39 ps and rate of 0.56 ± 0.08 ps, which is not changed across the different solvent conditions. These kinetics are also tracked as a function of sample position within the evanescent wave of the ATR technique and as a function of pump excitation fluence. Although significant changes to the coupled vibrational lineshape are observed through the Fano asymmetry constant q with changing coupling through the evanescent probe and solvent continua, the kinetic growth of the coupled mode remains the same across all these conditions. This work shows that the energetics of oxyl formation are defined by the local surface environment rather than the availability of solvent interaction.

Surface phonon polaritons (SPhPs) arise from the coupling of light to optical phonons on the surface of a crystal lattice. ATR spectroscopy provides an avenue for this coupling to occur

through a matching of the wavevector of the light to that of the optical phonon. SPhPs have been measured in the mid-infrared region on transition metals oxides for decades. This work measures a previously unreported SPhP in rutile TiO_2 along with an associated excited state signal that arises on the photoexcited surface. A comparison is made to a similar signal observed on SrTiO_3 , where a ground state SPhP has been previously reported.

Dedication

I would like to dedicate this thesis to the friends and family whose love and support has made this all possible.

First, to my amazing friends who have made my time in Colorado unforgettable, I would not have made through these years without you.

Thank you Raythe for all those long nights on zoom in our first year working on problem sets and studying for exams. You and Cheyenne have truly made me feel like family all these years, I couldn't have done it without you.

Thank you to my family who supported my love of science and made me feel like I could do anything I wanted. To my older sister, Katie, who pushed me to be excellent even if she didn't realize it. To my lovely nieces, who I always look forward to seeing and who bring such joy into my life. To my grandparents who were always interested in the work I was doing, even if they didn't understand it. To my father, who I wish could be here see this. And to my amazing mother, who made me the person I am today and believed in me no matter what, I am so grateful for the life you have given me.

Finally, and most importantly, to my loving fiancé Kelly. Thank you for being there for me through all the times I struggled. For believing in me even when I didn't myself. For always pushing me to be the best person I could be. For moving across the country, thousands of miles from your home and family to be with me. I couldn't have done any of this without your love and support.

Thank you.

Acknowledgments

I would first like to thank my advisor Dr. Tanja Cuk for the opportunity to be a part of her group and perform the work described here. This would not have been possible without her guidance, expertise, and especially her patience throughout the years spent on this project. I would also like to thank the two post-docs I had the privilege to learn from over the years: Ilya Vinogradov was always there in the lab to answer questions about optics and spectroscopy when I first began my graduate journey, and Moritz Lang, who came to the group later in my time and always encouraged thought provoking discussion of any topic. Of course, I must thank my fellow researchers over the years in Suryansh Singh, Michael Paolino, Casey Boyd, Elizabeth Lander, Christen Courter, and most importantly, James Stewart, who struggled with me through many difficulties on this project for years. I must also acknowledge the financial support of US Department of Energy, CEDARs, and the University of Colorado Boulder Chemistry department, without which none of this would be possible. Lastly, I would like to thank the members of my thesis committee, Andres Montoya-Castillo, Adam Holewinski, Niels Damrauer, and David Jonas for their time and feedback on my thesis.

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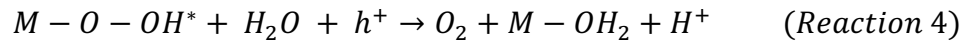
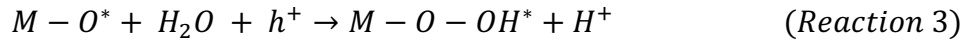
Chapter 1: Introduction

The drive for advancement of environmentally clean, renewable energy sources continues to be at the forefront of the scientific community to combat climate change and the coming energy crisis. Along with the need to harvest energy from renewable sources comes the requirement to store this energy as an accessible fuel source. One such fuel is energy dense and clean burning molecular hydrogen. If hydrogen can be produced in an environmentally carbon neutral manner, the whole process would present an entirely clean fuel cycle.

Water splitting produces hydrogen with only a single byproduct, oxygen. The idea of splitting water into its molecular components for fuel is hardly novel, having been around since electrochemical water splitting was discovered in the early 19th century. However, even now the process remains energetically inefficient due to the nature of the two redox reactions that make up the process: the Hydrogen Reduction Reaction (HRR) and the Oxygen Evolution Reaction (OER). It's the latter half-reaction that is generally considered the more energetically demanding and results in the inefficiency. Continual advancement into technologies allow us to study the mechanism of these reactions and determine conditions that improve their efficiency.

Water splitting can be driven electrochemically, with HRR occurring at the cathode and OER at the anode. Oxygen evolution at a single metal site on a catalyst surface can be described by the proposed mechanism given in Reactions 1-4¹. Each reaction describes a single proton and electron transfer, with four total being required for OER. At each step, a meta-stable intermediate species is formed and then consumed in the next reaction until the final products are achieved. The first intermediate, M-OH*, formed upon the initial proton and electron transfer from (or hole [h⁺] transfer to, as is shown in Reaction 1-4) a surface bound water molecule, has only recently been observed experimentally²⁻⁴. The free energy of the formation of the first reaction intermediate is

frequently used to describe the activity of catalytic systems such as metals and metal oxides⁵. Figure 1.1a shows the free energies in eV of all four mechanistic steps of OER.¹ While the overall theoretical potential needed to conduct OER is 1.23 V, the practical potential required is significantly higher due to the requirements of each mechanistic step. The minimum applied potential needed is determined by the rate limiting step, that which requires the highest applied potential or has the highest free energy. Transition metal oxides such as titanium and ruthenium oxide (TiO₂ and RuO₂) are considered the most effective materials for OER catalysis^{5,6}. RuO₂ is highly efficient with a low required overpotential to drive OER^{7,8}, while TiO₂ is very effective for photocatalysis due to its stability under oxidative conditions and the nature of its band structure for charge separation^{9,10}. The volcano plot in Figure 1.1b compares the efficiencies of common OER catalysts based on the free energies of the first intermediate formation as a function of the required applied potential⁵.



The suggested mechanism for OER involves the formation of meta-stable intermediate populations at multiple steps. It can occur as a single site (Reactions 1-4) or multi-site mechanism and is extremely environment specific^{1,11}. Varying conditions such as pH, ionic strength of solution, nature of the spectator ions, etc. for a given catalyst can change the rate limiting step and evolution of the intermediates while resulting in a similar product yield. Direct observation of the mechanistic steps of OER is still in the early stages, with much more information required to fully understand the effects of varying specific conditions. The sheer number of factors that can be tuned

to influence the catalytic process makes studying the mechanism experimentally challenging and requires very systematic, careful tuning of variables. That these variables can be used to optimize a catalyst's environment to meet the goals of an observer leads to the necessity to study each variable systematically on a model catalytic system. If one can reach an understanding of the optimal conditions for each mechanistic step, the entire OER process can be tailored to specifically meet needs.

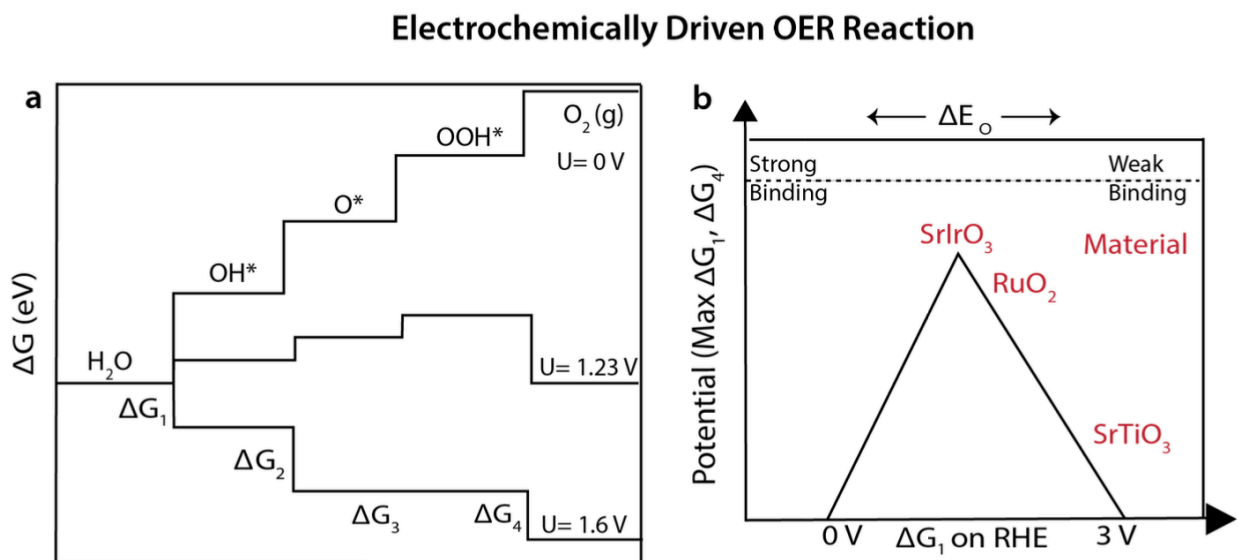


Figure 1.1: (a) Free energies of the four reaction steps involved in OER plotted for three different potentials applied to the electrode for a purely electrochemically driven OER reaction. (b) Volcano plot showing the free energy of the first proton-electron transfer step of OER to define overall OER catalytic activity.

Although much work has been done previously by both theory and experiment to understand catalytic reaction intermediates¹², directly resolving each reaction step in time remains a challenge. Doing so would yield pertinent information about reaction rates and meta-stable intermediate populations. Creating a system of experiments that provide both the time-resolution and the ability to vary the catalytic environment would allow for optimization of the system in terms of reaction selectivity and product evolution. In order to do so, the experiments must trigger

the overall reaction at a distinct time point, be sufficiently time-resolved and surface-sensitive, and finally be appropriately analyzed to extract relevant, meaningful spectral and kinetic information.

An ultrafast trigger is ideal for such time-resolved experiments since charge trapping on a catalyst surface can occur in less than a picosecond. The process must be triggered at a distinct point in time and initiate a fully spontaneous reaction such that each step in the catalysis proceeds sequentially without further input. Thus, a time axis is created that tracks the reaction coordinate of the systems potential energy surface (PES). That the reactions occur sequentially after a distinct time point is essential in capturing the initial formation of each intermediate separated from each other.

Similar to the trigger, the spectroscopic probe must also provide the time-resolution to observe the meta-stable intermediates from birth to decay for the sequential reactions. To fully classify the intermediate species, multiple techniques need be utilized to study both the electronic and vibrational excited state modes. An optical spectroscopy observes a broad set of electronic transitions over a given frequency regime independent of the molecular geometry present. Meanwhile, a vibrational spectroscopy can target more specific vibrational modes present with particular intermediate geometries. The combination of the two can provide a more wholistic kinetic picture of the catalytic reactions. These probes must also be sensitive to the catalyst surface where the intermediates form and progress through the sequential reaction steps. This is achieved using a reflectance of the optical probe and an attenuated total reflectance (ATR) geometry in the mid-infrared regime. The work presented here will focus on the mid-infrared vibrational study of these intermediates.

Above bandgap excitation of transition metal-oxide materials results in the formation of hole polarons^{13–15}. A hole polaron is a quasi-particle defined by a localized electron vacancy that

results in a distortion of the surrounding atomic lattice. These electron vacancies, or holes, are produced upon ultrafast UV excitation. They can then “trap” or localize on defect sites within an atomic lattice to form the polaron states¹⁶. The transition metal oxides used here for OER catalysis, SrTiO₃ and TiO₂, are n-doped semiconductors, doped with Niobium, which have surface oxygen sites both within the lattice and as adsorbed H₂O and OH⁻ groups¹⁷. These surface oxygen species serve as defect sites for the formation of hole polaron states that serve as the intermediates of OER¹⁵. Time-resolved spectroscopy can measure the formation of these intermediates through changes in the electronic energy levels of the species^{3,18,19} or, as will be done here with the mid-infrared vibrational probe, through changes in the vibrational signatures of the distorted lattice².

Previous work done by the Cuk group has studied OER on n-doped strontium titanate, SrTiO₃, and been able to identify significant information particularly regarding the first reaction intermediate. Time-resolved optical spectroscopy using a broadband visible probe found that the electronic energy levels of the reactive intermediates lie within the STO band gap and tracked the timescale of the formation and decay of these midgap states³. Optical studies have also identified the effects of reaction conditions such as ionic strength and pH on the kinetics associated with these intermediates, identifying in particular a strong pH dependence with an associated onset pK_a^{18,20}. Initial studies using time-resolved vibrational spectroscopy in the mid-IR region were able to directly observe a specific OER intermediate on the STO surface. A new excited state subsurface vibration was found and associated with a terminal oxyl radical (Ti-O*) on the surface with the help of DFT calculations². This vibrational signature exhibited a distinct Fano lineshape and was observed to be meta-stable on the order of nanoseconds^{2,21}. However, the exact picosecond growth kinetics remain to be tracked to fully understand the formation of this first intermediate

species. The goal of this work is to isolate and define the factors that drive the formation of the oxyl radical's vibrational signature.

Following this introduction, Chapters 2 and 3 will provide relevant background on the transient experiments and conditions of the OER reaction. A description of the experimental setup being used to investigate OER intermediates on catalytic surfaces will be provided, along with the pertinent information of the spectroscopic techniques used, namely time-resolved ATR spectroscopy. A background on the semiconductor/aqueous interface being studied as it behaves before and during photoexcitation will also be described in Chapter 2. Following that, Chapter 3 will expand on the previous work done to assign the oxyl's vibrational signature to the subsurface titanium-oxygen bond and characterize the equilibrated spectral shape through the Fano Resonance². A basic introduction to the Fano Resonance will be provided, along with the effects of introducing the electrolyte librational continua which can modify the observed vibrational lineshape through coupling with the vibrational mode²¹. The observed effects on the lineshape lead to the question of how the introduction of electrolyte can modify the kinetic growth of the oxyl's vibrational cross-section. Marcus theory can be applied to understand how solvent reorganization defines the energetics of an electron transfer reaction through two regimes: an "inner" reorganization of molecules and ligands directly bound to a transfer site and an "outer" reorganization of bulk solvent whose dipoles can reorient²². In bulk aqueous conditions, such as with hexaquo cations undergoing photoemission of electrons or $\text{OH}^- \rightarrow \text{OH}^*$ reactions in bulk water, the energetic contributions of the outer reorganization were found to be significant²³. However, in systems approaching a surface such as the example of excited state electron injection between indium tin oxide and bound RuP complexes, the outer reorganization is observed to be much reduced, and the inner reorganization dominates the energetics²⁴. While theory has suggested

that the inner reorganization dominates the energetics of hole-polaron formation on a metal oxide surface¹⁵, this work will provide much needed experimental evidence towards this hypothesis.

The remainder of this work in Chapters 4-6 will be divided into three different projects: extracting the time-dynamics of the oxyl's vibrational signature at the n-STO/air interface, interpreting the kinetic growth of the oxyl's vibration cross-section through the introduction of electrolyte, and characterization of a photo-induced surface phonon polariton on both STO and Rutile TiO₂. The first two projects work to expand on our understanding the energetics involved in the first mechanistic step OER through on the formation dynamics of the Ti-O* intermediate on the STO surface. The final project will characterize a different excited state vibrational mode observed on metal-oxide surfaces associated with a surface phonon polariton. This signal occurs in a similar frequency region as the oxyl on STO, and on rutile TiO₂ surfaces where the vibrational mode of the oxyl is not observed.

With the first two works in Chapters 4 and 5, the growth of the oxyl's vibrational cross-section will be defined through the exhibited Fano resonance. At the n-STO/air interface, the growth kinetics of the coupled vibrational mode can be defined through two time-dependent parameters of the Fano formula, the coupled continua excitations (A) and the coupling factor (Γ), while the kinetics of the bare vibrational cross-section can be extracted through an integrated spectral weight (S). Relevant time parameters for the vibrational growth through each of these regimes are extracted using a logistic fit to define the formation of the oxyl's vibrational cross-section. With the introduction of electrolyte, which can couple to the mode through the librational continua of water, Chapter 5 will examine the vibrational growth through changing reaction conditions. The reaction interface will be changed across four conditions: air, pH 7, pH 13, and pD 13. This will systematically modify the outer sphere through the availability of bulk solvent to

reorient. The resulting reaction kinetics are interpreted from a Marcus theory perspective to define the driving force behind the formation of the titanium oxyl.

The final study will focus on the discovery and characterization of a surface phonon polariton (SPhP) signal on Rutile TiO_2 . A discussion of both the ground state vibration and an associated excited state signature that arises following above band-gap UV excitation will be provided. A comparison of the surface TiO_2 mode will be made to a known SPhP signature observed on SrTiO_3 to compare the spectral behaviors observed in the ground state. The photoexcited signature will be reported for both samples and discussed in relation to the vibrational signature of the oxyl, which appears in a similar frequency region on STO but not on rutile TiO_2 . The future direction of the project towards understanding the source and observed behaviors of the photoexcited signal will be given.

Chapter 2: Experimental Methods and Background

In order to examine the mechanism on OER spectroscopically, a system is needed that not only conducts OER but that allows for selective study of OER in time without significant contamination from other reactions while also allowing for variation of relevant environmental factors (e.g. pH). The bulk of this work will focus on the study of the catalytic surface of niobium doped strontium titanate (abbreviated n-STO or STO). STO was chosen over other catalytic materials for multiple reasons. First, it is very selective for OER with limited competition from side reactions in comparison to other potential choices. For example, ruthenium oxide (RuO_2) and Iridium oxide (IrO_2) are more efficient OER catalysts but support other processes and side reactions that could increase the difficulty in isolating OER intermediates^{5,25,26}. STO also has a very high quantum efficiency of charge separation under bandgap photoexcitation, with efficiencies greater than 75%, and is commercially available as a single crystal in different sizes and doping densities. Finally, the surface is TiO_2 terminated, relevant since TiO_2 is one of the more commonly researched materials in the study of OER while being less available commercially in terms of doped single crystal samples. Combining these factors makes STO an ideal model system to study such that the techniques and analyses used can be applied to other potentially more complex systems, particularly other metal oxides used in oxidative reactions. This work will mostly focus on the use of STO doped with 0.7% Nb by weight. The final chapter will examine other doping densities of STO along with rutile TiO_2 , which exhibits similar characteristics for selectivity of OER and efficient charge separation.

2.1 Time Resolved Spectroscopy

Time-resolved pump probe experiments require the overlap of two incident beams both spatially and temporally. The pump pulse excites the system to some higher energy state, while the probe measures the system spectroscopically at some time before, during, or after the pump has excited the system. It is the variation of when the probe hits the sample relative to the pump that allows for time resolution of spectroscopic signatures. In the system studied here, a high energy 266 nm pump pulse photoexcites the sample at the semiconductor-aqueous interface generating electron-hole pairs in the semiconductor. These photo-induced charge carriers have the ability to trigger reactions at the interface. After a chosen time delay, the probe pulse is directed onto the same spot on the sample such that it interacts with the location where these reactions are triggered by the pump. The attenuated probe pulse for that time delay is then collected on a spectrometer. To understand the effect of the pump on the system, it is essential that the ground state system is also probed at each time delay for comparison. During an experiment, a “pump off” shot is collected with no exposure to the pump to obtain a spectrum for the equilibrated ground state of the system. A “pump on” shot is thus collected when the probe pulse interacts with the pump excited system at a given delay in time. Figure 2.1 shows a depiction of the different pulses and shots as a function of acquisition time, the total time over which a dataset is collected.

The excited state signal is taken as the difference between the measured on and off shots. This value is defined as the change in absorbance, ΔA , calculated as $\Delta A = -\log(R_{\text{on}}/R_{\text{off}})$, where R is the measured reflectance. For each on and off shot, a reference is also collected to account for any fluctuations in the probe intensity. Over the course of an experiment, many probe shots are collected for a given time delay and averaged, typically 4,000-5,000 shots to achieve a good signal to noise ratio. For lower signal strengths, more shots may be collected for greater averaging. Figure

2.2 provides a schematic diagram of the basic laser table setup for the mid-infrared vibrational studies.

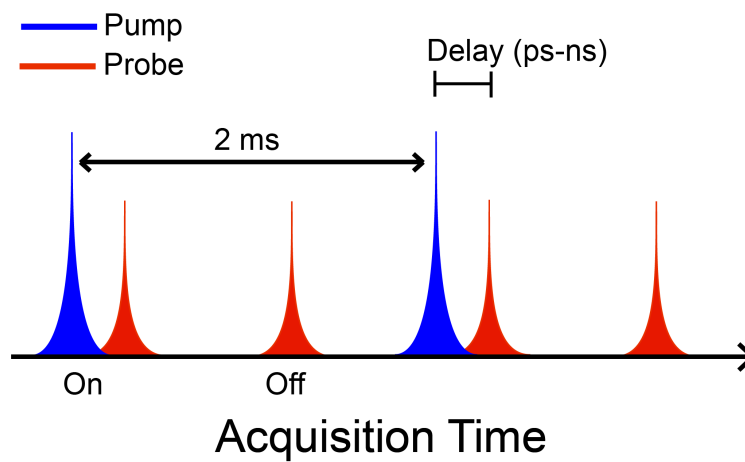


Figure 2.1: Cartoon depicting the on and off shots used in time-resolved pump probe spectroscopy. Probe pulses occur at twice the frequency of the pump. The delay time represents the time between the pump and probe pulses for the pump on shot with the bottom axis being the total acquisition time to collect all the shots taken.

The time delay between the pump and the probe for the pump on shot is varied using a motorized delay stage (MTM 150CC1, Newport) on the pump line to achieve an experimental time axis. By changing the distance that the pump travels before reaching the sample while leaving the probe timing unchanged, the time between the two pulses reaching the sample is changed. The number of points collected and the time difference between those points thus determines the extent of the time range post pump excitation that is probed spectroscopically. Collection of all delays for a given time range is considered one repeat, and multiple repeats may be collected and averaged in a given experiment.

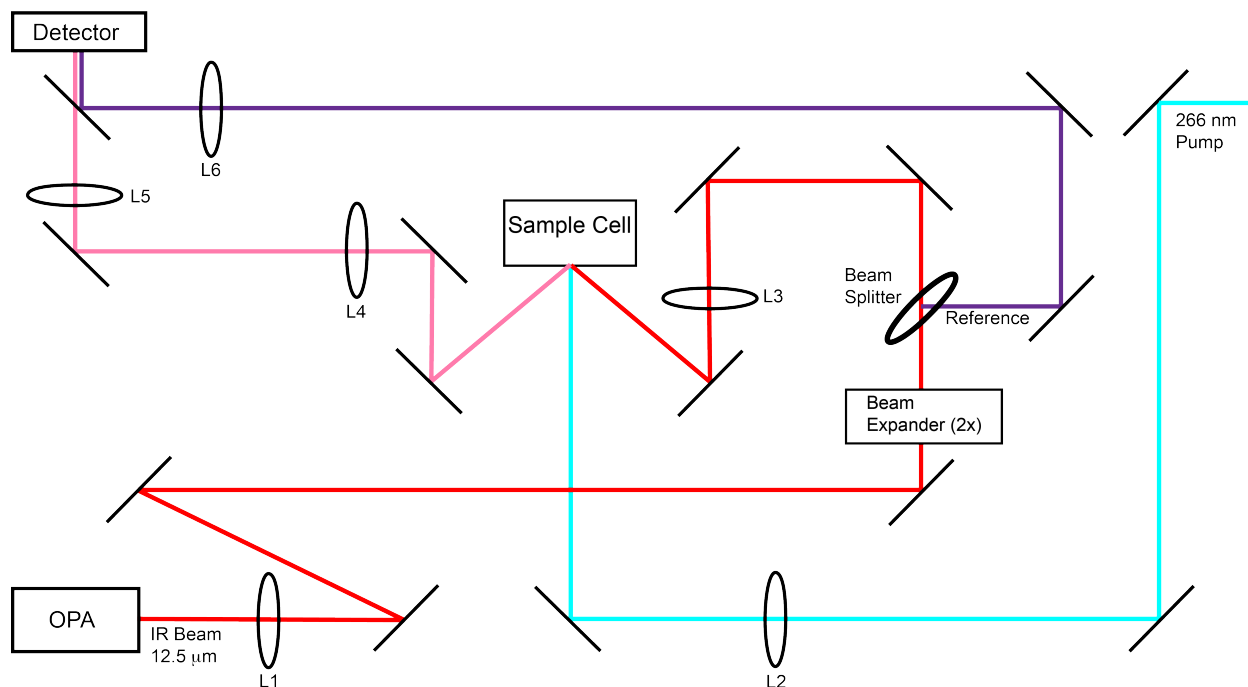


Figure 2.2: Schematic overview of time-resolved ATR setup on the optical table. The beam geometries of the pump and probe on the sample along with important optics are illustrated. Referencing of the probe is also shown. The sample and reference IR line enter the detector colinearly with a vertical offset. Further details about the generation of the IR probe and UV pump are given below.

The resolution of the experiment both spectrally and temporally is determined by the nature and timing of the two pulses. The spectral resolution is determined by the energetic width of the probe. This work makes use of a narrow vibrational probe spanning $\sim 80 \text{ cm}^{-1}$ in a typical experiment. However, other work in the Cuk group makes use of a broad band optical probe spanning the visible range of light. Use of the narrower vibrational probe allows for direct observation of specific vibrations associated with OER intermediates in comparison to the broader optical probe that views many electronic transitions without specific structural resolution.

The temporal resolution is determined by two factors. First, the pulse duration of the pump will determine on what time scale changes to the sample can be observed. A shorter pulse duration allows for resolution on a faster time scale. This work is done on what will be referred to as an ultrafast time scale, with a pump pulse duration of 400 femtoseconds, giving resolution on a

picosecond timescale. Data shown here will mainly focus on the 0-10 ps time regime of signal growth, with some data extending to approximately 4 ns, all with the ultrafast pulse. Examining longer time scales would require use of a pump with a longer pulse duration (nanoseconds or longer). Second, the resolution will depend on the delay steps between the pump and probe pulses on the time axis. This condition can be more easily controlled as long as the delay stage used can achieve small enough steps on the time axis. As an example, changes in ultrafast signals may occur on the order of a few picoseconds, thus delay steps on the order of tens of femtoseconds are needed to properly resolve signal changes in time. The delay stage used here for ultrafast studies allows for time steps on the order of ~ 10 s of fs, and the full temporal range of the stage is ~ 4 ns.

2.2 Pump Generation: 266 nm pump via Third Harmonic Generation (THG)

The pump utilized here is a 266 nm UV ultrafast pulse at a 500 Hz pulse rate generated by two sequential sum frequency generation (SFG) processes on an 800 nm beam. The 800 nm beam is produced using a Coherent Elite amplifier Ti:sapphire laser. The output pulses have a 150 fs temporal width and a 1 kHz repetition rate. A portion of this 800 nm beam is directed through a 0.5 kHz chopper and into the third harmonic generation area of the optical table. The optics used for the THG are from a commercially purchased kit from Eksma Optics, the Femtokit Basic FK-800-200-M. The first SHG process doubles the frequency of the 800 nm beam to produce 400 nm pulses along with leftover 800 nm pulses. These are then corrected for polarization mismatch and temporal walk-off using a waveplate and a birefringent material respectively. They then undergo the second SHG process wherein the 400 nm and leftover 800 nm pulses are summed to produce 266 nm pulses. The final output after the second SHG process is three colinear beams (266, 400, and 800 nm light). The desired 266 nm pump is then separated using harmonic mirrors that reflect

only the desired wavelength or a Pellin-Broca Prism. This process is depicted in Figure 2.3. The resultant beam has a 400 fs pulse beam width, as determined by a cross-correlation of the pump with an 800 nm pulse, as shown in Figure 2.4.

Input: 800 nm, 150 fs

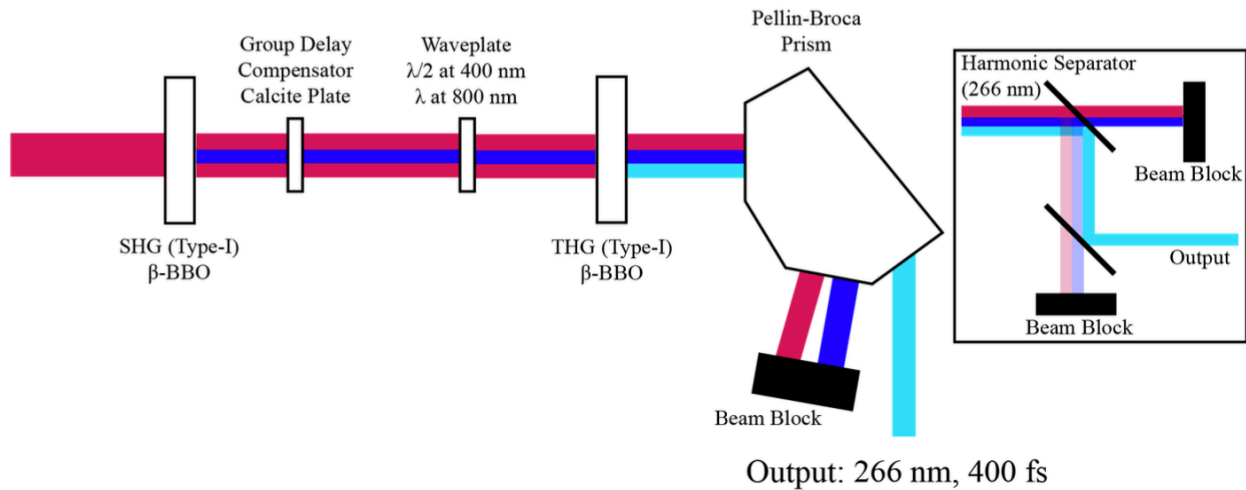


Figure 2.3: Depiction of the third harmonic generation setup used to create and isolate the 266 nm UV pump on the optical table. The boxed section on the right shows separation of the beams using harmonic mirrors, the method implemented in a standard measurement.

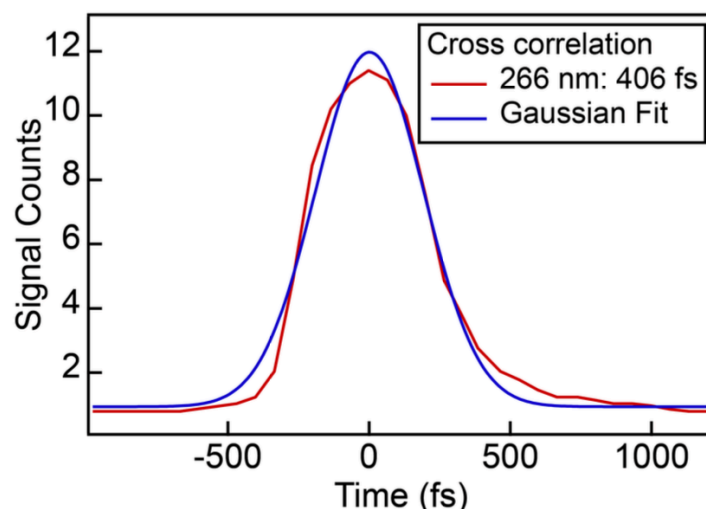


Figure 2.4: Cross correlation of the 266 nm pump used to calculate the time resolution and instrument response function (IRF) with a 400 fs temporal width.

2.3 Probe Generation: Mid-IR Probe using Optical Parametric Amplifier (OPA)

The Mid-IR probe is generated by directing a portion of an 800 nm beam into an Optical Parametric Amplifier (OPA). The output wavelength of light can be chosen and set by the experimentalist for the desired region of the near or mid-IR. Experiments outlined here will be in the mid-IR region centered around 12,500 nm (800 cm^{-1}), with some spectra extending over a range from $\sim 700\text{--}900\text{ cm}^{-1}$.

An 800 nm beam with a 150 fs pulse width is directed into the entrance of a Coherent OPerA-SOLO set to DFG2 (difference frequency generation). DFG is commonly used to produce mid-IR light, particularly for time-resolved spectroscopy, as direct laser sources are uncommon for this region of light. When the 800 nm beam enters the OPA, it is split into two beams, one containing up to 98% of the power, the other containing the remainder. The weaker beam is directed into the first of two parametric amplifier stages. It is split again into two beams, one of which is converted into a white light continuum (WLC) in a sapphire plate. The two beams are overlapped in a nonlinear crystal and the second beam, the “pump”, amplifies an overlapping

portion of the WLC, producing the signal beam on the output. It also creates an idler, which is a frequency equal to the difference between the pump and the signal beams.

The signal beam is directed to the second parametric amplifier stage where it goes through another amplification in a nonlinear crystal with the remainder of the 800 nm light separated out upon entering the OPA. This produces a new signal and idler beam, both of which are directed into the DFG section of the OPA. The signal and idler are overlapped in a DFG generator, or “mixer”, in which the difference frequency of the two beams is produced. It is this difference frequency that is the desired wavelength of mid-IR light (in our case centered at 800 cm^{-1}) and is directed out of the OPA and onto the optical table for use. The output beam is p-polarized with a 150 cm^{-1} bandwidth. Cartoon diagrams of parametric amplification and DFG are given in Figure 2.5.

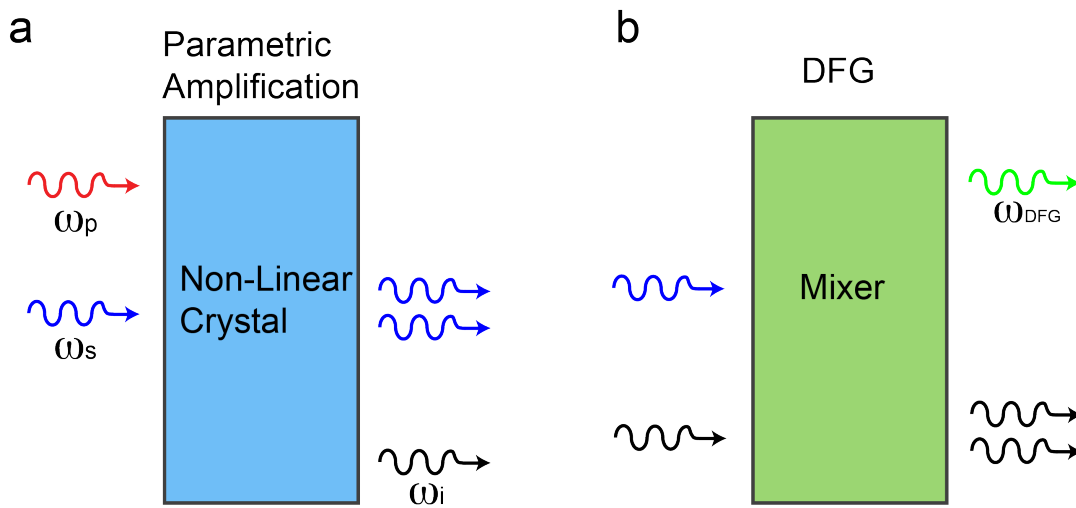


Figure 2.5: Diagram of parametric amplification (a) and Difference Frequency Generation (b) processes occurring in the OPA. Parametric amplification boosts the power of a signal frequency (ω_s) through a nonlinear crystal and occurs twice in the OPA. DFG produces the difference between two input frequencies, a higher frequency ω_s (signal) and lower frequency ω_i (idler). It also results in a boosted ω_i as for every signal photon destroyed it creates an idler photon and a difference photon.

2.4 Sample Cell and Attenuated Total Reflection Spectroscopy

The time-resolved ATR experiments are performed in a custom-built ATR photoelectrochemical cell, displayed in Figure 2.6. The bulk of the cell is made of polyether ether ketone (PEEK), a plastic resistant to solutions of interest to these studies, namely basic aqueous hydroxide solutions. The three holes in the top allow for a complete three electrode electrochemical system with working (sample), counter, and reference electrodes. The front of the cell is sealed by attaching a Piketech GladiATR front plate with a single-bounce diamond internal reflection element (IRE). The diamond is trapezoidal with a 45° cut. The front facet measures 1 mm in width while the side facets are 1.4 mm wide. Diamond is chosen for several reasons. It is transmissive to light both in the mid-IR (probe) and UV (pump) ranges, with approximately 25% of the pump power making it through the diamond. It has a very high refractive index ($n = 2.38$), important for the conditions of ATR measurements to create an evanescent wave (discussed more below). Finally, it is unaffected by aqueous and basic conditions in which our sample will be submerged. A rubber O-ring is in place between the front plate and cell wall to achieve the needed liquid tight seal to introduce electrolyte into the gap between the IRE and the sample.

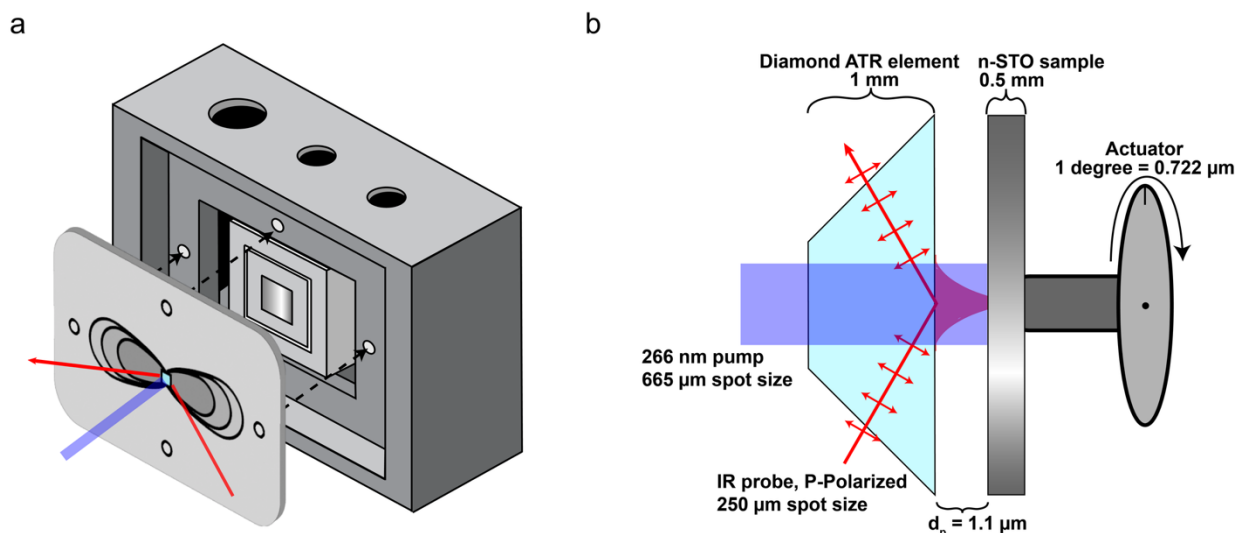


Figure 2.6: (a) Schematic of the custom built ATR photoelectrochemical cell used. A single crystal sample sits in the center of the cell and the metal front plate containing the diamond ATR element screws onto the front, creating a liquid tight seal. (b) Diagram of beam geometry entering the diamond ATR element. The 266 nm pump enters normal to the front facet of the diamond and sample. The mid-infrared probe enters through the side facet and totally internally reflects off the back of the diamond, creating the evanescent wave that probes the sample. An actuator on the back of the cell controls the distance between the sample and the diamond.

A titanium oxide single crystal sample is mounted onto a holder that screws into the center post of the cell. The position of the sample relative to the IRE is controlled by a Thorlabs Polaris P20 actuator on the back of the cell. All samples are single crystals that measure $10 \times 10 \times 0.5 \text{ mm}^3$ in size, with a front side polish to an arithmetic mean roughness of ~ 0.5 Angstroms. The sample mounting process involves applying a liquid resistant epoxy (Loctite 615) to the center of the holder while in the cell and placing the sample on the epoxy. The front plate is then screwed on, and the sample is pushed forward using the actuator until it comes into contact with the diamond IRE (determined by feeling of pressure on actuator). The epoxy is allowed to dry in this position such that the sample and crystal should be approximately parallel with each other, a condition that must be met to within a few hundredths of a degree for signal observation (discussed in detail below). Once a sample is mounted, the holder can be removed and replaced within the cell while maintaining this approximate alignment. Although the epoxy used to secure the sample is liquid resistant, it can swell enough to affect the precise alignment of the sample. A liquid electrical tape

(Gardner Bender LTR-400) is applied to the edges of the sample to seal off the epoxy and avoid this swelling.

The zoomed in sample and beam geometry with the ATR element is shown in Figure 2.6b. The 266 nm UV pump beam with a 665 μm FWHM and a 400 fs temporal width is directed through the front facet of the diamond IRE to excite the surface of the sample. After a set time delay, the IR probe (typically centered at 12.5 μm) with a 250 μm FWHM and a 150 fs temporal width is directed into the side facet of the crystal at a 60° angle. The critical angle for total internal reflection is defined by Equation 2.1 as:

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right) \quad \text{Equation 2.1}$$

For the diamond/air interface ($n_2 = 1$, $n_1 = 2.38$), this equates to 24.85°, well below the 60° in our geometry (for the diamond/aqueous, $n_2 = 1.33$ and $\theta_c = 33.97^\circ$). The chosen angle is also large enough to ensure that there is no chance of the probe making a double bounce within the diamond, which could interfere with the time-resolved measurements. This angle creates an evanescent wave with a penetration depth of 1.1 μm in air (1.3 μm in solution) as defined by Equation 2.2. This evanescent wave probes vibrations near the sample surface while probing very little of the bulk as the sample is three orders of magnitude larger than the penetration depth. The probe is P-polarized as the vibrations probed here are only excited in that polarization and disappear in S-polarized light.

$$d_p = \frac{\lambda}{2\pi(n_1)\sqrt{\sin^2(\theta) - \left(\frac{n_2}{n_1}\right)^2}} \quad \text{Equation 2.2}$$

After passing through the IRE, the probe is collimated and focused into the entrance slit of an Acton SP-2300 spectrograph (Princeton Instruments), where it is dispersed onto the top row of a dual-array 64-element detector (MCT-12-64, Infrared Associates), as shown in Figure. The

reference beam is directed into the bottom array of the detector. The signal is amplified using a boxcar amplifier (femtosecond pulse acquisition system boxcar integrator) and sent to a computer. The measured probe is normalized using the reference line to account for shot-by-shot differences and fluctuations.

The evanescent wave created upon total internal reflection of the IR beam at the diamond/air (or diamond/liquid) interface is a non-propagating electromagnetic wave that oscillates parallel to and decays in energy exponentially away from the interface. In order to be created, the ATR element must have a higher refractive index than the other side of the interface. If not, the light will propagate through the bordering medium rather than totally internally reflecting. The non-propagating nature of the wave does not allow for coupling to bulk propagating modes in the sample. The momenta of an evanescent wave produced during total internal reflection also allows for coupling to surface modes that have a higher wavevector than light travelling in free space. These conditions, along with the micrometer scale penetration depth mentioned previously, make ATR ideal for measuring surface modes.

The measured transient differential signal is calculated as a change in absorbance on the evanescent probe by^{2,27,28}:

$$\Delta A = -\log \left(\frac{I_0 - \left(\frac{n^{on} \kappa^{on} |t_{12}|^2}{n_1 \cos(\theta) \sqrt{n_1^2 \sin^2(\theta) - n_2^2}} \right) e^{\frac{-2\Delta Z}{dp}}}{I_0 - \left(\frac{n^{off} \kappa^{off} |t_{12}|^2}{n_1 \cos(\theta) \sqrt{n_1^2 \sin^2(\theta) - n_2^2}} \right) e^{\frac{-2\Delta Z}{dp}}} \right) \quad \text{Equation 2.3}$$

Here, n^{on} , κ^{on} , n^{off} , and κ^{off} represent the real and imaginary indices of refraction of the sample with and without photoexcitation of the pump (pump on and pump off shots). The ΔZ component highlights the dependence of the observed signal strength on the position of the sample relative to the crystal, with larger distances defining a smaller change in absorbance (Figure 2.7).

The change in absorption defined by Equation 2.3 changes in a complex way with the indices of refraction. In the case of a weakly absorbing sample, Equation 2.3 can be simplified to a purely absorptive change in κ defined by $(\kappa^{\text{on}} - \kappa^{\text{off}})$. However, the n-doped STO samples are not weak absorbers and the free carriers and plasma oscillations in the ground state can absorb the probe significantly, as can the librational continua of the electrolyte. By the Kramers-Kronig relation, changes in the imaginary part of the refractive index through κ^{on} also modifies the real part through n^{on} . Photoexcitation can modify n and κ over a large frequency region and thus, to truly calculate the absolute change in the absorptive cross-section the Kramers-Kronig relation must be incorporated into Equation 2.3 over this large region. This is not attempted in this work, and the sign of the signal is instead interpreted through the Fano lineshapes and changes observed there, as will be discussed later in Chapter 3.

The decay of the signal away from the IRE defined in Equation 2.3 should reflect the same exponential decay as the evanescent wave defined by the penetration depth (Equation 2.2). This is observed in Figure 2.7, which shows the signal strength for data measured here in ΔmOD as a function of z-distance from the IRE in μm . The signal is observed to decay exponentially away from the IRE with a decay rate corresponding to the penetration depth of the evanescent probe ($\sim 1.1 \mu\text{m}$). The distances given in Figure 2.7 are not absolute distances from the IRE, but rather relative distances between measurements with the maximum signal set as “zero” μm in distance. Absolute distances in this geometry of ATR have been calculated using white light interferometry²⁹, but that technique was not available to us in this work. The relative distances still allow for control of sample position between measurements, even without the knowledge of the absolute distance of the sample from the IRE.

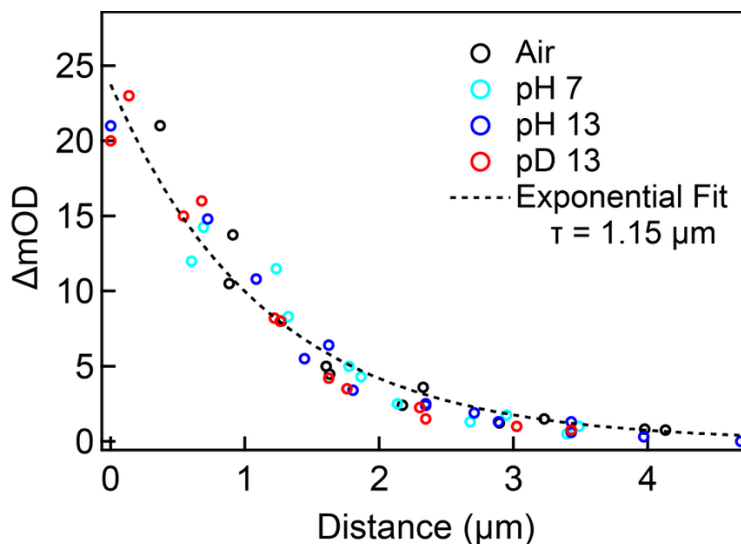


Figure 2.7: Exponential decay of the Oxyl's vibrational signature with z-distance from the ATR element. The signal strength decays with a rate equivalent to the penetration depth of the evanescent wave ($\sim 1.1 \mu\text{m}$).

The overall absorption of the sample will also be largest near the diamond due to the electronic continua in the semiconductor available in the same infrared region, which will absorb more of the probe intensity closer to the diamond. One must be careful about pushing the sample too close given the refractive index. STO has a relatively high refractive index of 2.4, almost the same of that of diamond at 2.38. As said previously, the ATR element must have a higher refractive index than the other material of the interface for creation of the evanescent wave. If the sample were to get too close to the crystal and eliminate all the air (or solution), the probe would begin to propagate into the sample and ATR would no longer occur.

Prior to data collection, the parallelism of the sample surface relative to the back face of the diamond ATR crystal must be checked. In order for the sample surface at the center of the diamond to be within the first penetration depth of the evanescent wave, the two surfaces must be parallel to within approximately 0.04° . The mounting process described previously is designed to get the sample close to this, and we can check how close using the back reflections of the pump. The pump beam will reflect off both the back of the diamond and the sample surface. To achieve

the needed parallelism, these two reflections must be nearly perfectly overlapped, with a slight offset expected due to the gap distance between the diamond and the sample. If the reflections are not overlapped, the tightness of the screws that fasten the front plate to the cell can be adjusted to tweak the position of the diamond relative to the sample, as allowed by the flexible rubber O-ring between the plate and the cell. In doing so, the reflections can be made to overlap, and a signal can be observed and then optimized. Figure 2.8 provides diagrams of the parallel and non-parallel alignments of the sample. If the sample is not parallel to the diamond, collected spectra and kinetics can be affected as the evanescent wave will be probing over different z-distances and thus different interfaces across the probe beam size. This can result in non-repeatable measurements that are an average over the different positions.

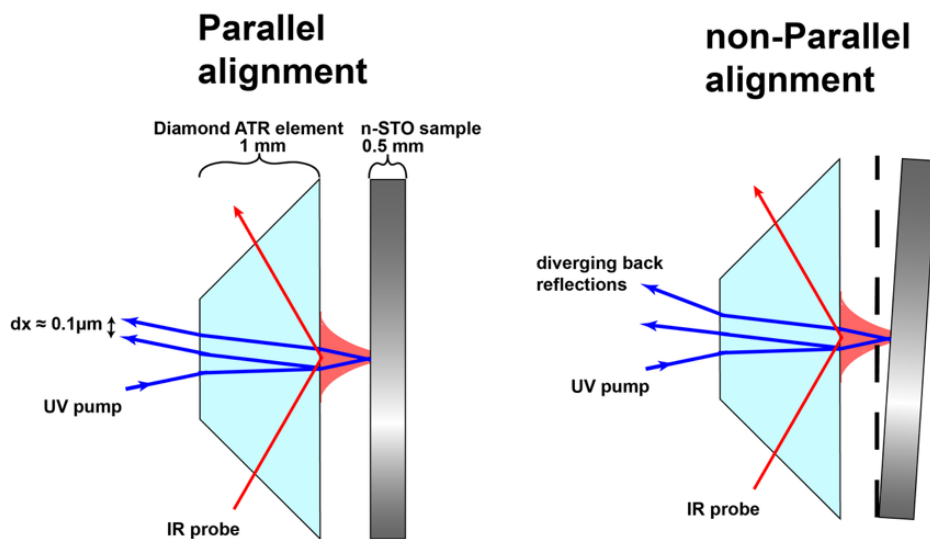


Figure 2.8: Parallel and non-parallel sample alignments for ultrafast ATR geometry. Back reflections of the UV pump, shown in blue, are used to determine sample alignment based on the divergence of the diamond and sample reflections. When the sample and diamond are parallel, the back reflections should emerge parallel with an offset determined by the difference in path length.

2.5 Electrochemical SrTiO₃/Aqueous Interface

When the n-doped STO sample is brought into contact with an aqueous solution, it naturally forms a Schottky barrier at the interface. A Schottky barrier is a potential energy junction formed when a semiconductor comes into contact with a material that contains an excess of charge carriers. Often that material is a metal, while here that is an aqueous solution. The non-semiconductor material involved must contain this large amount of charge carriers such that the fermi level does not change significantly when exchanging such carriers with the semiconductor. The barrier forms naturally when the chemical potential of electrons in the semiconductor equilibrates with the charged species in the solution. In doing so, the conduction band (CB) and valence band (VB) bend at the interface, creating an electric field over an area called the depletion region, which has a width W . In the absence of other redox species in the solution, it is the O₂/H₂O redox reaction that levels the chemical potential across the interface and the resulting ions both adsorbed on and collecting near the surface form what is called the Helmholtz layer. A diagram of this system is shown in Figure 2.9.

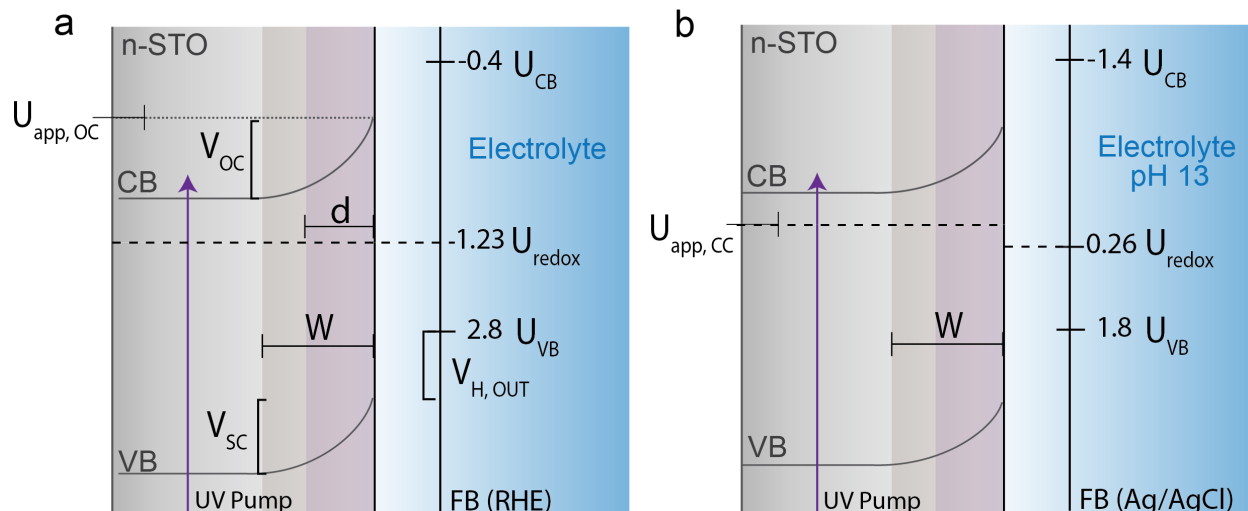


Figure 2.9: Diagram of the n-doped SrTiO₃ interface with aqueous electrolyte in (a) open circuit conditions on an RHE scale and in (b) closed circuit conditions on a Ag/AgCl scale. In (a), the open circuit potential of the conduction band under photoexcitation is shown by $U_{app, OC}$ as a dotted line. V_{SC} shows the voltage drop across the semiconductor while $V_{H, OUT}$ shows the voltage drop across the Helmholtz layer of electrolyte. The redox potential of water is shown as equal to the equilibrated chemical potential across the interface by the dotted line between the valence and conduction bands. In (b), $U_{app, CC}$ represents the applied voltage at the back of the electrode in a closed circuit geometry. U_{redox} here sits slightly below the Fermi level of the n-STO electrode, indicating a forward bias regime.

Upon photoexcitation with an above band-gap laser pulse, this built in electric field results in charge separation in the semiconductor wherein holes in the valence band are pushed toward the surface while excited electrons in the conduction band are shuttled to the back of the sample. Figure 2.9a shows an “open circuit” configuration (OC) for SrTiO₃, where a complete electrochemical circuit is not present. All chemical potentials in OC are shown on a reversible hydrogen electrode (RHE) scale. In vacuum conditions, the conduction band potential (U_{CB}) and valence band potential (U_{VB}) are -0.4 V and 2.8 V vs. RHE respectively. These are higher than at the edge of the STO sample as they are defined at the edge of the Helmholtz layer, depicted by the vertical line separating the light and darker blue of the electrolyte. The Helmholtz layer is defined at the surface by ions both adsorbed on the sample (inner Helmholtz layer) and in solution (outer Helmholtz layer) which screen the charge in the depletion region. Photoexcitation of sufficient fluence in OC conditions will counteract the built-in electric field, resulting in a flattening of the

valence and conduction bands. The potential at the rear of the electrode in OC conditions is given by $U_{app,OC}$ in Figure 2.9a.

When a complete electrochemical circuit is present, a potential can be applied to the back of the working electrode (sample). In this “closed circuit” configuration (CC), shown in Figure 2.9b, the bending of the bands is preserved under photoexcitation such that most of the photogenerated charge carriers are shuttled in their respective directions. This allows for OER to occur on the semiconductor surface and for electrons to travel to the counter electrode and perform hydrogen evolution (HER). In this scenario with the band bending preserved, far more holes will be shuttled to the surface when compared to the OC conditions, which will have a much larger amount of charge recombination once the bands flatten.

The initiation of OER in the semiconductor under UV excitation is dependent on the ability of the built-in electric field at the interface to separate charge. Thus, it is essential that the excitation occur within the region of this electric field, termed the depletion region (W). The depletion width is given by:

$$W = \sqrt{\frac{2\epsilon\epsilon_0}{e_0 N_d} \left| V_{SC} - \frac{k_B T}{e_0} \right|} \quad \text{Equation 2.4}$$

Here, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the vacuum permittivity, e_0 is the electronic charge, N_d is the doping density of the semiconductor, k_B is the Boltzmann constant, T is the temperature, and V_{SC} is the potential drop across the region of the semiconductor. For 0.1% Nb STO, $N_d = 8 \times 10^{18} \text{ cm}^{-3}$ and $V_{SC} = 0.85 \text{ V}$, yielding a depletion width $W \sim 25 \text{ nm}$. This width will decrease for higher doping concentrations of STO.

For effective charge separation to occur, the penetration depth (d) of the UV pump should be within this depletion region. Equation 2.5 approximates d as a function of the excitation wavelength λ and the imaginary part of the refractive index of the semiconductor κ . For the 266

nm pump and a 0.1% Nb STO sample, a penetration depth $d \sim 17$ nm is calculated, smaller than the depletion width. This will similarly decrease with doping density as the semiconductor will be more absorptive (higher κ).

$$d = \frac{\lambda}{4\pi k} \quad \text{Equation 2.5}$$

In order to examine processes occurring at the semiconductor/electrolyte interface, one must have an understanding of the electrical and optical properties of the material at said interface. Figure 2.10a shows the results of cyclic voltammetry (CV) measurements on 0.1% Nb STO in pH 13 electrolyte vs a Ag/AgCl reference electrode. CV measures the current through the STO sample while scanning the electric potential across the diode. The red curve shows the light-on measurement, where the STO sample is photoexcited by above band-gap UV pump with a fluence of 0.04 mJ/cm^2 , while the black curve shows the results in the dark (no UV pump). The light-on measurement shows current even at zero potential due to the efficient charge-separation in the depletion width under photoexcitation. Both light-on and dark curves show typical diode behavior where current is independent of potential until a certain voltage is reached, after which current flows essentially resistance free. For cathodic voltages more than -0.85 V , the electric field in the depletion layer that separates electron-hole pairs has decreased in width such that photocurrent no longer evolves. At anodic potentials, this width is at a maximum, and current is independent of potential.

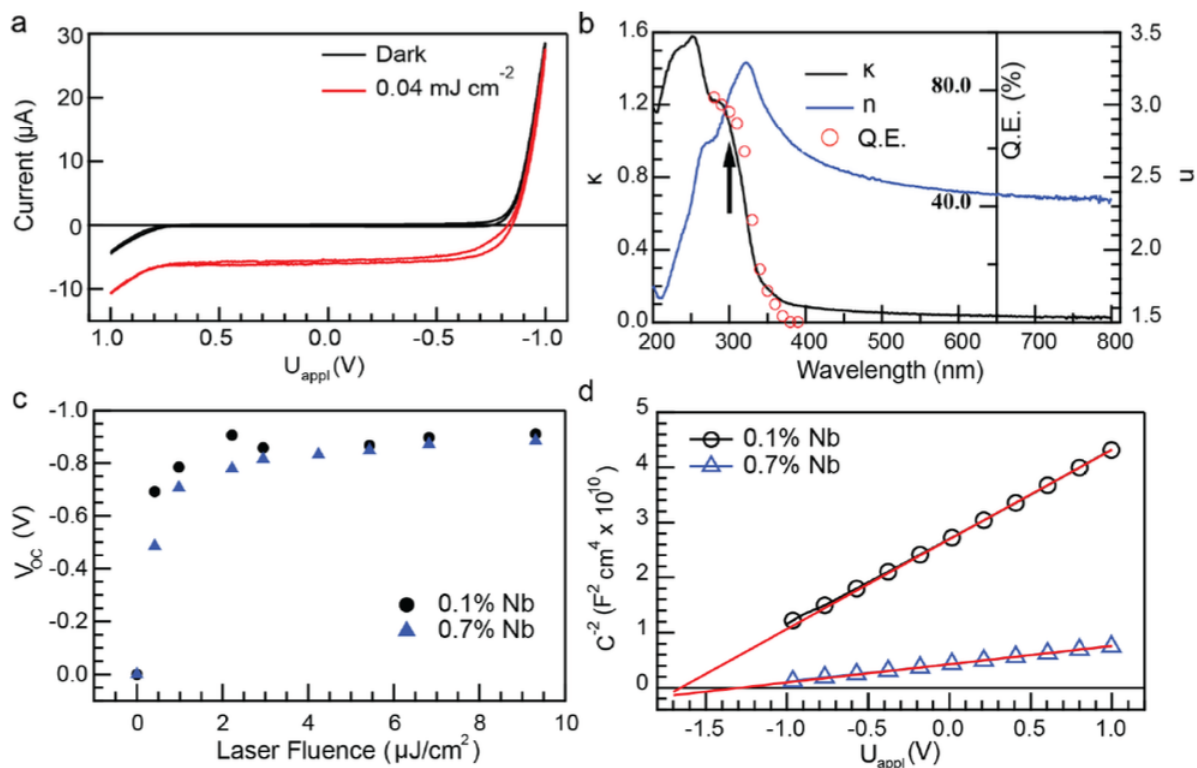


Figure 2.10: Photoelectrochemical response of n-STO at the pH 13 electrolyte interface. (a) current-voltammogram under dark and light (photoexcited) conditions for 0.1 % Nb STO. (b) Real (n) and imaginary (κ) indices of refraction and quantum efficiency for charge separation (red circles) for 0.1% Nb STO shown as a function of wavelength. (c) Open circuit photovoltage and (d) Mott-Schottky plots for 0.1% Nb and 0.7% Nb STO. Figure reproduced from reference 30. Copyright 2014 American Chemical Society.

The real (n) and imaginary (κ) parts of the refractive index are shown in Figure 2.10b as a function of wavelength for 0.1% NB STO. We see that κ , which represents light absorption in the sample, increases dramatically around 380 nm, which corresponds to the bandgap of STO (3.25 eV). Also increasing sharply at the same wavelengths is the quantum efficiency (QE), which represents the efficiency at which photons are converted to charge carriers in the material and closely follows κ . This is calculated as the ratio of photo-induced charge carriers, calculated from the amount of charge induced under photoexcitation, to the number of incident photons, as determined by the laser fluence and beam size. Quantum efficiencies for n-STO samples used in this study are calculated at >70%.

Open-circuit photo-voltage (V_{oc}) measurements for both 0.1% and 0.7% Nb STO in pH 13 conditions are given in Figure 2.10c as a function of UV pump fluence. We see that V_{oc} , which represents the voltage change across the sample in open circuit after photoexcitation, saturates at low pump fluences at -0.85 V. This indicates that even at low fluences, sufficient fluence has been applied to separate enough charge to completely flatten the valence and conduction bands, resulting in no further increase in charge separation with fluence.

Mott-Schottky plots for both n-STO samples are shown in Figure 2.10d. This analysis is a measure of total capacitance across both the semiconductor and the Helmholtz layer. Equation 2.6, as derived by de Gryse³¹, shows the Mott-Schottky equation to define the relationship between the total capacitance and the flatband potential (U_{FB}) of the semiconductor, which is the potential needed to flatten the valence and conduction bands. The capacitance is also dependent on the doping density of the material (N_d), the applied potential (U_{app}), and the capacitance of the Helmholtz layer (C_H). For transition metal oxides, one can apply 20 $\mu\text{F}/\text{cm}^2$ for C_H ³⁰ and from the linear fit in Figure 2.10d extract N_d from the slope and U_{FB} from the intercept. Here, in pH 13 UFB is equivalent to -0.5 V vs RHE.

$$\frac{1}{C^2} = \frac{1}{C_H^2} \left[1 + \frac{2C_H^2}{q\epsilon N_d} \left(U_{app} - U_{FB} - \frac{kT}{q} \right) \right] \quad \text{Equation 2.6}$$

The capacitance of the Helmholtz layer can be treated as a parallel plate capacitor, where one side is the charge on the electrode and the other arises from ions in the electrolyte. In the case of a metal oxide semiconductor, the Helmholtz layer can be divided into two parts, an Inner and outer layer. The inner Helmholtz layer is defined by ions adsorbed on the surface (OH^- , H^+) while the outer layer is derived from free counter ions in the solution (such as SO_4^{2-} , OH^-) along with oriented dipoles in the solution that screen the positive charge in the depletion region of the semiconductor³². While Equation 2.6 treats the Helmholtz layer as having a single capacitance,

these layers have capacitances C_{H-in} and C_{H-out} respectively, with corresponding voltage drops V_{H-in} and V_{H-out} ³³.

The pH of the solution can modify the inner and outer Helmholtz layer through deprotonation of surface adsorbed species at higher pH³⁴. To calculate the energetic quantities of the layers, we can consider the open circuit conditions for the n-STO/electrolyte interface under changing pH conditions. In OC, the floating potential at the back of the electrode will equilibrate with the redox potential of water (U_{redox}), where the voltage across the interface is calculated as that needed to achieve this equilibration by $U_{redox} - U_{FB}$. Both U_{redox} and U_{FB} change equivalently with pH by -59 mV/pH due to the proton transfer between the surface and the electrolyte³⁴, such that the potential drop across the interface remains constant with pH. This potential drop is calculated as the sum of the potentials across the interface, i.e. that of the semiconductor (V_{SC}), the inner Helmholtz layer (V_{H-in}) and the outer Helmholtz layer (V_{H-out}) such that:

$$U_{redox} - U_{FB} = V_{SC} + V_{H-in} + V_{H-out} \quad \text{Equation 2.7}$$

The contributions of each layer of the interface will change with the protonation of the surface. The open-circuit photovoltage (V_{OC}) measurements discussed previously with Figure 2.10c are a measure of the potential drop across the semiconductor and the inner Helmholtz layer such that $V_{OC} = V_{SC} + V_{H-in}$. Since the potential across the whole interface is unchanged with pH, any change to $V_{SC} + V_{H-in}$ will be compensated by a change in V_{H-out} . So, by measuring pH changes in V_{OC} one can calculate the pH dependent values of V_{H-out} using Equation 2.6 along with the values of U_{Redox} (1.23 V vs RHE) and U_{FB} (calculated from the Mott-Schottky analysis).

2.6 Pump exposure and sample degradation

An important aspect of a pump-probe spectroscopy that involves averaging over many pulses is that the sample must always return to its initial state before photoexcitation prior to each subsequent pulse. If this is not the case, then the reaction is not being triggered at a distinct time point and tracked from that point on, and any kinetic measurements taken will be contaminated by other effects. One must be concerned when taking such measurements about whether there is any lasting damage to the sample surface after repeated exposure to the high energy pump. In fact, photo-induced catalytic OER is known to restructure the catalytic surface, caused by a number of possible reasons such as side reactions occurring on the same surface, and can result in a decrease in catalytic activity. Such changes do occur in the STO system under pump exposure. In a CC configuration, changes in the reflectivity are observed to occur on a minute timescale. However, in an OC configuration, no significant restructuring of the surface is observed, likely due to the increased electron-hole recombination reducing the extent of reactions occurring on the surface³⁵.

A common method to avoid such restructuring issues is to apply a scanning methodology wherein the sample is moved a predetermined distance over time such that each sample spot is only probed for a small amount of time. This can be done by moving continuously or in steps, the amount of time each sample spot is exposed to the pump is determined such that no degradation will occur and affect measurements. While this can often be implemented without too much difficulty in a standard reflection or transmission spectroscopy, the nature of ATR experiments makes this extremely difficult, if not impossible. For one, since the size of the ATR element is so small and both the pump and probe beams need to enter very precisely, the sample would have to be moved without moving any other part of the cell. So rather than attaching the cell to a moving stage, one would have to create movement of the sample within the cell while also remaining

water-tight. Second, due to the decaying nature of the evanescent wave, the sample must maintain an extremely precise distance from the ATR element while moving. This means that the entirety of the sample area scanned across must be perfectly parallel to the crystal, and that neither the parallelism nor the absolute sample distance from the crystal can change during experimentation. If this is not achieved, the signal strength and interfacial conditions could change significantly as the sample moves and alter the measured kinetics in unknown ways.

Given the challenges involved in applying such a scanning methodology, the ATR technique used here will focus on measurements under OC conditions where sample reconfiguration is not a concern. In the instance where CC conditions are required using the current electrochemical cell, one would have to consider the amount of pump exposure time that is acceptable for a given sample spot. Given that experiments performed here take significant time and averaging to fully complete, such CC conditions would impose many further difficulties and are not explored in this work.

Chapter 3: The Oxyl Radical's Vibrational Signature and Interfacial Nature

3.1 Measurement of the Oxyl in n-STO

Attenuated total reflectance (ATR) spectroscopy has been used to detect a vibrational mode associated with the presence of a terminal oxyl ($\text{Ti-O}^{\bullet-}$) on n-STO following UV photoexcitation of the sample surface. The signature is assigned to the subsurface Ti-O bond directly below the terminal oxyl and is centered around 800 cm^{-1} . When the hole traps on a surface bound water species, the subsurface lattice is distorted, resulting in a new Ti-O subsurface infrared mode as shown in Figure 3.1².

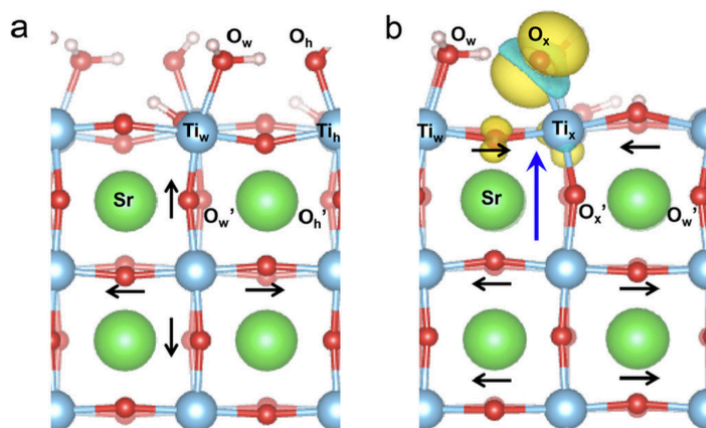


Figure 3.1: Subsurface vibrational modes in SrTiO_3 . (a) Ground state breathing modes (black) in STO beneath hydrated surface. (b) STO surface with oxyl formed on a terminal oxygen species. The subsurface modes are distorted compared to the ground state, and the associated subsurface vibration of the Ti-O bond is shown in blue. Figure adapted from reference 2. Copyright 2016 nature Springer Ltd.

It is important to characterize the ground state response of the sample in the same frequency regime to understand the nature of the excited state signal. Unpolarized reflection spectra of various Nb-dopings of STO are shown in Figure 3.2a. Using a Kramers-Kronig analysis, the frequencies of a transverse optical (TO) and a longitudinal optical (LO) phonon can be extracted

as 535 cm^{-1} and 795 cm^{-1} , as previously reported in literature³⁶. Increasing doping density changes the reflectance spectra as the LO phonon couples to the dopant plasma density. Reflectance spectra for 0.1% Nb STO are given in S and P polarized light in Figure 3.2b, showing no dependence on polarization.

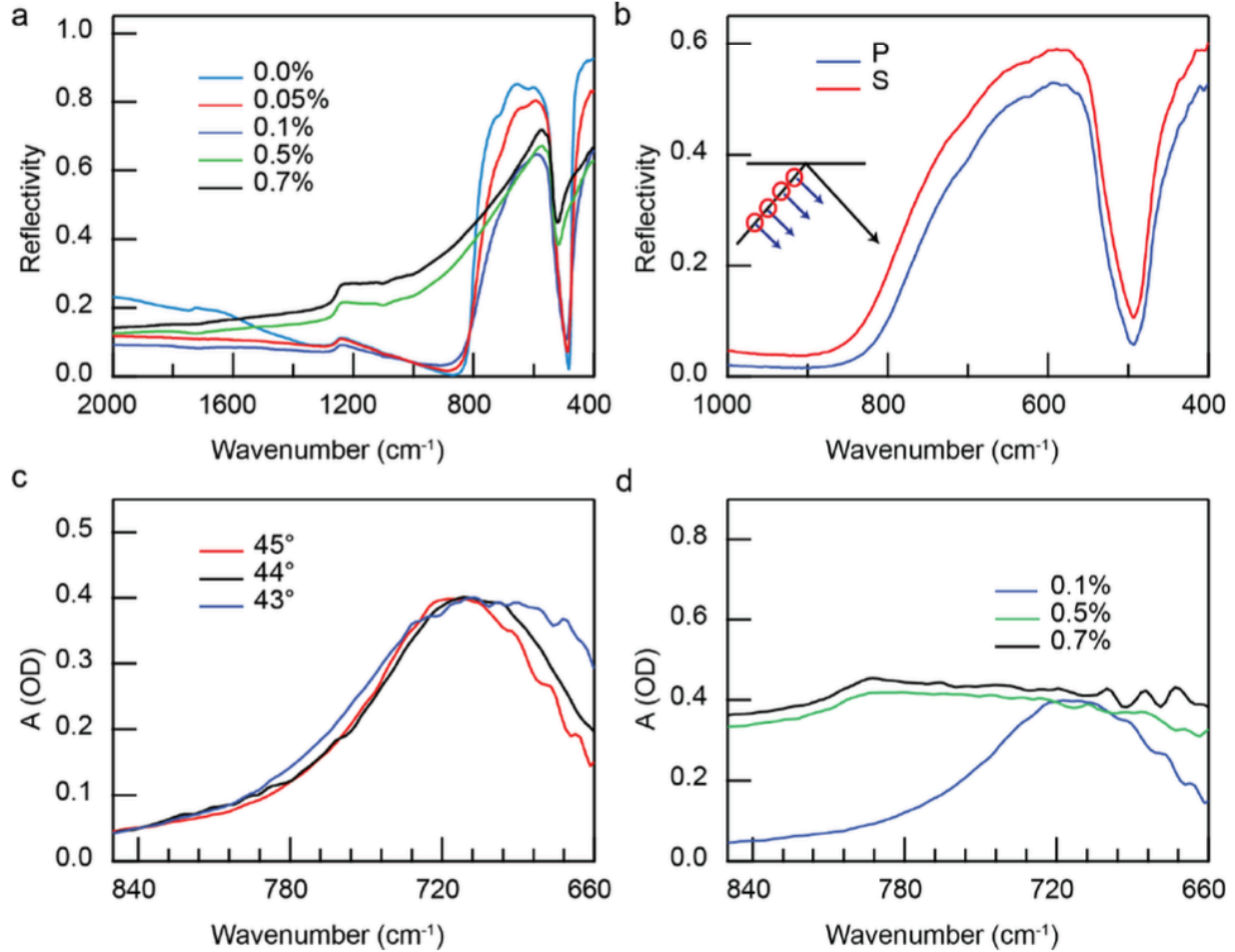


Figure 3.2: Infrared reflectance of SrTiO₃. (a) Reflectance spectra as a function of Nb doping. (b) Polarization reflectance measurements of 0.1% Nb STO in air. The cartoon inset shows the S and P polarized light vectors in the reflectance geometry, with the red circles representing vectors perpendicular to the plane of incidence. (c) P-polarized ATR measurements of 0.1% Nb STO as a function of incidence angle. (d) P-polarized ATR measurements as a function of Nb doping of STO. Figure adapted from the supporting information of reference 2². Copyright 2016 Nature Springer Ltd.

Ground state ATR spectra in air for n-STO are given in Figure 3.2c as a function of incident angle on 0.1% Nb STO and in Figure 3.2d as a function of doping density. The peak observed in 0.1% Nb STO has been previously assigned to a surface phonon polariton³⁷. This is supported by its dependence on incident angle, polarization dependence (only appears in P polarized light), and broadening with increased dopant density shown in Figure 3.2d, likely due to coupling to the dopant plasma density.

Figure 3.3 shows the spectrum of the oxyl mode at an air (black) and pH 13 (blue) interface with 0.7% Nb STO. Spectra are shown for both P and S-polarization of the infrared probe, where the signal is observed to disappear under S-polarization. The peak of the spectra appears between 790 cm^{-1} and 805 cm^{-1} , close to the frequency of the LO phonon mode observed in the ground state³⁶. This infrared region is also known for Ti-O vibrational stretches. Given that in the ground state ATR spectra only the surface polariton appears closer to 700 cm^{-1} , and that the LO phonon near 800 cm^{-1} is not polarization dependent, the appearance of the mode in solely P-polarized light identifies it as a new transient vibrational species with a dipole perpendicular to the sample plane. The STO crystal is isotropic and thus the crystal orientation has no effect on the measurement.

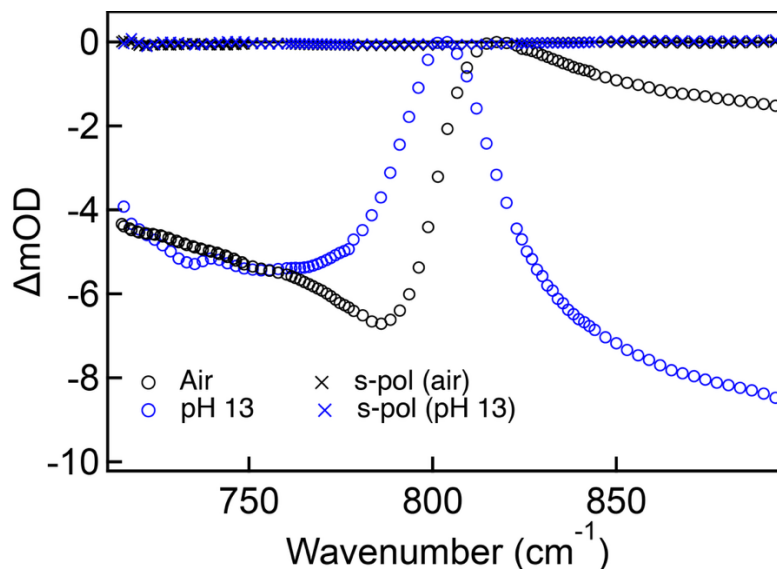


Figure 3.3: ATR spectra of the oxyl's vibrational mode at an air (black) and pH 13 (blue) interface with 0.7% Nb STO. The circles show the spectra for P-polarized infrared light, while the x's show the spectra for S-polarized light where the signal disappears. Any background has been subtracted from the spectra.

It is necessary to properly attribute the new mode to a hole-trapped surface species. First, the mode only appears under photoexcitation of samples that have a good affinity for charge separation, that is n-doped samples. No signal is observed in undoped or p-doped samples. Second, the mode is relatively long-lived, with lifetimes in the ns regime, eliminating the possibility of a highly excited surface Ti-O mode of the ground state, which would decay more rapidly. Figure 3.4 shows the lifetime of the signal as a function of methanol concentration in water. Methanol is a hole-scavenger and will accept a hole more readily than water. That the transient signal decays more rapidly with the introduction of methanol indicates a hole-trapped species. Finally, the ATR signal was correlated to O₂ evolution, where the measured population was observed to increase as the current for O₂ evolution does with excitation fluence².

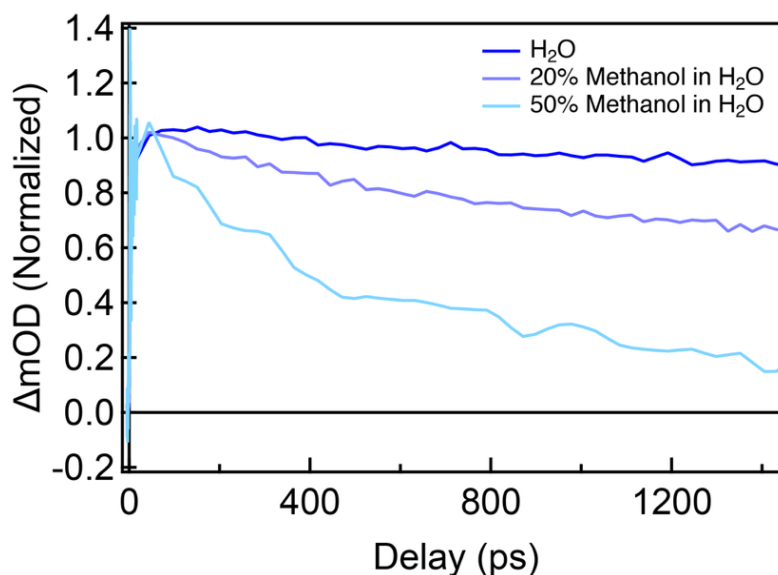


Figure 3.4: Decay of Oxyl's vibrational signal at the 0.7% Nb STO/liquid interface. The signal is stable in water on the ~1.5 ns timescale, but decays significantly faster with the introduction of methanol, a hole scavenger.

To corroborate the experimental evidence of the oxyl's subsurface vibrational mode, theory is required to make the particular assignment for the vibrational mode. Theoretical DFT calculations examined the infrared activity of both a ground state configuration and an oxyl configuration of an STO slab². In the oxyl configuration, a hole was placed on a terminal surface oxygen species. It was found that the significant difference in infrared activity between the two configurations occurred at 846 cm⁻¹, where the subsurface oxygen beneath the oxyl (see Ox' in Figure 3.1b) decoupled from the other subsurface oxygen motions (Ow' and Oh' in Figure 3.1a). The result is the assignment of the new infrared activity observed experimentally to the Ti-O subsurface vibration for the following reasons: (1) it appears at a frequency ~10 cm⁻¹ above the bulk LO phonon (835 cm⁻¹ in the theory); (2) it is associated with the hole-trapped site of the oxyl radical; (3) it is associated with a new absorption cross-section not observed in the ground state; (4) the frequency of the mode does not involve a proton (H/D exchange does not change the frequency of the mode, discussed more later); and (5) the infrared activity comes from the

subsurface layer with motion perpendicular to the sample plane (p-polarized) and can readily couple to water librations (discussed more later).

3.2 Modification of Continua Density of States and The Fano Resonance

The photoinduced vibrational lineshape observed at the n-STO surface is observed to change with interface when moving from air to pH 13 in Figure 3.3. In fact, the surface mode is sensitive to both sides of the interface, and the observed line shape is altered by moving from air to electrolyte, modulating that electrolyte (H/D exchange), and modulating the doping density of the semiconductor. Given this sensitivity, and the asymmetry of the observed lineshapes in Figure 3.3, it becomes relevant to introduce the Fano lineshape, or Fano resonance. A Fano resonance occurs in a vibrational spectroscopy when a narrow vibrational mode couples to a broad continuum that is excited in the same infrared region²¹. In the case of the semiconductor/aqueous interface, this continuum can be electronic continua in the semiconductor from dopant plasma and free carrier excitations³⁸, as well as librational continua in the liquid. Figure 3.5 depicts a diagram of the relevant vibrational mode (Oxyl) and continua (semiconductor, aqueous) present in the system defined here.

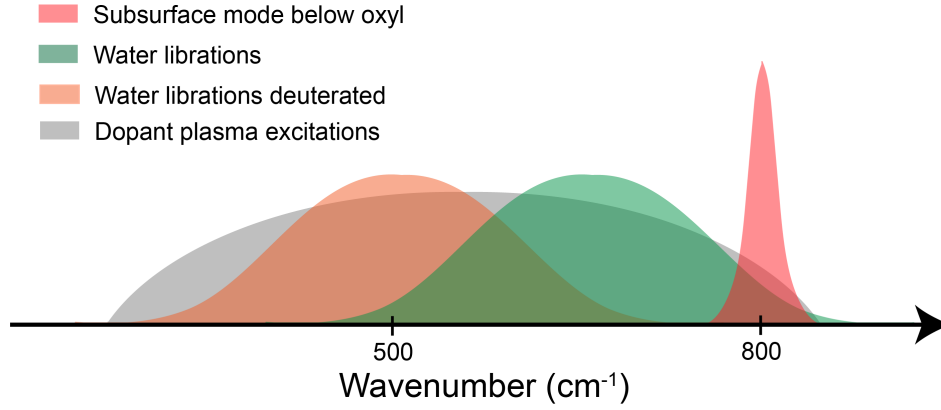


Figure 3.5: Diagram of relevant mode and continua excitations that contribute to the Fano resonance observed at the n-STO interface. The semiconductor and electrolyte continua are broad and overlapping in frequency with the narrow vibrational mode of the Oxl.

The Fano lineshape is defined by Equation 3.1. On the left side of the equation, ψ represents the wave function of the vibration coupled to the mode. As such, $|\langle \Psi | T | i \rangle|^2$ is defined as the square of the transition dipole moment, where T is the dipole operator and i is some initial state, and represents the intensity measured by the spectroscopy for the coupled vibrational mode²¹.

$$|\langle \Psi | T | i \rangle|^2 = \frac{A \left(\frac{2(\omega - \omega_0)}{\Gamma} + q \right)^2}{1 + \left(\frac{2(\omega - \omega_0)}{\Gamma} \right)^2} + Y_0 \quad \text{Equation 3.1}$$

On the right side of the equation, we have a function of frequency ω with five relevant variables: A , ω_0 , q , Γ , and Y_0 . ω_0 is the resonant frequency of coupled vibrational mode, and as such will be determined by both the frequency of the uncoupled mode and the nature of the coupling to the continua involved. Γ represents the spectral width of the coupled mode and is defined as the square of the coupling constant of the mode to the continuum. A in Equation 3.1 is a measure of intensity defined as $|\langle \psi | T | i \rangle|^2$. ψ here represents the wave function of the continuum, and therefore A defines the intensity of the continuum light excitations that are coupled to the mode. Y_0 is an additive background independent of frequency that represents the same intensity as A , but for the continuum excitations that are not coupled with the mode.

When a discrete state is spectrally overlapped with a continuum, the spectrum is generally asymmetric. The final parameter in the Fano equation, q , defines this asymmetry. Mathematically, q is the ratio of two different types of light excitations defined in Equation 3.2. The numerator, $|\langle\phi|T|i\rangle|^2$, represents the excitations of the bare but dielectrically screened mode. Meanwhile, the denominator is defined as the coupled continuum light excitations, $|\langle\psi|T|i\rangle|^2$, multiplied by a factor of Γ , the spectral width, thus representing the number of continuum excitations within the spectral width that contribute to the resonance.

$$q^2 = \frac{2|\langle\phi|T|i\rangle|^2}{\pi|\langle\psi|T|i\rangle|^2\Gamma} \quad \text{Equation 3.2}$$

When no continua are present, a discrete mode is often seen as a symmetric, Lorentzian lineshape. Indeed, if we examine Equation 3.2 in the limit where the continuum excitations go to zero, q goes to infinity and the Fano equation produces a Lorentzian shape. The other case of symmetry for the Fano equation is the limit where the continuum excitations are much larger relative to the mode excitations. In that scenario, q approaches 0 and the Fano equation produces a symmetric Lorentzian dip centered at the resonant frequency. Figure 3.6 depicts Fano lineshapes for several different values of q where the asymmetry is observed to increase with increasing magnitude of q . The y-axis, which represents a spectral intensity, along with the values of q are shown as negative for better comparison to the data presented in this work.

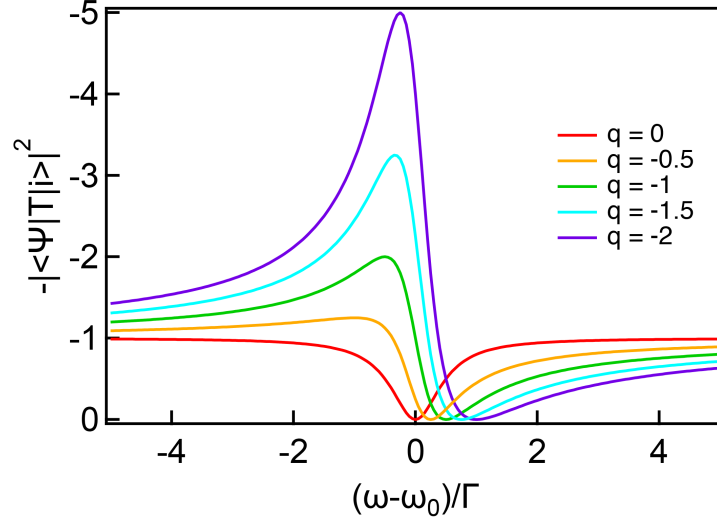


Figure 3.6: Family of Fano lineshapes with different values of the asymmetry constant q . For each q , the vibrational cross section is plotted as a function of the difference in frequency from the resonant frequency divided by the spectral width Γ . Negative q values are chosen as they better reflect the actual data collected. The coupled continuum excitations (A parameter) are normalized.

The continuum excitations density of states (DOS) can be modulated significantly by the environment. The electronic continuum in the semiconductor can be varied by doping percentage³⁸. Since the STO samples used here are n-doped with Nb, increasing the level of doping will increase the electronic DOS, thus lowering the value of q and the asymmetry. Results of spectral fitting with Equation 3.1 for different Nb doping densities of STO at air and electrolyte interfaces given in Table 3.1 summarize the effects of modifying the doping density². The resulting q -values are observed to decrease with increasing Nb doping density as anticipated.

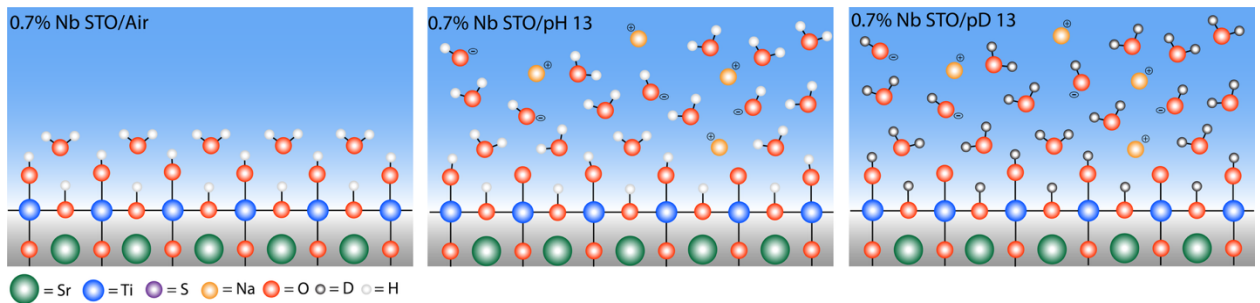


Figure 3.7: 0.7% Nb STO interfaces with air, pH 13, and pD 13. In air, the surface is largely hydroxylated with at least one layer of water bound to the surface¹⁷. The surface remains hydroxylated as electrolyte is introduced through pH and pD conditions.

Similarly, we can modify the air/electrolyte interface to change the observed asymmetry. Figure 3.7 shows molecular diagrams of the 0.7% Nb STO interface with three different conditions: air, pH 13, and pD 13. Going from air to aqueous conditions adds a second continuum in the region of interest, that of the water librations shown in Figure 3.5. The addition of a second continuum lowers the value of q drastically and results in a much more symmetric spectral shape. Examples of spectra for the 0.7% Nb STO interface with air, pD 13, and pH 13 are given in Figure 3.8, highlighting the effect of adding the second continuum. The most asymmetric spectrum is seen in air, where a single continuum is present. In pH conditions, with the added water librational continua, the spectrum is nearly symmetric, and pD conditions lay in between as the deuterated librational continua is farther from the resonance (see Figure 3.5). The fit parameters are for each spectrum are given in Table 3.2, confirming the spectral changes are reflected in the changing q parameters.

Condition	Doping	ω_0 (cm^{-1})	q	A (ΔmOD)	Γ (cm^{-1})	Y_0 (ΔmOD)	S ($\text{cm}^{-1} \Delta\text{mOD}$)
Air	0.7% Nb	807.7	-1.62	-1.58	29.6	1.25	120.41
	0.5% Nb	802.3	-2.29	-0.35	31.0	0.24	72.97
	0.05% Nb	797.6	-1.93	0.16	53.2	0.38	37.30
Electrolyte (1 M NaOH)	0.7% Nb	809.7	-0.16	-5.34	34.5	5.60	281.60
	0.5% Nb	808.9	-0.07	-3.97	31.5	4.50	195.68
	0.05% Nb	797.9	-1.98	0.09	44.5	0.32	18.80

Table 3.1: Equilibrated Fano parameters for different Nb doping densities of SrTiO_3 at air and electrolyte interfaces. The integrated spectral weight (S) of the equilibrated spectra is also included. Table adapted from the supporting information of reference 2. Copyright 2016 Nature Springer Ltd.

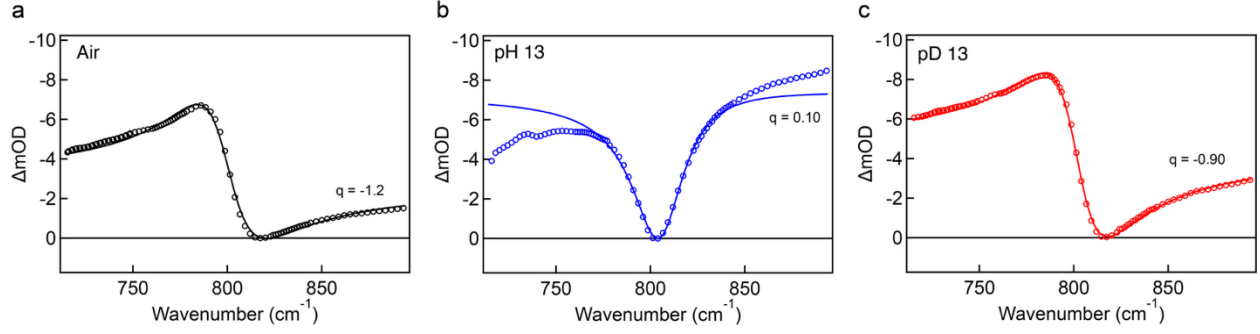


Figure 3.8: Spectra taken at the 0.7% Nb STO interface with air (a), pH 13 (b) and pD 13 (c). The corresponding Fano fits are provided by the solid lines. Any frequency independent background (Fano Y_0) has been subtracted out.

Condition	ω_0 (cm^{-1})	q	A (ΔmOD)	Γ (cm^{-1})	Y_0 (ΔmOD)	S ($\text{cm}^{-1} \Delta\text{mOD}$)
Air	799.5	-1.17	-5.72	36.2	2.64	815.2
pH 13	805.6	0.10	-7.28	33.4	10.06	942.2
pD 13	802.0	-0.90	-6.29	34.0	3.54	609.5

Table 3.2: Equilibrated Fano parameters for different interfaces with 0.7% Nb STO corresponding to the spectra shown in Figure 3.7.

The negative sign of q and changes in the magnitude across different conditions can be interpreted through the contributions of the electronic and librational continua in terms of the wave functions and matrix elements involved. The matrix elements that define q can be written in a form using the wave function of the bare vibration with no continua present, φ , and the combined wave function of both continua, ψ , such that^{21,39}:

$$q = \frac{\langle \varphi | T | i \rangle}{\pi(V_E + W_E) \langle \psi_E | T | i \rangle} + \frac{\int \frac{dE' (V_{E'} + W_{E'}) \langle \psi_{E'} | T | i \rangle}{E - E'}}{\pi(V_E + W_E) \langle \psi_E | T | i \rangle} \quad \text{Equation 3.3}$$

Here, V_E and W_E represent the coupling constants of the vibration to the electronic and librational continua, which contribute to the overall spectral width Γ . E is the energy corresponding to the resonant frequency ω_0 , while E' is the energy that spans through both continua and corresponds to the frequency axis of the spectrum ω . Thus, the first term results from the phases of the involved wave functions, while the second term represents the screening of the bare vibration by the

continua. This screening term is positive whenever the continua DOS peaks below the resonant frequency, as is the case here for both the electronic and librational continua. As the DOS of the continua that crosses E increases, this term increases and becomes more positive.

Given the mostly negative values of q observed here (Tables 3.1 and 3.2), the first term must therefore be dominant and negative. It follows that as the DOS of the continua increases, the magnitude of the first term decreases as the continua are represented in the denominator, while the contributions of the second, screening term simultaneously increases. This explains the drop in the magnitude of q observed with increased Nb doping (increased electronic continuum contributions), and the drop when moving from air (larger than 1) to solution (near zero) with the addition of the librational continuum. These librational contributions would also decrease with H/D exchange in the electrolyte, as seen with the increase in the magnitude of q from pH to pD conditions. These results are summarized in Tables 3.1 and 3.2. If one increased the continua DOS enough that the second, screening term became larger than the first term, q could become positive. This is observed in some pH conditions shown in this work and is dependent on the sample position, as will be shown later in Chapter 5.

Along with modifying the value of q, the addition of a second continuum also leads to a large, frequency independent background superimposed on the Fano lineshape. In this case, Y_0 is given by^{21,39}:

$$\sqrt{V_E^2 + W_E^2} * |\langle \psi_E | T | i \rangle|^2 \quad \text{Equation 3.4}$$

While in the case of a single continuum Y_0 is a background from uncoupled continuum excitations, for the case of two continua in Equation 3.4, the background arises from coupled continua excitations that are not resonant with the mode. For the case of 0.7% Nb STO in electrolyte conditions, a large, positive Y_0 results from the fits compared to air as anticipated (Table 3.2). This

background has been subtracted from the spectra given in Figure 3.7 for better comparison to the Fano lineshapes given in Figure 3.6 but will be reflected in data taken later in this work where spectra in electrolyte conditions will appear as Lorentzian peaks rather than the dips predicted by the Fano equation without a background.

The signal amplitude, given by the coupled continuum excitations A , is negative for the highly doped STO samples in Table 3.1 and positive in the 0.1% Nb case. This sign change is related to the nature of the measured differential signal in the ATR geometry, discussed previously in more detail in Chapter 2.4. One can explore another set of fits where A is positive for all conditions, which results in an interpretation where $q \rightarrow \infty$ for the Lorentzian dips in highly doped samples. This result is not matched by the physical conditions of having multiple continua present. It also results in large Y_0 backgrounds being added to the fits in air, where only a single continuum is present.

3.3 Marcus Theory and Solvent Reorganization Energy

Given the changes in the vibrational lineshape with the electrolyte interface and the goal of resolving the growth kinetics of the vibrational signature, it becomes relevant to introduce Marcus theory of electron transfer. Marcus theory is used to define the rates of electron transfer reactions where no bond formation or breaking occurs^{22,40}. Instead, the theory uses the reorganization of solvent to define the Gibbs free energy of activation ($\Delta G^\ddagger$) based on Equation 3.3, where ΔG° is the Gibbs free energy of the redox reaction and λ is the reorganizational energy of the solvent.

$$\Delta G^\ddagger = \left(\frac{\lambda + \Delta G^\circ}{4\lambda} \right)^2 \quad \text{Equation 3.3}$$

This reorganizational energy can be divided into two parts: an “inner” reorganizational energy (λ_{in}) corresponding to the ligands immediately surrounding an electron transfer site, and an “outer” reorganizational energy (λ_{out}) corresponding to the free solvent outside of the inner sphere. These two energies sum to the overall reorganizational energy of the solvent λ . A cartoon diagram of these spheres is shown in Figure 3.9 for an arbitrary electron transfer from a negative to a positive state in a water environment.

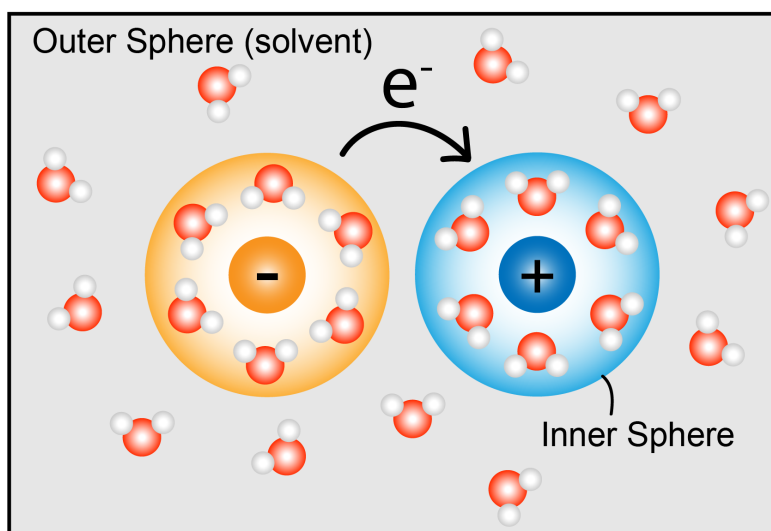


Figure 3.9: Cartoon of Marcus picture of electron transfer in solvent environment. The large blue and orange circles represent the inner sphere around the transfer site where bound ligands are involved. The outer sphere is represented by the free solvent around the inner spheres, where molecular dipoles can reorient in response to an electron transfer.

The outer sphere reorganizational energy reflects changes in the polarization of free solvent molecules as a result of the electron transfer²². It is defined in Equation 3.4 by the radii of the two reactants and the dielectric properties of the solvent where:

$$\lambda_{out} = \frac{(\Delta e)^2}{2} \left(\frac{1}{a_1} + \frac{1}{a_2} + \frac{1}{R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad \text{Equation 3.4}$$

Here, a_1 and a_2 represent the radii of the two reactants, R is the distance between the two, Δe is the charge transferred in the reaction, ϵ_{op} is the optical dielectric constant of the solvent, and ϵ_s is the static dielectric constant of the solvent. One can see from Equation 3.4 that the size of the

species involved and the distance between them has a large effect on the magnitude of λ_{out} , with larger distances reducing the reorganization energy. Also important is the relationship between the static and optical dielectric constants. If ϵ_s is much greater than ϵ_{op} , the outer reorganization energy will be larger. In polar solvents like water, ϵ_s is often quite large (78-80 in water^{41,42}), resulting in a larger λ_{out} . If ϵ_s is on the same order of magnitude as ϵ_{op} , λ_{out} will be much reduced.

The inner sphere reorganization energy is related to changes in bond lengths and angles of the reactants and molecules or ligands directly bound to the transfer site²². This can be expressed using a harmonic oscillator approximation as:

$$\lambda_{in} = \frac{1}{2} \sum_i k_i (\Delta x_i)^2 \quad \text{Equation 3.5}$$

Where k_i represents the normal mode force constants and Δx_i represents the difference in bond lengths between the initial and final states of the redox center.

Whether the total reorganization energy will be dominated by λ_{out} or λ_{in} will be dependent on the system. Figure 3.10 depicts specific systems in both bulk aqueous conditions (Figure 3.10a) and at interfaces (Figure 3.10c) where these energies have been studied, along with the system described here (3.10b). In aqueous conditions, the outer reorganization energy is expected to be quite large, as was shown in hexaquo metal cation complexes undergoing photoemission of electrons shown in Figure 3.10a where the inner and outer reorganization energies were calculated at around 1 eV each²³. At an interface, the outer reorganization energy can be much reduced. Studies of ITO materials undergoing excited state electron injection from surface bound RuP complexes, depicted in Figure 3.10c, found that by varying the electron transfer length, the outer reorganization energy was modified significantly, with contributions to the outer reorganization becoming negligible at transfer distances below 4 Angstroms^{24,43}. This work will interpret the formation of the titanium oxyl, a hole-polaron state on a terminal oxygen on the semiconductor

surface shown in Figure 3.10b, in terms of the contributions of the inner and outer reorganization energies. This will be done by systematically introducing the availability of free solvent (outer sphere) to reorient to the polaron formation based on the interfaces with 0.7% Nb STO shown in Figure 3.7, moving from air to electrolyte (pH 13), and deuterating that electrolyte to modify the coupling of the observed mode through the Fano resonance.

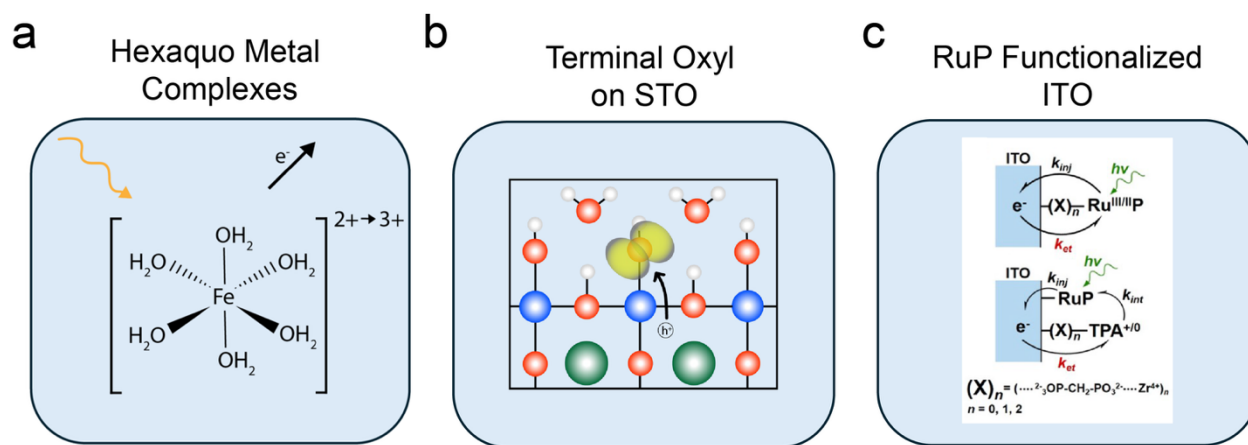


Figure 3.10: Bulk and interfacial systems of electron transfer reactions. (a) Hexaquo metal cation complexes undergoing photoemission of electrons in bulk aqueous conditions. (b) Terminal oxyl formation of SrTiO₃ surface. (c) Excited state electron injection between ITO and surface bound RuP complexes. (X)_n represents a molecular spacer to change the electron transfer distance from the interface. Part c was adapted from reference 24²⁴. Copyright American Chemical Society 2019.

The formation energetics of the titanium oxyl on TiO₂ have been previously studied by theory¹⁵. Figure 3.11 shows the Marcus diagrams of photoinduced electron transfer for the two-energy curve picture (Figure 3.11a) and for an extended picture including the valence band states of a semiconductor (Figure 3.11b). In the two-curve picture, the system is initially excited from the ground, reduced state (a) to an excited, oxidized state surface (c), represented by the purple vertical arrow. At this point, the oxidized state must reorganize with some energy, λ_o , to the minimum energy of the curve, shown by the dashed black arrow. The difference between the minima in the reduced and oxidized states, shown by the blue arrow, represents the overall energy

change of the electron transfer reaction. In this linear-response picture, the reorganization of the oxidized and reduced states requires the same energy such that $\lambda_O = \lambda_R$, shown in the energy levels on the far right of the figure.

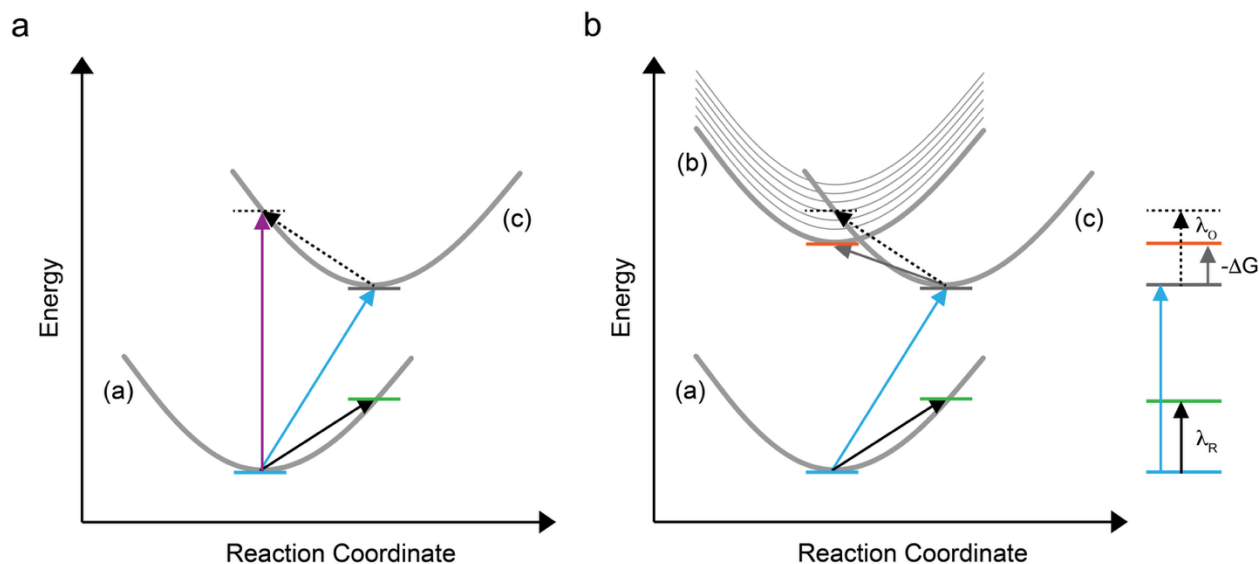


Figure 3.11: Marcus potential energy diagrams for the two curve (a) and semiconductor (b) pictures. In a, the purple arrow represents photoexcitation of the system from the reduced state (a) to the oxidized state (c). The black solid and dashed lines show the reorganization energies of the reduced (λ_R) and oxidized (λ_O) states respectively. The blue arrow shows the energy change of the reaction. In b, the valence band states are included such that state (b) represents the oxidized state of the system before reorganization has occurred. Here, a delocalized hole can thermalize to the valence band edge, resulting in a lowering of the reorganization energy to the free energy of the reaction (ΔG) shown by the gray arrow. The energy level diagram on the right depicts the different reorganization energies.

In the expanded picture for the semiconductor shown in Figure 3.11b, the inclusion of the valence band states in the Marcus picture can modify the reorganization of the oxidized state. If we consider the system examined by J. Cheng and M. Sprik of a hole trapping event on a surface Ti-OH^- group¹⁵, we have the reduced surface (a) with an associated Ti-OH^- with an energy that exists within the valence band, the oxidized surface with a delocalized valence band hole formed upon photoexcitation (b), and the oxidized surface once the system reorganizes to a hole trapping on the Ti-OH^- to form Ti-OH^* (c). If the hole transfer occurs directly from the Ti-OH^- , λ_O is the same as in the two curve picture in Figure 3.11a, and the reorganization of the oxidized and reduced

states remains symmetric. However, since the surface $\text{Ti-OH}^\cdot$ exists at an energy level within the valence band, the hole can thermalize to the valence band edge (energy level in orange in Figure 3.11b). In this case, λ_{O} is reduced compared to λ_{R} , resulting in a non-linear response regime. Here, reorganization energy for the oxidized state is shown to be equal to minus the free energy of hole-trapping $(-\Delta G)^{15}$. Thus, by Equation 3.3, the activation free energy is zero and the hole-trapping event is barrier-less.

While the hole-trapping event from the semiconductor to the surface species is thus predicted to be barrier-less, the question of what predominates the reorganization energy λ_{O} still remains. While theory has suggested in calculations of free energies of this reaction on TiO_2 and STO surfaces that the inner reorganization dominates^{13,15}, experimental evidence is still needed to support this. This work will modify the availability of free solvent through changing reaction conditions at the n-doped STO interface, illustrated in Figure 3.7, to systematically examine the contributions of the inner and outer reorganization energies to the hole-trapping energetics at the surface.

Chapter 4: Formation of the Oxyl's Potential Energy Surface by the Spectral Kinetics of a Vibrational Mode

4.1 Original Publication

This work has been previously published as Stewart, J.*; Zayka, P.*; Courter, C.; Cuk, T. Formation of the Oxyl's Potential Energy Surface by the Spectral Kinetics of a Vibrational Mode. *The Journal of Chemical Physics* **2024**, 160 (16), 164202. *These authors contributed equally to this work

4.2 Introduction

Surface oxygen intermediates form the basis of reaction mechanisms of heterogeneous catalysis on metal oxides. Their coverages and formation rates guide the evolution of reactants into products. One of the most reactive surface oxygen species is considered the oxyl radical with an electronic configuration of $O^{\bullet}$. For example, the oxyl radical has been invoked to explain O-O bond formation within the oxygen evolution reaction (OER) from water^{12,44}. In bi-radical recombination, two oxyls reduce their electron deficiency by forming a bond between the two radicals^{45,46}.

On a surface, the oxyl radical is bound to a metal site, forming a terminal $M-O^{\bullet}$. When produced electrochemically during OER, electrons and protons are taken from a water adsorbed species within the hydration layer of the metal-oxide^{47,48}. The microscopic details of how the electron and proton transfers^{49,50} arise determine the oxyl's binding energy and kinetic stability with respect to the initial catalyst surface⁵¹ and, therefore, its ability to catalyze the rest of the cycle. To arrive at these microscopic details, it would be important to follow how the excited state potential energy surface (PES) of a stable population of oxyls forms.

When photons drive the electrochemistry by photo-electrochemistry at a semiconductor-liquid interface, the necessary time resolution exists to track radical formation. In recent years, diverse optical probes of photo-electrochemically excited OER from an electron doped SrTiO₃/electrolyte interface have investigated the formation of surface oxygen intermediates^{2,3,18,19,30,52}. A critical one is the mid-infrared probe of the vibrational structure of the surface bound oxyl radical². A new molecular vibration near the longitudinal optical phonon of SrTiO₃ was observed to form upon valence band hole transfer to (or electron transfer from) a hydroxylated site; this vibration does not exist in the ground state of SrTiO₃². The hole transfer occurs alongside proton transfer from the hydroxylated group to a neighboring, bare oxygen site. The assignment was made using experimental correlations, density functional theory calculations of the excited state PES, and connections between them. The detailed theoretical calculation was required, because unlike an oxo such as Co=O⁵¹, a new bond is not created when the intermediate is formed. One of the experiment-theory connections is the spectral shape of the mode, which exhibits a Fano resonance²¹. In a Fano resonance, a narrow vibrational mode couples to a broad continuum (*e.g.* excitations of delocalized carriers) that are also excited by the infrared probe. For example, Fano resonances describe plasmonic interactions between quantum nanocrystals and colloidal molecules⁵³ and adsorbed molecular catalysts⁵⁴.

Here, we use the oxyl radical's vibration and the associated Fano resonance to determine the reaction kinetics by which the hole traps and the oxyl radical forms. The reaction kinetics are obtained through three characteristics and associated parameters of the Fano lineshape: the anti-resonance (the kinetics of the coupling factor), the resonance (the kinetics of the coupled continuum excitations), and the frequency integrated spectrum (the kinetics of the normal mode's cross-section). That all three perspectives yield a logistic function growth with a half-rise of 2.3

+/- 0.3 ps and time constant of 0.48 +/- 0.09 ps suggests that we are tracking the formation of the excited state PES through its underlying quantum states. To show the methodology, a particular electron doping (0.7% Nb) and an air interface is chosen; the air interface contains a hydration layer but no solvent. The logistic function describes an exponential growth rate at the very initial stages ($t \sim 0$) that quickly decreases towards zero as a limiting oxyl coverage is reached. A transient, non-equilibrium signal exists that is separated out in the analysis. While such non-equilibrium effects are anticipated and intrinsically interesting, we focus on the logistic growth that resolves a dynamic activation barrier in the formation of an excited state PES.

4.3 Spectral kinetics of Oxyl radical formation

An ultraviolet light pulse first excites the wide-band gap semiconductor SrTiO₃ (STO) to create delocalized electrons and holes in the conduction and valence band respectively. In Figure 3.1a, this is depicted by the pump pulse that takes the ground state of the perovskite (1) to the excited state (2) containing delocalized holes on the largely O 2p valence band. The holes can preferentially trap at a distorted reaction coordinate in early transition metal oxides^{16,55,56}. If they form on hydrated sites, they can form reactive surface oxygen species (3) trapped by the polarization of the distortion^{15,57}. At the new reaction coordinate, the vibrational transitions (3→4) are characteristic of the surface oxygen species created.

That such a process is relevant to Nb-doped SrTiO₃ (n-STO) and creates meta-stable oxyl radicals was investigated previously. Figure 3.1b summarizes the results by showing the density functional theory calculation of the vibrational structure of the surface of the metal-oxide for the ground state PES, with the hydration layer alone (left) and for the excited state PES (right), containing a coverage of terminal titanium oxyl radicals (Ti-O•)². In place of the symmetric

breathing mode in the ground state, an optically active one appears due to the sub-surface oxygen motion perpendicular to the surface and directly underneath the oxyl radical. The experimental conditions introduced methanol scavengers and correlated the observed vibration with O_2 evolution to show that the mode occurred when holes could efficiently trap to water species absorbed on a surface². The experimental conditions also varied the doping of the semiconductor². For electron doped STO by Nb, the electric field at the interface drives holes to the surface and the mode is observed, while hole doped STO by Fe, the electric field is in the opposite direction and the mode is not observed. As probed by its vibrational mode, the oxyl radicals were found to be stable through nanoseconds.

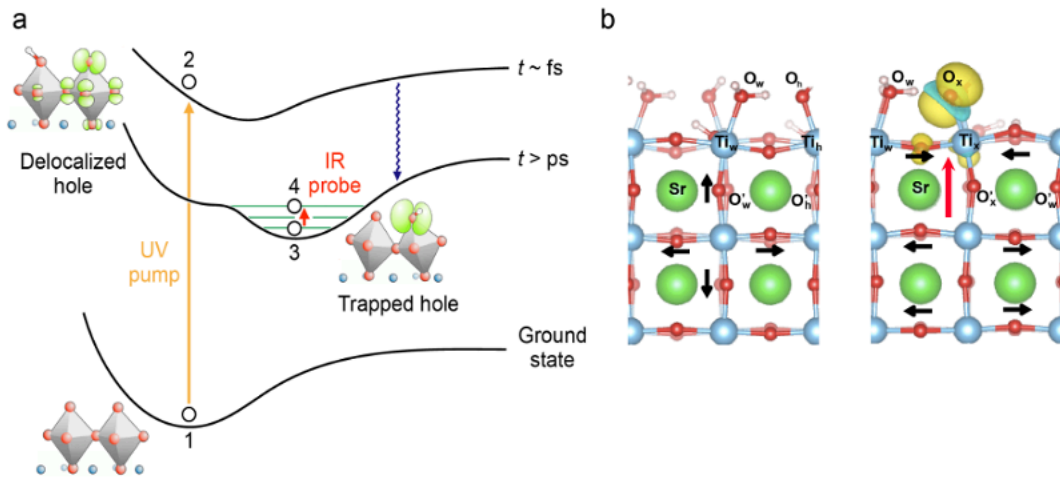


Figure 4.1: Potential energy surface (PES) and vibrational probe of the oxyl radical. a) PES of the ground state of $SrTiO_3$ at its minimum (1), the excited state PES of delocalized holes upon UV photoexcitation (2), and after the PES equilibrates, such that the hole traps in a new minimum of the reaction coordinate (3) that can be probed by a mid-infrared vibration (4). b) On the right, the oxyl radical's (yellow, spin orbital) subsurface vibration (red arrow) formed from a linear combination of dark (black, breathing) modes prior to excitation of the hydrated surface on the left.

As introduced above, the vibrational mode exhibits a characteristic Fano resonance in which the mode couples to neighboring continua. The Fano resonance is formed when the infrared probe excites both the vibration and the continuum excitations coupled to it. In the case of the oxyl radical's vibration, the resonance exists both with the continuum of the solid (a plasma

excitation, delocalized carrier excitations) and of the liquid (a librational excitation of water). Previous work makes this conclusion by modulating the extent of the continuum involved through doping the solid, comparing air to liquid interfaces, and deuterating the water². That the vibration couples to continua within the solid and the liquid shows that it truly sits at the interface, connecting the experimental phenomenology to the density functional theory calculations. In the following work, we have chosen the air interface and the highest doping, 0.7 wt. % Nb, for which the continuum of the solid dominates. When coupled to the vibrational mode, the plasma oscillations of the doped electrons are polarized to screen the vibrational dipole; the signal of both the mode and the continuum are seen only in p-polarization when the incoming light beam has a component perpendicular to the sample plane².

In-situ ultrafast IR spectroscopy in an attenuated total reflectance (ATR) geometry measures the subsurface vibrational mode. In this technique, an evanescent wave formed by total internal reflectance between the ATR crystal, a single bounce diamond, and air probes the sample surface²⁸. As opposed to a propagating wave, the evanescent wave cannot couple directly to optical phonons of a bulk crystal due to a spatially decaying Poynting vector, such that the signal is dominated by surface modes. The STO crystal is brought close enough to the diamond to be within the $\sim 1 \mu\text{m}$ evanescent decay of the mid-infrared probe³⁷. The data is reported at each time delay as a change in the probe reflectance (ΔR) before and after above band gap pump (266 nm) excitation, calculated using optical density or $\Delta\text{mOD} = -\log(\Delta R/R) \times 10^{-3}$. The beam is p-polarized with a 60° angle to the sample normal. At the excitation energies used, degradation of the metal oxide is not observable by optical or electron microscopy in open circuit conditions³⁵. A more detailed description of the experimental configuration can be found in Figure 2.6.

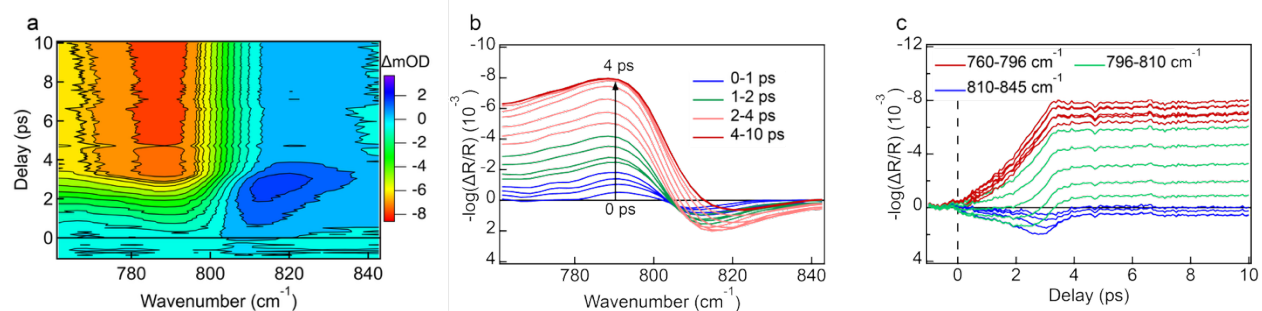


Figure 4.2: Time evolution of the vibrational signal of the n-STO air interface in the first ten ps following excitation. The 2D contour plot (a) and associated spectra (b) and kinetic traces (c) depict the picosecond rise of the oxyl radical's vibration. The vibrational peak begins to take shape within the first picosecond and reaches its final, converged lineshape by 4 ps. The y-axis of (b) and (c) correspond to the ΔmOD color scale of the contour plot (a) and represent a change in absorption based on Beer's Law, or $\Delta mOD = -\log(\Delta R/R) \cdot 10^{-3}$ where R is the reflectance.

The initial ten picoseconds of the oxyl radical's formation is illustrated in Figure 4.2. In the contour plot (Figure 4.2a), substantial changes occur within the first four picoseconds until the signal converges to a final, unchanging spectral shape. The contour plot exhibits a distinctively asymmetric spectral shape, with a peak optical density (red) at 786 cm⁻¹. On the higher frequency side of the peak, the optical density drops sharply while on the lower frequency side, it drops gradually. This asymmetry aligns with expectations for a Fano resonance, as will be explored in more detail below. The optical density of the Fano peak is negative due to the refractive indices involved in the attenuated total reflection geometry, as discussed elsewhere¹². A transient background also exists—the short-lived positive optical density (dark blue) on the higher frequency side of the peak.

Spectral slices at specific delays are shown in Figure 4.2b. While the signal grows in, the spectral width also increases as seen by the peak to valley distance in the blue (0-1 ps) versus pink (2-4 ps) spectra. The transient background, with a positive maximum near 810 cm⁻¹, grows in and then decays. Kinetic traces at specific frequencies are shown in Figure 4.2c. There are three regimes: green for frequencies near the Fano resonance (796-810 cm⁻¹, as will be determined below), red for frequencies below this Fano resonance (760-796 cm⁻¹), and blue for frequencies

higher than this Fano resonance ($810\text{-}845\text{ cm}^{-1}$). For the wavenumbers covered within the blue frequency regime, the transient background dominates while for those covered by the red frequency regime, the signal of the Fano peak dominates. For both the spectral slices and the kinetic traces, the data demonstrate a converged signal by 4 ps.

The presented data underwent two separate procedures to eliminate artifacts and background signals. First, regular oscillations in wavenumber are observed, likely due to the mid-infrared detection electronics. Since these oscillations have a constant frequency spectrum in time and are additive to the oxyl signal, they can be removed using a low pass FFT filter, as shown in Figure A.1a. Second, a background due to the pump-probe response from the diamond ATR crystal is taken without the presence of the STO sample after each measurement and subtracted out. While the bandgap of diamond is above that of the pump beam (5.5 eV vs 4.7 eV), pump-probe responses in the IR range at similar pump wavelengths (273 nm, 310 nm) and peak fluences ($\sim\text{GW}/\text{cm}^2$) have been attributed to two photon absorption^{58,59}. Since the diamond response is also generally a narrow, symmetric peak about time zero, it has been used as an autocorrelation measurement of the pump and probe⁵⁹. We have a similarly symmetric peak (Figure A.1b) and use it to determine time zero by a gaussian fit (Figure A.1c).

The instrument response function (IRF) was measured previously by a cross-correlation of the pump pulse (266 nm) with a 150 fs, 800 nm pulse, determining a pulse width of 0.4 ps (Figure A.2a). This resolution is sufficient to accurately resolve the rise without distorting the kinetics. A convolution of the IRF with the logistic function used for fitting the reaction kinetics (discussed below) yielded a fit that is unchanged in comparison to the non-convolved logistic function (Figure A.2b).

In parallel to the data presented in Figure 3.2 and analyzed within the manuscript, two other data sets taken with the same experimental conditions were measured and analyzed. The contour plots, spectral slices, and kinetic traces of all three data sets are shown in Figure A.3, highlighting the reproducibility of the measurements. While the overall signal strength varied due to the ATR geometry's sensitivity to the distance between the ATR crystal and the sample, the time-dependent spectra are consistent across the three data sets.

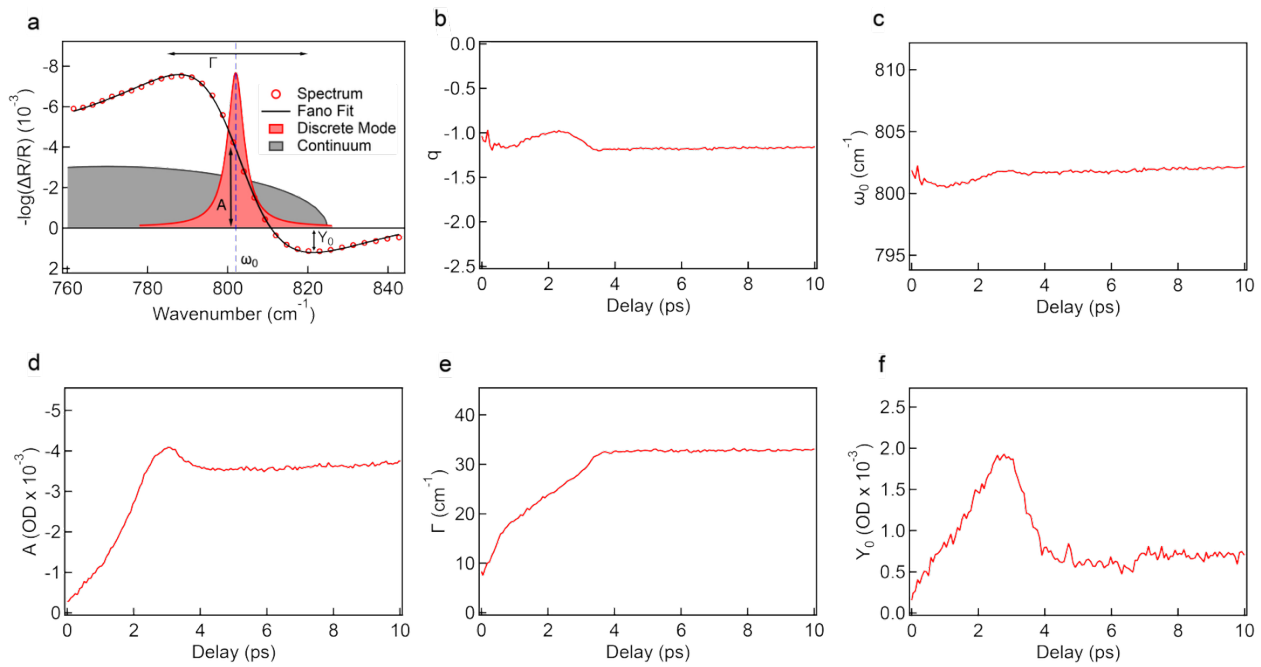


Figure 4.3: Free-form Fano fits of the spectral kinetics. (a) Illustrates the Fano fit (black line) that results from excitation of the discrete mode (gray) and the coupled continuum (gray) by the infrared probe to detect the resulting asymmetric spectrum (red dots). (b)-(f) show the time evolution of the Fano parameters obtained from free fits: (b) The Fano asymmetry constant (q), (c) the resonant frequency (ω_0), (d) the coupled continuum excitations (A), (d) the coupling factor (Γ), and the uncoupled continuum excitations (Y_0).

Next, we turn to examining the data using the Fano lineshape, whose form is given by Equation 4.1. There are several quantum mechanical wave functions involved in the Fano equation²¹. Ψ represents the vibrational wave function coupled to the continuum, such that $|\langle \Psi | T | i \rangle|^2$ is the square of the transition dipole moment or intensity measured by the spectroscopy for the coupled vibrational mode; T is the dipole operator and i is the initial state. ψ is the quantum

mechanical wave function of continuum and A in Equation 4.1 denotes $|\langle \Psi | T | i \rangle|^2$, or the intensity of the continuum light excitations coupled to the mode. Y_0 is the same, but for the uncoupled continuum excitations; it is an additive, constant background in the region of the mode frequency. The lineshape is a function of $(\omega - \omega_0)/2\Gamma$. ω_0 is the resonant frequency of the mode after coupling to the continuum. Γ is equal to the square of the coupling constant of the mode to the continuum and is a measure of the spectral width; with $q=0$, the Fano equation simplifies to a Lorentzian. For a given Γ , the light frequency ω probes the Fano lineshape through the resonance. As the vibrational mode involved in the Fano lineshape is not present in the ground state, it can be freely fit using Equation 4.1. The continuum, Ψ , involved includes that present in the ground state and any pump-induced continuum transients that couple to the mode. Here, since any uncoupled continuum in the ground state is subtracted in the difference spectrum, Y_0 represents a pump induced continuum transient.

$$|\langle \Psi | T | i \rangle|^2 = \frac{A(t) \left(\frac{2(\omega - \omega_0)}{\Gamma(t)} + q \right)^2}{1 + \left(\frac{2(\omega - \omega_0)}{\Gamma(t)} \right)^2} + Y_0 \quad \text{Equation 4.1}$$

Figure 4.3a shows representations of the bare vibrational mode, the continuum excitations, and the Fano lineshape of the coupled vibrational mode. Fano parameters A (an intensity at $\omega = \omega_0$), Γ (a spectral width), ω_0 (the resonant frequency), and Y_0 (constant background) on the Fano lineshape are depicted. The main continua contributing to the Fano lineshape come from electron plasma and delocalized carrier excitations in the STO substrate³⁸. The electronic plasma continuum is a broad peak centered at 400-500 cm^{-1} and extends past the 802 cm^{-1} vibrational mode, as represented by the gray spectrum. In addition to this, there are delocalized carrier excitations due to both dopant electrons and electron-hole pairs created upon pump excitation.

The coupling between the mode and the continuum results in an asymmetric lineshape when light simultaneously excites the mode and the coupled continuum. That asymmetry is defined by the parameter q :

$$q^2 = \frac{2|\langle\phi|T|i\rangle|^2}{\pi|\langle\psi|T|i\rangle|^2\Gamma} \quad \text{Equation 4.2}$$

Thus, q^2 is proportional to the ratio of light excitations of the bare but dielectrically screened mode ($|\langle\phi|T|i\rangle|^2$) to that of the coupled continuum light excitations ($|\langle\psi|T|i\rangle|^2$). The denominator represents the number of continuum excitations that contribute to the Fano resonance within the width of the mode, given by Γ ; ψ is reported as a density of states such that q is unitless. For our data, with a q value near -1 , Γ is the difference between the maximum and minimum of the Fano peak, as depicted in Figure 4.3a.

The difference spectra shown in Figure 4.2b were freely fit at each time delay with the Fano lineshape, which fully encapsulates the observed spectra as the new vibrational mode is not present in the ground state. The quality of the fits for the main manuscript data are shown in Figure A.4. The resulting time-dependence of the Fano parameters are shown in Fig. 4.3b-4.3f. Interestingly, the asymmetry parameter q (Fig. 4.3b) and the resonant frequency ω_0 (Fig. 4.3c) are fairly time independent. The coupled continuum excitations of A (Fig. 4.3d) and the coupling factor defined by Γ (Fig. 4.3e) both exhibit rising kinetics that converge to a final value by 4 ps, while the uncoupled continuum excitations of Y_0 (Fig. 4.3f) rise and decay by 4 ps. In addition, a transient can be seen in A before the kinetics stabilize.

Free fits performed on all three data sets are shown in supplemental Figure A.5. While overall similar trends for each parameter are shown, some parameters are highly correlated and changing one can be compensated by changing another. An example of when this occurs is the

third data set for which q becomes time dependent, and A has a different time dependence than that shown in Fig. 4.3d. Thus, one set of free fits is not necessarily unique.

4.4 Extracting time-dependence of Fano parameters: $A(t)$, $\Gamma(t)$, $S(t)$

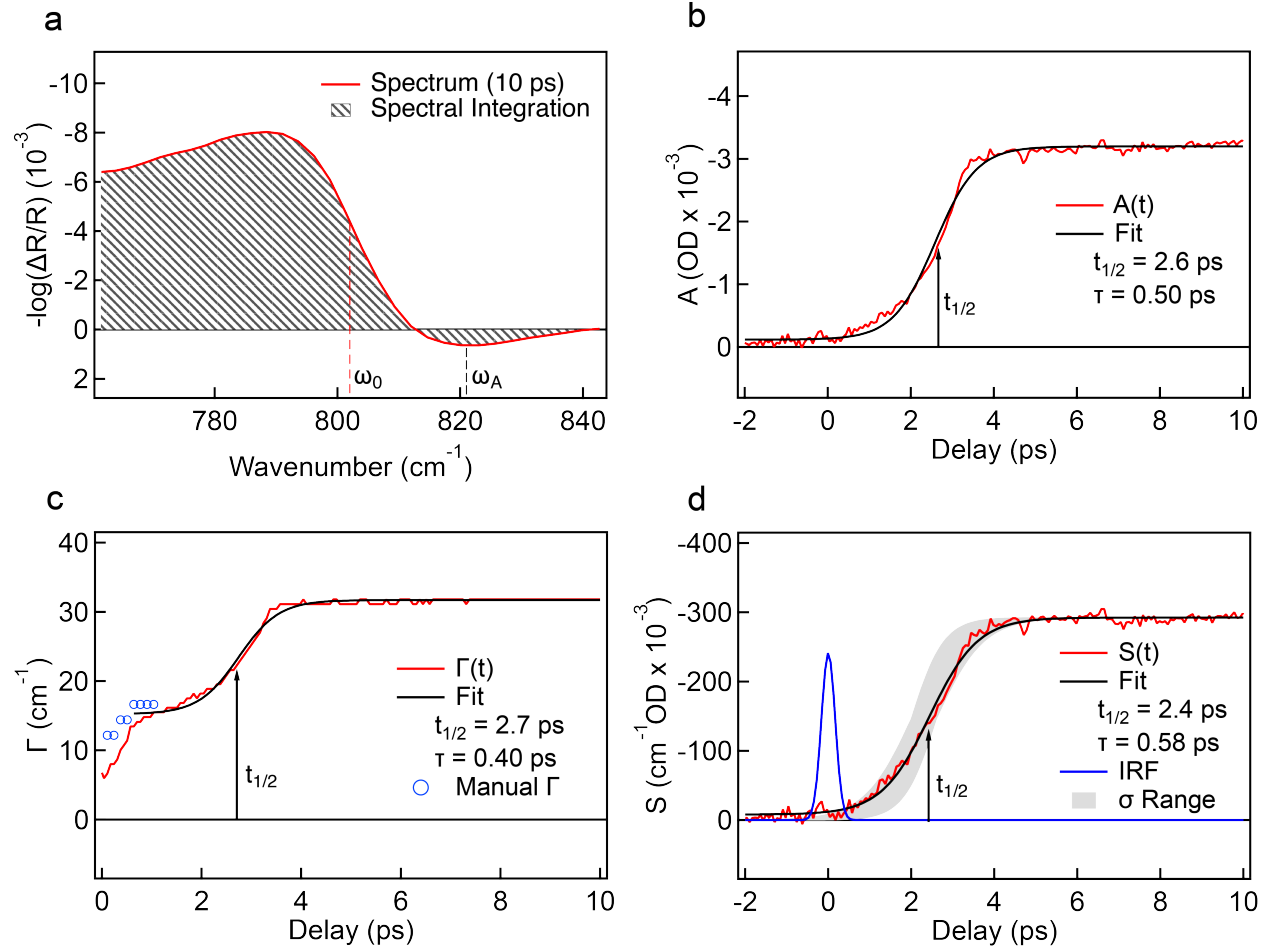


Figure 4.4: Extraction of $A(t)$, $\Gamma(t)$, and $S(t)$ by frequency regimes of the Fano resonance. (a) Depicts the resonant frequency (ω_0) and anti-resonant frequency (ω_A) used to determine $A(t)$ and $\Gamma(t)$ respectively on the 10 ps spectrum. The frequency integrated spectrum is $S(t)$. (b-d) show the time evolution of $A(t)$ (b), $\Gamma(t)$ (c), and $S(t)$ (d) along with the corresponding logistic fits and associated time constants. The manual determination of $\Gamma(t) < 1$ ps is shown in (c). The instrument response function (IRF) and standard deviation range of the data (σ range) are given in (d).

Fortunately, distinct frequencies within the Fano lineshape uniquely determine $A(t)$ and $\Gamma(t)$ if q and ω_0 are constant. The constancy of q and ω_0 is on the one hand supported by the free

fits, for which it generally occurs. On the other hand, conceptually the constancy of q can be understood by its construction from the underlying quantum mechanical wave functions of the two parts contributing to the Fano resonance: a ratio of the light excitations of the bare mode (the numerator) to those of the coupled continuum within the mode's width (the denominator). If as the bare mode forms, it couples at each instant to the continuum, then q should be constant in time. Similarly, if the coupling occurs at each instant, the resonant frequency should be constant in time. A justification for such an instantaneous coupling is that the electronic response to atomic motion is considered fast on the time scale of the atomic motion itself. The Born-Oppenheimer approximation is an example of such a justification, albeit for how electrons in a bond respond to atomic motion. We will return to this justification below with data itself and a frequency integration of the Fano lineshape.

If q and ω_0 are time-independent and there is no Y_0 offset, then the Fano lineshape evaluated at the resonant frequency ($\omega = \omega_0$) uniquely extracts the time evolution of the coupled continuum excitations ($A(t)$). Since the offset Y_0 extracted is a transient (Fig. 4.3f) that decays to a small value past 4 ps, we set it to zero in order to isolate the spectral kinetics involved in the formation of the meta-stable state. At the resonant frequency and with $Y_0 = 0$, Equation 4.1 simplifies to:

$$|\langle \Psi | T | i \rangle|^2 = A(t) \cdot q^2 \quad \text{Equation 4.3}$$

From the free fits, ω_0 and q were determined to be 802 cm^{-1} (Figure 4.3c) and -1.2 (Figure 4.3b) respectively. For a q near -1, ω_0 is located at approximately the half-rise of the peak (Figure 4.4a). Using Equation 4.3, $A(t)$ is calculated at the resonant frequency of 802 cm^{-1} and the q value of -1.2 and is shown in Figure 4.4b. $A(t)$ exhibits an S-shaped growth that saturates beyond 4 ps and does not contain the transient of the free fits (Figure 4.3d).

Similarly, the anti-resonance frequency (ω_A) can be used to determine the time evolution of the coupling factor ($\Gamma(t)$). The anti-resonance is located at the minimum of the concavity in the Fano lineshape, as labeled in Figure 4.4a. In the absence of a constant offset (Y_0), ω_A occurs at the frequency for which the Fano lineshape is zero. Assuming a nonzero $A(t)$, the frequency that zeroes the numerator of Equation 4.1 obtains ω_A in terms of Γ , ω_A , and q :

$$\omega_A = \frac{-q\Gamma(t)}{2} + \omega_0 \quad \text{Equation 4.4}$$

Given the existence of an offset, extracting ω_A from the data is done by taking the first and second derivatives of the spectrum to find the frequency at which the first derivative is zero and the second derivative is negative (Figure A.6a); the concavity identifies the same relationship for ω_A in Equation 4.4. Once this frequency is extracted at each time delay, $\Gamma(t)$ is derived from Equation 4.4 with $\omega_0 = 802 \text{ cm}^{-1}$ and $q = -1.2$. The resulting time evolution is shown in Figure 4.4c and like $A(t)$, exhibits an S-shaped growth that saturates by 4 ps.

At the earliest time delays, the data do not fit perfectly to a Fano lineshape which especially affects the extraction of $\Gamma(t)$. The method to extract ω_A uses the Fano fits of each spectrum rather than the data itself because the point density in the fit is much greater than the data (taken at each pixel of the detector) and produces a comparatively smooth $\Gamma(t)$ (Figure A.6b). This results in a value of Γ that does not accurately reflect the anti-resonance at the earliest time delays (Figure A.6c). Therefore, for these time delays, ω_A are extracted manually and the resulting Γ values are shown as blue circles in Figure 4.4c. Nonetheless, a change in $\Gamma(t)$ is noticeable below 0.75 ps. Even faster processes could be at play in the hole trapping reaction, and we do not attempt to ascribe their origin here.

We now turn to one more way of extracting the time dependence of the Fano parameters and that is through integrating over the measured frequencies ($760 \text{ cm}^{-1} - 840 \text{ cm}^{-1}$) of the spectrum

at each time delay. The resulting $S(t)$ is shown in Figure 4.4d. Interestingly, like $A(t)$ and $\Gamma(t)$, $S(t)$ exhibits an S-shaped growth that saturates. As derived by U Fano²¹, the integration, S , of the Fano lineshape represents the cross-section of the bare, screened mode after a simple subtraction of the coupled continuum excitations (A), integrated over the same frequency range. Without this correspondence, the frequency dependence of the underlying parameters invalidates the derivation of the Fano resonance. That $S(t)$ exhibits a regular growth and one that resembles $A(t)$ supports the applicability of the Fano resonance here. Furthermore, it suggests that the cross-section of the bare, screened mode is created essentially at the same time as that of the cross-section of the coupled continuum excitations, which helps justify the constancy of q and ω_0 described above.

The S-shaped growth of $A(t)$, $\Gamma(t)$, and $S(t)$ suggests the use of a logistic growth function (Equation 4.5) to describe the kinetics. This yields two-time constants, along with the saturation of the growth (max): τ , which describes the rate of the rise, and $t_{1/2}$, which defines the half-rise of the growth⁶⁰. The logistic function used to fit the data is:

$$f(t) = \frac{max}{\left(1 + \exp\left\{\frac{t_1 - t}{\tau}\right\}\right)} + base \quad \text{Equation 4.5}$$

Base is a constant background used especially for fitting $\Gamma(t)$ starting at 0.75 ps. The fits, shown on top of the data in Figure 4.4, nicely describe the growth kinetics of all three Fano parameters.

Furthermore, they all exhibit similar τ and $t_{1/2}$ values. Each of the three data sets yields three evaluations of these time constants by $A(t)$, $\Gamma(t)$, and $S(t)$. The results are shown in Figure A.7 and the time constants are compiled in Table A.1. The nine separate determinations of the time constants lead to the following average values and standard deviations: $\tau = 0.48 \pm 0.09$ ps and $t_{1/2} = 2.3 \pm 0.3$ ps. The range of logistic curves given by the average values $\pm$ one standard

deviation is displayed in Figure 4.4d in gray and detailed in Figure A.8, which also describes the effect of changing τ and $t_{1/2}$ individually. The IRF on Figure 4.4d shows that the time-resolution would not affect the fits.

An exponential rise of the form $1 - e^{-t/\tau}$ (Equation A.2) is often used to fit the reaction kinetics of similar systems following light excitation. To explore the validity of such a fit, $A(t)$ extracted at the resonant frequency (802 cm^{-1}) (Figure A.9a) and the kinetic trace at the Fano peak maximum (786 cm^{-1}) (Figure A.9b) were each fit by an exponential rise. A time-zero offset between 0 ps and 2 ps was included to account for any time dynamics that were not measured by the probe (*e.g.* of delocalized carriers). For the exponential rise to capture the second half of $A(t)$, the fit must be initialized with an offset of 2 ps, which results in a failure to capture the initial time delays at all. The same occurs for the kinetic trace at the peak maximum, which rises faster than $A(t)$ and yet, the simple exponential cannot fully capture both ends of the time trace. Thus, the logistic function represents a more accurate and holistic function with which to model the oxyl formation kinetics by its specific vibration.

The logistic formation is different than the rising exponential fits of the visible stimulated emission or the coherent terahertz oscillations that provide information respectively on the electronic levels³ and the continuum lattice strain⁵² due to trapped holes on n-STO. These rising exponential fits are for the liquid interface and find a 1.3 ps time constant. Further, the visible probe is a more collective probe, for which different geometries of trapped holes are not yet well-distinguished by the broad spectrum. We also note that the kinetics at the Fano peak maximum (Figure A.9b) and away from resonance are different than that extracted by the Fano parameters.

4.5 Reaching an equilibrium potential energy surface of Oxyl radicals

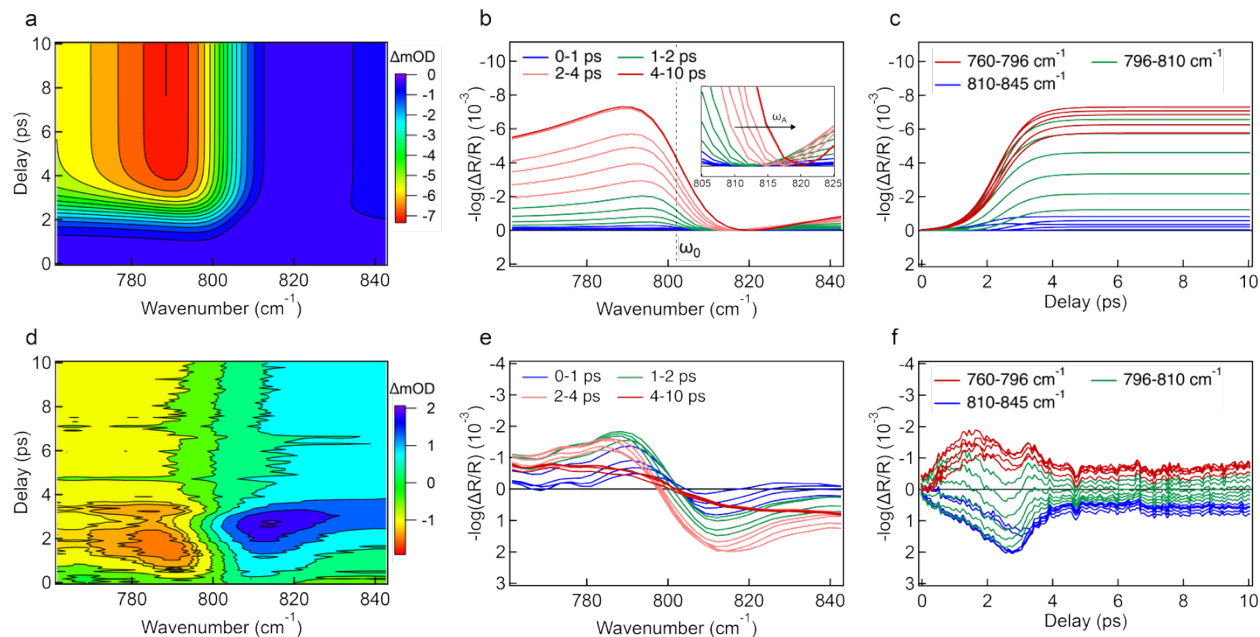


Figure 4.5: Modelling the equilibrated PES of the oxyl and the non-equilibrium transient. (a) Contour plot of the Fano resonance of the equilibrated PES with associated spectral slices (b) and kinetic traces (c). The input parameters for q , ω_0 , $\Gamma(t)$, and $A(t)$ are described in the text. (d)-(f) show the difference between the raw data (Figure 2) and the model for the equilibrated PES (a-c), which extracts the contour plot (d), spectral slices (e), and kinetic traces (f) of the non-equilibrium transient.

By using the kinetics extracted by the resonant frequency for $A(t)$, of the shift in the anti-resonant frequency for $\Gamma(t)$, and the frequency integrated spectrum for $S(t)$, a common logistic function rise was found with a τ of 0.48 ps and a $t_{1/2}$ of 2.3 ps. Since the logistic function exhibits a smooth increase that then saturates, it cannot itself describe transients within the data. In the following, we utilize this finding to separate components of the data that describe an equilibrium reached by a meta-stable excited state surface from a decaying transient. We then consider what the kinetics of this equilibration say about the mechanism of hole-trapping to create the excited state PES of oxyl radicals.

To separate out the formation of the excited state PES, a Fano lineshape is built from the two time-independent parameters, q and ω_0 , and the two time-dependent parameters, $A(t)$ and $\Gamma(t)$.

Figure 4.5a shows the contour plot of a Fano equation with $q=-1.2$ (Figure 3.3b), $\omega_0=802\text{ cm}^{-1}$ (Figure 4.3c), and logistic function growths for $A(t)$ and $\Gamma(t)$ with $\tau = 0.48$ and $t_{1/2} = 2.3$. For $A(t)$, the logistic function rises from zero (base) to a maximum of 3 mOD (max) as derived from Figure 4.4b. For $\Gamma(t)$, a base of 15 cm^{-1} rises by 15 cm^{-1} (max) to saturate at 30 cm^{-1} as derived from Figure 4.4c.

Select spectral slices at 1-2 ps, 2-4 ps, and 4-10 ps are shown in Figure 3.5b. As depicted there, ω_0 is constant, while ω_A redshifts. The redshift is anticipated from Eq. 4.4 as Γ grows in time. While such a redshift can be seen in the data itself (Figure 4.2b), it becomes clearer in the modelling for which the transient Y_0 is not included. Select kinetic traces prior to ω_0 , near ω_0 , and through ω_A are shown in Figure 4.5c. Both the kinetic traces and the spectral slices for $\omega > \omega_A$ more clearly show the tail of the Fano lineshape obscured in the data by the transient Y_0 (Figure 4.2c). Overall, the spectral and kinetic traces follow that of the raw data (Figure 4.2b-c) when the uncoupled background is avoided either in frequency ($< 800\text{ cm}^{-1}$) or in time ($> 4\text{ ps}$).

To identify the transient in the data, we have subtracted this equilibrium model from the raw data to obtain the contour plot in Figure 4.5d. The spectral slices and kinetic traces are shown for select time delays and frequencies in Figure 4.5e and Figure 4.5f. The entirety of the signal is transient and there are two components: a peak in the region of the anti-resonance, and a fairly symmetry peak of opposite sign below the resonance. Interestingly, at the resonant frequency, there is a negligible transient. The two components reflect the transient $Y_0(t)$ and the transient within $A(t)$ seen in the free Fano fits of Figure 4.3f and 4.3d respectively. While the background to the Fano lineshape is then frequency dependent, it is also of a particular shape such that the kinetics extracted at ω_0 , by the shift in ω_A , and the integrated spectrum isolate the kinetics of the

meta-stable surface. The non-equilibrium component is avoided at the resonant frequency, does not appreciably change the anti-resonant frequency, and being approximately symmetric across the resonance, integrates to $\sim$ zero within the frequency window. While this is the outcome of the data analysis using the distinctive Fano lineshape, why such a clean separation is possible is not a priori clear and would require an atomistic understanding of how non-equilibrium transients couple to the vibration as the PES forms. Possible origins of the non-equilibrium transient are pump-induced electron-hole excitations or excited continuum states that couple to the vibration temporarily before they decay.

We now turn to how to visualize populating an electron doped semiconductor surface with oxyl radicals using a logistic function rise and further, one that is consistent across several Fano parameters. Each of the parameters have a distinct physical meaning, as discussed in detail above. $S(t)$ is a measure of the transition dipole of the bare, screened vibration while $A(t)$ and $\Gamma(t)$ are measures of how that vibration couples to its surroundings. Since they all rise with a similar logistic function suggests that as the oxyl forms, the vibration simultaneously couples to the electronic continuum. One could rationalize this result by the time required for a change in the vibrational dipole moment to couple to the electronic continuum, which could be instantaneous at the time-resolution of the experiment.

On the other hand, the logistic function growth is itself more difficult to describe, since it means that the reaction kinetics change in time as the oxyl forms. In the $t=0$ limit, the rate of growth is exponential, $e^{t/\tau}$. That growth rate decreases towards zero as the oxyl fully forms and a limiting coverage is reached. As cartooned in Figure 4.1, the process is initially barrier less, but as the reaction coordinate extends to form the oxyl, an activation barrier grows in. Since the formation of the oxyl in the theoretical calculation requires a $\sim 10\%$ extension of the titanium-

oxygen bond^{2,15}, an activation barrier would be anticipated for the fully formed oxyl due to the polarization that traps the hole. In terms of the ergodicity of the hole-trapping reaction, there is no barrier to release energy to the surroundings initially and that grows as the reaction coordinate of the oxyl forms.

Another way to understand how the growth rate slows is through the interaction between oxyls. In the experiments, a population of oxyls is created and this population saturates with the photoexcitation fluence, as shown previously. Since a larger population of photoexcited holes does not create a larger oxyl population, the oxyl coverage is surface limited^{3,52}. Likely, this surface limitation comes from their repulsive Coulombic interaction. To what extent repulsive interactions between a surface coverage of oxyls or the reaction coordinate polarization itself leads to the observed logistic growth would require atomistic simulations of the hole-trapping event.

Understanding a barrierless hole-trapping event occurring at the initial stages of a logistic function growth introduces an issue with how one would usually interpret a rise in a time-resolved signal. If the initial hole-trapping is barrier-less, why would the measured signal for the oxyl coverage be small? One hypothesis is that although the actual formation of the hole-trapped states and the oxyl is barrier-less, the oxyl's vibrational optical dipole takes time to grow in and therefore, its cross-section is initially small. Since the measured signal is a function of both the population and its cross-section, a low signal strength does not necessarily reflect the oxyl population that exists and could be limited by the vibrational cross-section before the PES is fully formed. To more clearly understand the population dynamics at the earliest times, a structural probe (such as x-ray) is recommended to directly time-resolve the reaction coordinate. Alternatively, one could try to follow the rapid decay of the delocalized hole population if it could be properly isolated from the trapped hole population by an optical probe at either lower or higher probe frequencies.

Finally, we shortly comment on these results from the perspective of Marcus theory of electron transfer for molecules on the one hand, and polaronic distortions in solids on the other. Marcus theory describes how molecular distortions within the molecule and its surroundings lead to a reorganization energy and driving force for electron transfer that together define its transition state and activation barrier⁴⁰. The reaction kinetics then follow a well-defined law that can be modulated experimentally by, for example, the solvent environment and bonding within the molecule. Ultrafast optical spectroscopy has played an important role in defining the scope of the theory by measuring electron transfer kinetics as a function of these parameters. However, Marcus theory deals with two states—an initial and final one—with a single activation barrier and so, it is not immediately clear how to apply the theory to a dynamically evolving one. On the other hand, more recently, ultrafast x-ray⁶¹ and multi-dimensional, optical spectroscopy⁶² of molecular electron transfer depict a multitude of dynamic structural distortions involved in forming the final reaction coordinate. On the solid-state side, ultrafast x-ray diffraction probes polaronic distortions and especially in the halide perovskites^{63,64}. The closest study we are aware of to a dynamic activation barrier are those that measure a radially expanding strain field due to picosecond polaron formation and its subsequent relaxation; corresponding ultrafast optical spectroscopy further associates a time-dependent effective mass⁶³.

4.6 Conclusions

The work identifies the formation of an excited state PES that reaches a meta-stable equilibrium for an oxyl radical surface coverage. As such, it describes how stable reactive oxygen intermediates form for oxygen evolution catalysis, among other important catalytic reactions. The formation of the excited state PES is identified through a vibration coupled to its immediate

surroundings. The coupling allows a Fano resonance and its associated parameters to be applied to the time-evolution of the spectral kinetics. Through the fitting of these parameters by the logistic function, the time dynamics show that holes initially trap with barrier-less kinetics until an activation barrier accumulates as the polarization due to a distorted reaction coordinate grows; the rates likely depend also on the Coulombic interaction between the trapped holes or oxygens.

4.7 Experimental methods

Sample and ATR Cell:

0.7% Nb-doped by weight SrTiO_3 single crystal samples with a (100) crystallographic orientation were acquired from MTI. The crystals measured 10 mm x 10 mm x 0.5 mm in size, with the front side of the sample polished to an arithmetic mean roughness of 0.5 Å.

For each measurement a custom-built ATR cell made of PEEK plastic was employed, shown in Figure 2.6. The internal reflection element (IRE) used was a single-bounce 45° trapezoidal diamond (GladiATR plate, Piketech) with a 1 mm front facet and 1.4 mm side facets. The STO samples were mounted within the cell using epoxy (Loctite 615). While the epoxy was still wet, the sample was lightly pressed against the IRE using a Thorlabs Polaris P20 actuator and allowed to fully dry, ensuring the crystals' alignment was parallel with the IRE.

Transient Infrared Setup:

The pump and probe beams were generated using a Legend Coherent Elite amplifier Ti:sapphire laser, emitting 800 nm pulses with a temporal width of 150 fs and a repetition rate of 1 kHz. A portion of the light was directed through a 0.5 kHz chopper and then converted through third harmonic generation to a 266 nm pump beam. The pump was directed through the front facet of the IRE at normal incidence to excite the STO sample. Before reaching the IRE, the pump was

focused and attenuated using a focusing lens and variable OD filters, resulting in a beam size of 665 μm FWHM with a fluence of 0.1 mJ/cm^2 at the sample position. With a 400 fs pulse beam width determined by a cross-correlation (IRF in Figure A.2a), this results in a peak fluence in the diamond of 1.14 GW/cm^2 .

Another portion of the 800 nm pulse was directed into an optical parametric amplifier (Opera Solo) to convert the light to infrared pulses with a center wavelength of 800 cm^{-1} and a 150 cm^{-1} bandwidth with P polarization. This polarization has a component perpendicular to sample and allows for exciting the oxyl vibrational mode that is likewise perpendicular to the sample surface. The IR beam was then split using a 50/50 beam splitter to create a probe and reference line. The probe, with a beam size of 350 μm FWHM, was sent through the IRE in the ATR cell at an incidence angle of 60° using a focusing lens. This resulted in an evanescent wave penetration depth of 1.1 μm at the diamond/air interface used for measurements.

After passing through the IRE, the probe was collimated and focused into an entrance slit for an Acton SP-2300 spectrograph (Princeton Instruments), where it was dispersed onto the top row of a dual-array 64-element detector (MCT-12-64, Infrared Associates). The reference beam was directed to the bottom array of the detector. The signal was amplified using a boxcar amplifier (FPAS boxcar integrator) and sent to a computer. The delay between pump and probe pulses was controlled by a delay stage (MTM 250CC1, Newport). The probe was normalized using the reference line to account for shot-by-shot differences.

Transient IR ATR measurements:

During the experiments, the sample was pressed into the 1.1 μm penetration depth of the evanescent wave at the diamond/air interface using the actuator. The sample was photoactivated

by the 266 nm 0.5 kHz pump and probed with the IR 800 cm⁻¹ 1 kHz probe. The absorbance was calculated using Beer's Law with $\Delta A = -\log(\Delta R/R)$, where ΔR is the change in reflectivity before and after exciting with the pump, and R is the initial reflection before excitation, measuring the change in reflectance of the sample before and after being pumped. Spectra were collected with a 67 fs step across the desired time range. Following each experiment, the sample was removed from the evanescent wave and a transient background was recorded under the same experimental conditions.

Chapter 5: Surface formation of oxygen radicals on titanium oxide determined by reorganization of nearby aqueous bonds, not free solvent

5.1 Introduction

The oxygen evolution reaction from water (OER) on surfaces is thought to occur through several metal-stable intermediates and the first is an electron and proton transfer from water to create a hydroxyl group (OH^*) or from a hydroxyl group to create an oxyl group (O^*). The formation energies of these intermediates have been computed for decades using an adsorbed layer at an otherwise vacuum interface, without free solvent reorganization and the computational hydrogen electrode; the activation barriers for formation are then constructed by assuming a linear scaling of the activation free energy^{1,5}. The question of whether implicit and/or explicit solvent effects play a role in the intermediates' formation energies or kinetics has lingered, even with the advent of more advanced computational methods. Oxygen production from OER has shown dependencies on pH and ionic strength, which suggests that role of free solvent is important⁴. The OER involves the four electron and proton transfer steps occurring from a complex hydration layer and any one of them could be involved in determining the product dependence.

Marcus theory has long been used to understand the role of solvation in rates of electron transfer for homogeneous molecules in solutions²². Reorganizational energy accounts for the free energy required to polarize molecules around the site that accepts or donates the electron. The reorganizational energy is divided into an “inner” and “outer” sphere: the inner sphere accounts for reorganization of bonds around the metal site, whether due to tightly bound solvent or chemical bonding to ligands, and the “outer” sphere accounts for the solvent molecules free to reorient their dipoles around the complex. For molecular transition metal complexes such as Fe cyanide in

metalloproteins, the outer sphere dominates by several electron volts⁶⁵. The outer sphere reorganizational energy also dominates for solvated electrons in high dielectric solvents; it is several eV also for alcohols, with the electron in one work being described as an electron “polaron” based on the dynamics exhibited by the solvent shell⁶⁶. On the other hand, for mixed-valence dimers of Ruthenium complexes, the first molecular solvent layer dominates the electron transfer kinetics via the incorporation of mixed solvents⁶⁷. For protein complexes and enzymes such as the blue copper proteins, cytochrome c oxidase, nitrous oxide reductase, and iron sulfur clusters, the inner sphere reorganization energy of the first bonded layer is also thought to determine the electron transfer kinetics, being 2 eV and higher⁶⁸. Probably the most analogous homogeneous system to that studied in this work heterogeneously are the hexaquo transition metal complexes. For the hexaquo cations of V^{2+} , Cr^{2+} , Fe^{2+} , six waters form the first molecularly bonded layer with inner sphere reorganizational energies of ~ 1 eV, as determined by photoelectron emission²³; for others, it is lower, being 0.2 eV for Tl^{+} . The outer sphere reorganizational energy is less dependent on the cation, being 1 eV for almost all the complexes, such that for many of the hexaquo cations the inner and outer sphere are on par²³. The inner sphere reorganizational energy is the most easily computed by theory, and therefore, the exact energies have been correlated and benchmarked with experiment, especially for the aqueous cations⁶⁹. The role of solvation has also been computed and compared to experiment for the $OH^-/OH^\bullet$ redox couple with ~ 0.1 eV inner sphere⁷⁰ and an overall ~ 3 eV reorganizational energy^{15,71} and for small inorganic redox couples such as $NO/NO^\bullet$ and O_2/O_2^- with ~ 1 eV inner sphere reorganizational energy⁷².

The outer sphere reorganizational energy could be much reduced at electrochemical interfaces, due to the inner Helmholtz plane (IHP) which requires the orientation of solvent molecules to sustain large electric fields (V/nm); while the outer Helmholtz plane (OHP) is less

structured, it still sustains a field⁷³. Electrochemical capacitance measurements suggest that the dielectric constant of water is much reduced at interfaces to 3-8 from 80⁷⁴. Several studies explicitly investigate the effects of outer and inner sphere solvation for electron transfer to or from molecular complexes attached to metal or metal-oxide electrodes. For Ru-bipyridyl complexes anchored to indium tin oxide, only when the molecules are tailored such that the electron transfer is outside of the IHP ($>15 \text{ \AA}$), does the outer solvent reorganizational energy appreciably change the electron transfer rate; the outer sphere contributed 0.1 eV below $4 \text{ \AA}$ ^{24,43,75}. For the electron transfer rate from TiO_2 to organic Mn complexes, the inner sphere was also found to be significant (2 eV) while the outer sphere was lower but still appreciable (0.7 eV)⁷⁶. Calculated reorganizational energies for electron transfer to self-assembled monolayers at electrochemical interfaces show that including the effects of the electric double layer and the ionic environment do not appreciably change the total reorganizational energy, even when including explicit solvent effects for the molecule-solvent boundary⁷⁷. Further, the measured rate of electron transfer from a photo-reduced ZnO nanoparticle to an organic radical was explained by calculations of the inner sphere reorganization at a vacuum interface, with the ZnO nanocrystal and organic radical contributing similar amounts⁷⁸.

Here, we consider explicitly surface oxygen radicals formed from the first hydration layer at a reduced titanium oxide surface. Whether reorganizational energy is dominated by the lower dielectric constant within the electric double layer, or whether the effect of the local charge extends for several water layers from the interface, such that solvent dipoles orient to screen the local charge, is not clear a priori. The studies of the electrochemical interface all consider complexes with ligands around the metal site as the source of the inner sphere reorganization. For the oxygen radical, the electron transfer is from the adsorbed water layer directly, and from oxygen rather than

the metal site. As summarized above, in bulk aqueous solutions, the outer sphere screening of small inorganic ions—beyond the first molecular layer—can be significant for anions, cations, and for redox couples. Finally, theory predicts that the surface oxygen radicals on titanium oxides are accompanied by strong distortions of the metal-oxygen bonds, being referred to as small hole-polarons^{13,15}. It would be important to experimentally substantiate whether free solvent motions are at all relevant to the polaron formation energies.

In the following, we investigate the formation of terminal oxyls at the Nb-doped SrTiO₃/aqueous interface by time-resolved attenuated total reflection infrared spectroscopy. The titanium oxyls are created after band-gap excitation that sends valence band holes to the interface. Previously, a vibration was assigned to the terminal oxyl radical by density function theory calculations of the anticipated infrared spectrum²; the vibration arises from the subsurface layer at 798 cm⁻¹, near the LO phonon. The experimental phenomenology of the line shape shows the vibration to be coupled to the nearby rotational-vibrational (librational) excitations of water by a Fano resonance. Therefore, the system is a good candidate to understand whether the electron transfer from the hydration layer is affected by the water molecules free to reorient in the outer layers. We find that the formation kinetics for the terminal oxyl are very much the same across air, pH 13, pH 7, and pD 13 interfaces which all change the coupled line-shape associated with the high frequency librational motion. While these are related to the high frequency, optical dielectric constant, both the static and optical dielectric constants determine the outer-sphere reorganizational energy²². The formation kinetics are analyzed with a logistic function, and given the results across conditions, the rise is interpreted in the context of a static planar polarization within the Helmholtz layer existing prior to excitation. Therefore, for oxyl radicals at aqueous titanium oxide surfaces, the inner sphere reorganization provided by a bound hydration layer is

enough to account for their stability; the same may be true for other small, hole polarons associated with OER.

5.2 Results

5.2.1 Detecting hole polarons at the Nb-SrTiO₃/aqueous interface

Hole-trapping on titanium oxides at aqueous interfaces has been proposed to occur by the formation of small hole-polarons on oxygen sites. Here, we first briefly recall the salient points of this process, which differs from Marcus-Gerischer approaches at metal interfaces⁷³ in that it occurs from the photo-generated holes in the bands of a semiconductor rather than a tunable electrochemical potential. Theoretical calculations show large spontaneous formation free energies for photo-holes to trap at de-protonated surface sites, leading to either holes on the oxygen lattice (e.g. bridge, lateral) or terminal to the titanium site (e.g. terminal, oxyl). Following the discussion by J. Cheng and M. Sprik^{15,71}, Figure 5.1a shows the Marcus diagrams associated with the reduced surface (PES a) that contains a Ti-OH⁻ within the hydration layer hybridized with the valence band, the oxidized surface with a valence band hole (PES b), and the oxidized surface with a hole-polaron on Ti-OH⁻ creating Ti-OH[•] (PES c). The reorganizational energies for oxidation, λ_O , and reduction, λ_R , are shown with black arrows for the reaction $\text{Ti-OH}^- + h^+ \rightarrow \text{Ti-OH}^\bullet$, when the hole transfer occurs directly from Ti-OH⁻. In the case that the hole first thermalizes to the VB edge, λ_O reduces, λ_O and λ_R are no longer symmetric, and the electron transfer is activation-less in the Marcus sense; this is shown by the gray arrow.

That metastable titanium oxylys are created on Nb-doped SrTiO₃ (n-STO) was investigated previously by ultrafast attenuated total reflection infrared spectroscopy. Figure 5.1b summarizes

the results by showing the density functional theory calculation of the vibrational structure of the metal-oxide for a hydrated surface prior to excitation and for the surface containing a coverage of terminal titanium oxyl after excitation². In place of the symmetric breathing mode in the ground state, an optically active one appears due to the sub-surface oxygen motion perpendicular to the surface and directly underneath the oxyl; it is polarized perpendicular to the surface. The experimental conditions introduced methanol scavengers to correlate the observed vibration with reactive surface oxygens at an aqueous surface². The experimental conditions also varied the doping of the semiconductor². For electron doped STO by Nb, the direction of the electric field drives holes to the interface and the mode is observed, while for undoped and hole doped STO (by Fe), the mode is not observed.

This process occurs in the context of an n-type Schottky barrier at the semiconductor/electrolyte interface, as depicted in Figure 5.1c. Importantly for this study, the vibration associated with the terminal oxyl on Nb-doped SrTiO_3 only occurs for n-doped semiconductors for which a larger inner Helmholtz layer with a polarization perpendicular to the surface plane exists at equilibrium. The equilibrium values of the band edges and the field in the semiconductor and electrolyte are shown vs. RHE²⁷. Upon band-gap light excitation at open circuit, a photo-voltage is created in the semiconductor that flattens the semiconductor bands at an ultrafast timescale; while the field in the Helmholtz layer will eventually respond to this perturbation, it is not directly photoexcited.

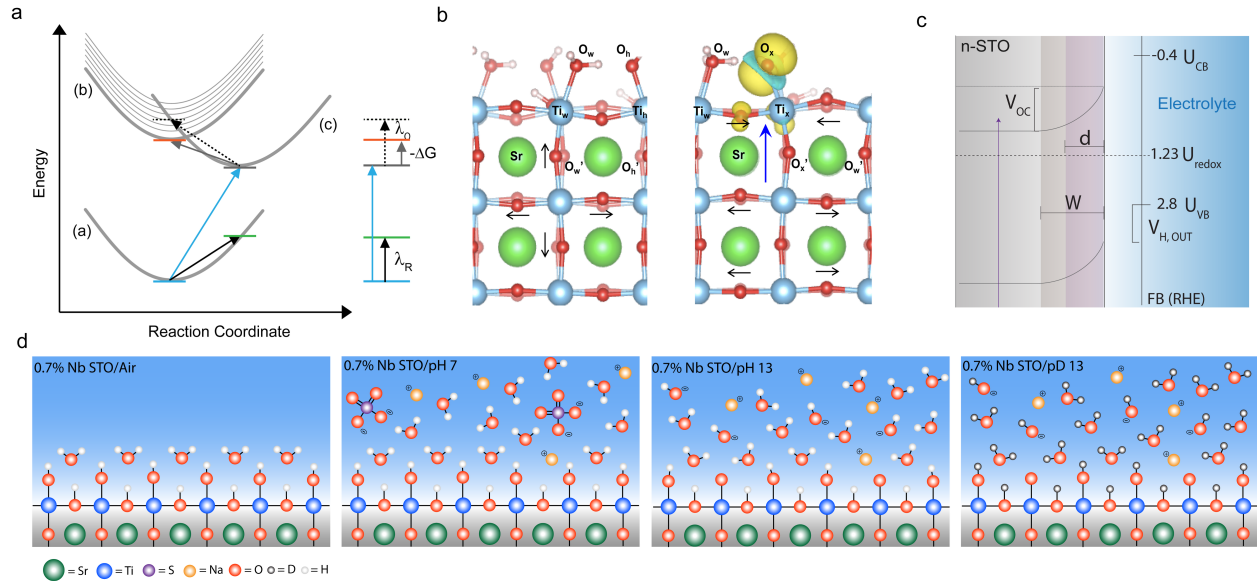


Figure 5.1: Hole-polaron formation, the titanium oxyl's vibration, and the electrolyte conditions at the n-STO/aqueous interface. (a) Marcus-Hush diagram of hole-trapping at an aqueous semiconductor interface as explained in the text with the reduced surface (a), oxidized surface with a delocalized hole (b), and the oxidized surface with the hole-polaron at a distorted metal-oxide coordinate (c) following ref. ¹⁵; λ_O , λ_R are the reorganizational energies for oxidation, reduction respectively and ΔG is the free energy of hole-trapping from the valence band edge. (b) From the reduced surface (left), formation of the titanium oxyl (yellow is the spin orbital) and its sub-surface vibration (blue arrow) as calculated by density functional theory (right) in ref. ² (c) n-STO/aqueous Schottky barrier, where V_{OC} is the open circuit photo-voltage, V_H the voltage drop across the outer Helmholtz layer, and U_{CB} , U_{redox} , U_{VB} are the conduction band, redox, and valence band potentials respectively; d is the excitation depth of the 266 nm light (purple arrow) and W is the depletion width. (d) depiction of the four interfaces probed at the 0.7% Nb-STO surface: air, pH 7, pH 13, and pD 13.

5.2.2 Attenuated total infrared reflectivity and the Fano Resonance of the titanium oxyl

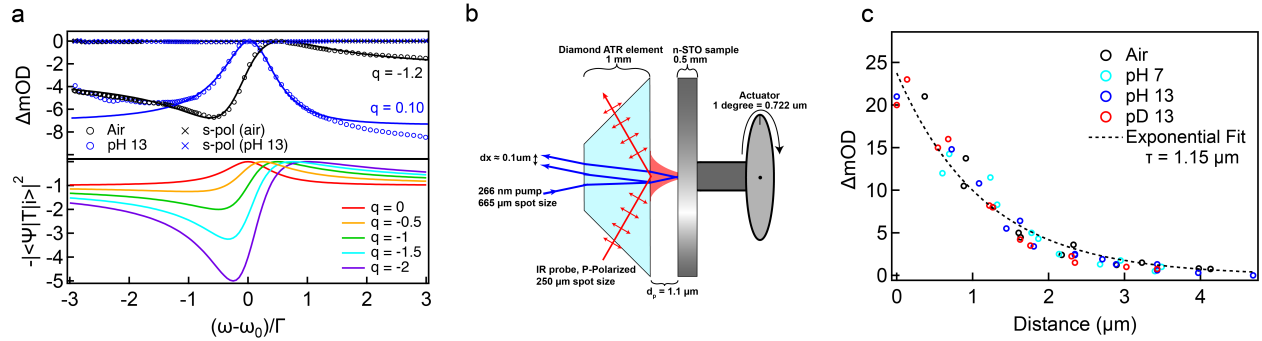


Figure 5.2: The Fano Resonance and experimental ATR geometry. (a) Experimental data taken at the interface of 0.7% Nb STO with air (black circles) and pH 13 (blue circles) with corresponding fits of the Fano lineshape in solid lines (top half). Spectra taken under the same experimental conditions but with the probe set to s-polarization instead of p-polarization are shown as x's. The bottom half of the graph shows a series of Fano line shapes with varying asymmetry factors (q). The sign of the intensity is negative to match the experimental data. (b) The experimental ATR geometry. (c) The experimental signal strength in ΔMOD as a function of the distance in μm between the sample and the ATR element. The distances are relative such that the smallest distance based on the measured actuator angles is set to 0 μm . The signal intensity decays exponentially away from the ATR element.

In the following, we probe the formation dynamics of this mode at the four electrolyte interfaces depicted in Figure 5.1d: air, pH 7, pH 13, and pD 13 with the cation and anion concentration adjusted to be 0.1 M (by $\text{Na}_2\text{SO}_4\text{:NaOH}$, or $\text{Na}_2\text{SO}_4\text{:NaOD}$). The observed vibrational mode of the oxyl exhibits a distinctive Fano resonance, which arises from the coupling of the mode to nearby continua when both are simultaneously excited by the infrared probe. The oxyl's vibration is an interfacial mode, able to couple both with the continuum of the solid (plasma excitations) and that of the liquid (librational excitations of water). Previous work supports a resonance with both continua through spectral comparison obtained by modulating the doping of the solid, comparing air and liquid interfaces, and deuterating the water^{2,39}. The top half of Figure 5.2a shows sample spectra taken at the n-STO interface with air (black) and pH 13 (blue). The bottom half of Figure 5.2a shows a family of Fano lineshapes at specific values of the asymmetry constant q ²¹. Only negative q values are pictured as that reflects the symmetry of the lineshapes studied here. With the introduction of liquid, not only does the vibrational lineshape change with

a second continuum to couple to, but a large constant background arises due to the infrared excitation of both coupled continua at energies not resonant with the vibration (subtracted from the data in Figure 5.2a for a direct comparison with the resonant Fano lineshape). Table 3.1 summarizes the results of also modifying the doping level in STO on the Fano fit parameters at both air and electrolyte interfaces.

In situ ultrafast IR spectroscopy in an Otto attenuated total reflectance (ATR) geometry measures the subsurface vibrational mode. This geometry is depicted in Figure 5.2b where the IR beam, directed into a single bounce diamond ATR crystal, totally internally reflects at the diamond/air (or diamond/liquid) interface. This creates an evanescent wave that probes the sample surface. Due to a spatially decaying Poynting vector, the evanescent wave cannot couple directly to bulk optical phonons in the crystal, such that the ATR signal is dominated by surface modes. The probe (red beam) can be p- or s- polarized at 45° incidence to the normal. The oxyl's vibration is only seen in p-polarization (Figure 5.2a), such that it is indeed a dipole perpendicular to the sample plane as depicted in the calculation (Figure 5.1c). The sample is made parallel to the crystal by aligning the back reflections of the UV pump of the ATR element and the sample, as shown by the blue beams in Figure 5.2b. The STO crystal is brought within the $\sim 1 \mu\text{m}$ evanescent decay of the probe using an actuator where the change in angle can be used to calculate a relative distance in μm 's. Thus, the change in the observed vibrational mode can be tracked as a function of changing z-position relative to the ATR element; the “zero” in z-position is when the diamond crystal and STO sample press against each other, such that the actuator no longer moves the independently from the diamond. Figure 5.2c shows the signal strength to decay exponentially as the sample is moved farther from the diamond, with a rate corresponding to that of the anticipated decay of the evanescent wave for the diamond/electrolyte interface ($1.26 \mu\text{m}$, Equation 2.2). Data

are reported as a change in the reflectance of the probe (ΔR) before and after above bandgap pump excitation (266 nm), calculated as a change in optical density (ΔmOD). A full description of the sample cell, geometry of the setup, and electrolyte conditions can be found in the experimental section and in the background (Figure 2.6).

5.2.3 Time-spectral evolution of the titanium oxyl's vibration across electrolyte conditions

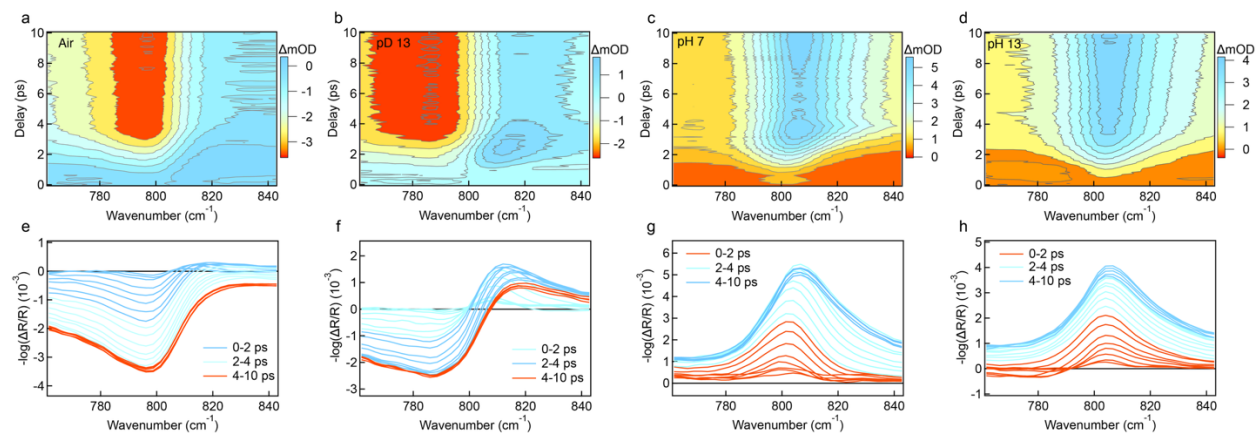


Figure 5.3: Time evolution of the vibrational signal of the n-STO interface in the first 10 ps following UV excitation for four different interfaces. The 2D contour plots depict the full growth of the signal in time for air (a), pD 13 (b), pH 7 (c) and pH 13 (d) interfaces. Select spectra from specific time regimes are shown in (e-h) to illustrate the growth of the spectral shape for each interface. The data is shown for similar z-distance from the ATR element for comparability. At all interfaces, the vibrational peak begins to take form in the first picosecond following excitation and converges to a metastable lineshape by 4 ps. The y-axis of (e-h) corresponds to the ΔmOD of the contour plots and represents a change in absorption based on Beer's Law, or $\Delta mOD = -\log(\Delta R/R) \times 10^{-3}$, where R is the reflectance.

The first ten picoseconds of the oxyl's formation are shown in Figure 5.3 for the n-STO interface with air, pD 13, pH 7, and pH 13. The contour plots for air (Figure 5.3a) and pD 13 (Figure 5.3b) depict an asymmetric spectral shape peaking just below 800 cm^{-1} , while the pH 7 (Figure 5.3c) and pH 13 (Figure 5.3d) contour plots exhibit more a symmetric peak with a maximum intensity slightly above 800 cm^{-1} . The shift in symmetry from highly asymmetric in air where a single continuum dominates to nearly symmetric with the addition of a second continuum in electrolyte aligns with expectations for a Fano resonance, as will be explained in more detail in

section 5.2.4. In all conditions, the signal grows entirely within the first four picoseconds before converging to a steady-state spectral shape.

Spectral slices corresponding to specific time regimes from the air contour plot are shown in Figure 5.3e. The spectral slices show the growth of the signal on the lower frequency side of the lineshape with a peak optical density at 796 cm^{-1} . The contour plot and spectral slices for the pD 13 interface (Figure 5.3f) also show a very asymmetric peak. The maximum negative optical density occurs at lower at 786 cm^{-1} , while the higher frequency side of the spectrum displays a positive peak at 815 cm^{-1} , not observed in air. The largely negative observed optical density can be explained by the refractive indices involved in measuring in an ATR geometry at the solid interface. The highly absorptive nature of the 0.7% Nb doped STO sample leads to changes in both the real and imaginary refractive indices upon photoexcitation due to the added charge carriers exhibiting their own dielectric frequency response. This modifies the reflected intensity of the material in addition to the response of the oxyl, which results in a non-trivial sign for the differential signal.

The spectral slices for pH 7 (Figure 5.3g) and pH 13 (Figure 5.3h) show a symmetric peak with a maximum intensity at 805 cm^{-1} . Both show a small asymmetry with optical density dropping slightly faster on the lower frequency side, reflecting a lower q value. That the peak is flipped from the air/pD13 interface is in alignment with the expectation of a q approaching zero (Figure 5.2a). Further, in the case of two or more continua, excitations of continua that are not resonant with the mode result in a large background superimposed on the Fano resonance²¹. When this background is removed with a consistent negative sign for the ATR differential signal for both air and

electrolyte, the spectrum appears as a dip rather than a peak (Figure 5.2a). The background also creates positive peak for pH 13, which if removed would instead approach zero.

The data underwent two procedures to remove artifacts and non-sample related background signals, as described in the experimental section and Appendix B (Figure B.1). Also shown in Figure B.3 is the growth of a transient signal measured in the same frequency range for gallium nitride (GaN). The GaN response begins to grow immediately following time zero with a significantly faster initial rate than that of the STO signal, demonstrating the time resolution of the experiment as measured by a cross-correlation (400 fs, Figure 2.4).

The presented contour plots were chosen at similar distances from the ATR element. Four more contour plots at different z-positions ranging from 0-2.5 μm are shown for each interface in the supplemental information (Figure B.3-contours and Figure B.4-spectra). Contours are largely consistent with z-position, showing similar growth kinetics. Smaller z-distances show larger signal intensity, as expected in an ATR geometry with a decaying evanescent wave. Small changes in the Fano asymmetry can be observed with peak optical density shifting to lower frequencies as the z-distance is shortened, which will be explored in section 5.2.4.

To extract the growth kinetics from a vibrational cross-section independent of the Fano parameters, each spectrum was integrated over the measured frequency range ($760\text{-}840\text{ cm}^{-1}$). A diagram of this integration for a single pH 13 spectrum is provided in Figure 5.4a. This integrated spectral weight, or S, is extracted at each time delay, thus yielding the kinetics of the spectral growth, S(t). Figure 5.4b depicts S(t) for both the air (black) and pH 13 (blue) interfaces for a range of above band gap pump fluences from 0.04 mJ/cm^2 to 0.5 mJ/cm^2 . Data was collected at a single z-position relative to the ATR element for each interface. For both air and pH 13 interfaces, the spectral weight begins to grow immediately after time zero. After a slow initial growth period, S

risers rapidly before reaching a saturation around 4 ps following excitation. The growth kinetics are unchanged with the addition of pH 13 electrolyte or with fluence in either air or pH 13. Similar plots for pD 13 and pH 7 are provided in Figure B.5, which also show unchanging growth kinetics. Due to the symmetry of the pD 13 signal around zero and the presence of a constant positive background, the Fano lineshape is first shifted and then the integration performed to obtain $S(t)$ as explained in Appendix B (Figure B.6).

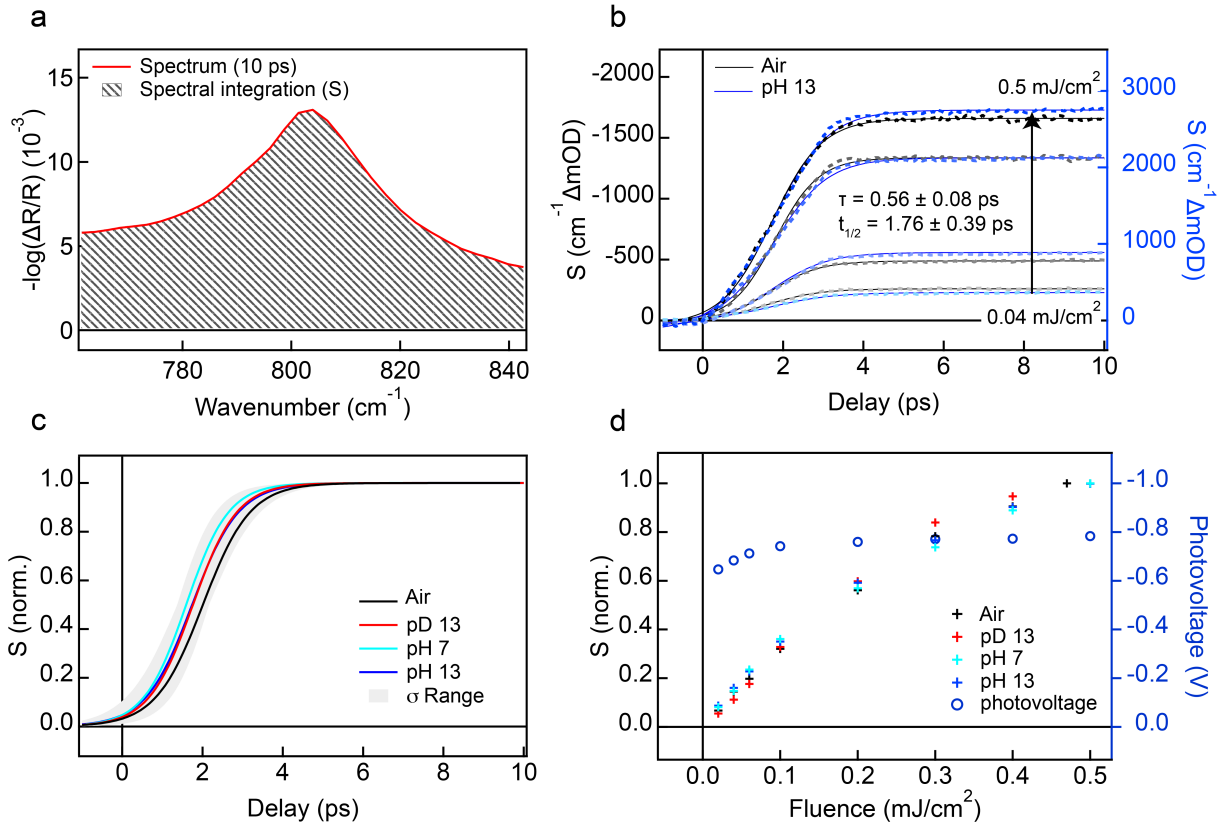


Figure 5.4: Extraction of time dynamics by spectral integration. (a) depicts the integration of a spectrum at the pH 13 interface to extract S , the integrated spectral weight. (b) shows the time evolution of $S(t)$ for air (black) and pH 13 (blue) interfaces along with their corresponding logistic fits for data taken at a single z -position with multiple fluences. The overall average rate (τ) of all the data is given as 0.56 ps. The normalized average fits for each condition are given in (c) based on the extracted rates (τ) and half-rises ($t_{1/2}$). The average for each condition fits well within the overall range of the data plus/minus one standard deviation of the average rate and half rise of all conditions (gray shaded region). (d) depicts the equilibrated value of S (taken at 10 ps) plotted against fluence for all conditions and normalized such that S at the highest fluence is one. For all conditions, S grows linearly at low fluences, while growth slows and begins to saturate at fluences above 0.2 mJ/cm^2 . Also shown on the right axis is the open circuit photovoltage for n-STO which is nearly saturated at 0.8 V at the lowest fluence taken (0.02 mJ/cm^2).

Previous work at the air interface²⁸ showed that the S-shaped rise in the kinetics is best fit using a logistic function (Equation 5.1). A logistic function is the solution to a differential equation for population growth that is barrierless and exponential near $t \sim 0$ but then slows down proportionally to the population. Using an exponential rise instead ($1 - e^{-t/\tau}$) that describes a first order rate law for a reactant does not fit the data, as shown previously for air⁷⁹. The logistic function includes both a growth rate ($1/\tau$) and population half rise ($t_{1/2}$), in addition to the asymptotic limit of the population (max):

$$f(t) = \frac{\text{max}}{1 + \exp\left\{\frac{t_{1/2} - t}{\tau}\right\}} \quad \text{Equation 5.1}$$

Figure 5.4b shows that the logistic fitting leads to unchanging ($1/\tau$) and ($t_{1/2}$) between the air and pH 13 interfaces, and this is consistent across the fluence range. Figure B.5 shows that the rate and half-rise remain consistent for pD 13 and pH 7. Figure B.7 shows that, like fluence, the z-distance does not modify the growth kinetics appreciably. A full list of fit parameters for all data sets can be found in Tables B.1 (fluence) and B.2 (z-dependent). Some data sets show a non-equilibrium transient in the kinetics, such as the z-dependent pD 13 data (Figure B.7c). While this transient can affect the quality of the logistic fits, the extracted rate and half-rise remain within the standard deviation of the data sets.

Figure 5.4c shows the normalized logistic fits for each interface plotted using the average τ and $t_{1/2}$ obtained using the full fluence- and z- dependent data sets. The average τ and $t_{1/2}$ for all interfaces results in $\tau = 0.56 \pm 0.08$ ps and $t_{1/2} = 1.76 \pm 0.39$ ps. The gray shaded region represents $\pm$ one standard deviation of both the rate and half-rise. While there is some variation between the interfaces, all are well within this standard deviation. A one-way analysis of variance (ANOVA) statistical test was performed to compare τ between conditions and showed no statistical

difference between the four interfaces with a P-value of 0.8. The full results of this test are given in Table B.3. Figure B.8 explores the effect of varying τ and keeping constant, and vice versa, within a standard deviation each.

The change in signal strength, expressed as a normalized spectral weight at ~ 10 ps, is given as a function of fluence for each interface in Figure 5.4d. The magnitude of S is normalized such that it equals one at the highest fluence taken for each condition (~ 0.5 mJ/cm²). Across all four conditions, the signal grows approximately linearly until around 0.2 mJ/cm², after which the growth slows and begins to saturate. The right axis of Figure 5.4d shows the open circuit photovoltage for 0.7% Nb STO taken in pH 13 electrolyte as a function of fluence. Unlike the signal strength, the photovoltage (0.8 V) saturates at the lowest measured fluence (0.02 mJ/cm²), which shows that the formation of the titanium oxyl and its vibration is not limited by the electric field driving holes to the surface.

5.2.4 Analysis of the time-evolution of the Fano resonance across electrolyte conditions

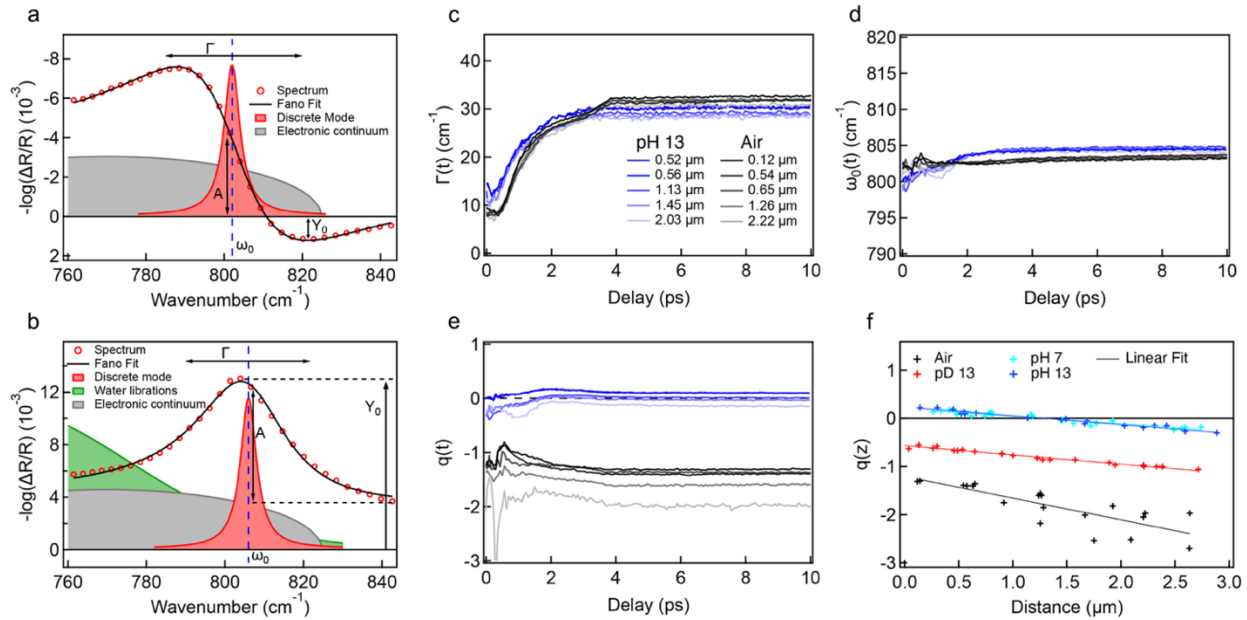


Figure 5.5: Free form Fano fits of spectral dynamics. (a) illustrates the Fano fit (black line) of the vibrational lineshape (red dots) that results from the excitation of a discrete mode (red) and the coupled continuum (gray) by the infrared probe at the n-STO/air interface. (b) shows the same for the pH 13 interface and includes the coupled water librational continuum (green). (c-e) show the time evolution of the extracted Fano parameters for the air (grayscale) and pH 13 (bluescale) interfaces: (c) the coupling constant Γ , (d) the resonant frequency ω_0 , (e) the asymmetry constant q . (f) provides the dependence of q on the distance between the sample and the ATR element in μm with corresponding linear fits.

Although the growth kinetics of the oxyl's vibrational signature extracted via $S(t)$ appear unchanged with factors such as interface and z -position, it is evident in Figure 5.4 that the spectral dynamics changes with the interface, and so it makes sense to examine the time-dependence of each of the Fano parameters that define it. Why the spectral lineshape changes so drastically with interface and noticeably with z -position yet exhibits no measurable difference in growth kinetics, is not a priori clear. Here, we extract these growth kinetics from the Fano resonance itself (Equation 5.2) rather than the integrated spectrum. The left side of Equation 5.2 is the intensity measured by the spectroscopy with Ψ being the wavefunction of the vibration coupled to the continua, T being the transition dipole operator, and i being the initial state of the system such that $|\langle \Psi | T | i \rangle|^2$ is the square of the transition dipole moment and thus the measured spectral intensity. This intensity is

dependent on the difference between the measured frequency (ω) and the resonant frequency (ω_0). ω_0 is the frequency of the discrete mode (the subsurface vibration) after coupling with the continua. The $A(t)$ term in Equation 5.2 represents the intensity of the coupled continua light excitations defined as $\langle \psi | T | i \rangle$ where ψ is the wavefunction of the continua. The Y_0 term is the same but for continuum excitations not resonant with the mode and is frequency independent in the region of the mode. The spectral width is defined by Γ which corresponds to the square of the coupling constant between the mode and continua. The Fano lineshape can be thought of as an asymmetrical Lorentzian with an asymmetry factor q . Indeed, when $q = 0$, Equation 5.2 simplifies to a Lorentzian and Γ is equal to the full width at half maximum (FWHM) of the peak. The spectra can be freely fit with Equation 5.2 without accounting for ground state bleach as the vibrational mode is not present in the ground state.

$$|\langle \Psi | T | i \rangle|^2 = \frac{A(t) \left(\frac{2(\omega - \omega_0)}{\Gamma(t)} + q \right)^2}{1 + \left(\frac{2(\omega - \omega_0)}{\Gamma(t)} \right)^2} + Y_0 \quad \text{Equation 5.2}$$

Figure 5.5a provides a depiction of the overlapping bare vibrational mode and the continuum excitations at the air interface, the coupling of which results in the observed Fano lineshape. Figure 5.5b depicts the same for the pH 13 spectrum, where there exists an additional continuum on the liquid side of the interface. In both cases, electronic plasma excitations of the doped substrate have a broad absorption peak centered at $400\text{-}500 \text{ cm}^{-1}$ (grey)³⁸ and extending past the narrow vibrational mode (red). For the liquid interface, regular water has a broad librational continuum centered at 675 cm^{-1} (green)^{80,81}. Also depicted are the Fano parameters ω_0 , Γ , A , and Y_0 and how they are reflected in the spectral shape.

Asymmetry of the lineshape arises when the coupled continua and mode are simultaneously excited by the infrared probe. This is defined by the q parameter and is proportional to the ratio of excitations of the screened mode ($|\langle\phi|T|i\rangle|^2$) to coupled continua excitations ($|\langle\psi|T|i\rangle|^2$) (Equation 5.3).

$$q^2 = \frac{2|\langle\phi|T|i\rangle|^2}{\pi|\langle\psi|T|i\rangle|^2\Gamma} \quad \text{Equation 5.3}$$

The denominator represents the number of excited states of the continua that are within the width Γ of the mode. As $|\langle\psi|T|i\rangle|^2$ is reported as a density of states, q is unitless. This q value is thus very dependent on experimental factors that change the density of states of the continua, such as the doping level of the material or the interface (air, liquid). At the STO/air interface, only one continuum (that of the semiconductor) is strongly present, resulting in the highly asymmetric lineshape observed in Figure 5.3. In the case of pH 13, the more symmetrical shape is a result of adding another broad continuum to the system, thus increasing the continuum excitations in the denominator and lowering the q value. The q -value of the STO/pD 13 interface lies in between. The librational continuum of D₂O peaks near 500 cm⁻¹,⁸² farther from the vibrational mode than that of H₂O (675 cm⁻¹). This results in a lower density of states near the resonant energy, thus less continuum excitations within the width Γ of the mode and a higher q value than at the pH 13 interface.

The negative optical densities for the 0.7% Nb doped STO sample discussed with Figure 2 reflect in the A coefficient, which defines the signal intensity and is negative for all data defined here. There does exist a second unique set of fits for all interfaces where A is positive³⁹. At the electrolyte interface, one must interpret the symmetric lineshape with positive A in the $q \rightarrow \text{infinity}$ regime, which does not align with the physical experimental conditions of having two continua present. In the case of negative A , q becomes negative at all interfaces, and near zero at the

electrolyte interface, which aligns with having multiple continua present in the system. The observed positive optical density in electrolyte is then readily explained by the presence of a large background, Y_0 , that appears with one or more continua are coupled to the mode²¹ (Figure 5.5b). With only the continuum of the semiconductor in air, Y_0 is a small experimental background.

The time dependence of the Fano parameters in the first ten picoseconds from free fitting Equation 5.2 is shown in Figure 5.5(c-e) for both the air and pH 13 interfaces at multiple z-positions. Sample spectra and corresponding Fano fits at specific time delays are given in Figure B.9 to show the quality of the fits. For both interfaces, Γ (Figure 5.5c) shows a consistent time-dependent growth, starting from a base of 10 cm^{-1} and growing to an equilibrium value of approximately 30 cm^{-1} by 4 ps. There is a small difference in the equilibrated value of Γ , with air and pD 13 having a larger width by $\sim 3 \text{ cm}^{-1}$ at a comparable z-position (see also Figure B.10).

Across all interfaces, q and ω_0 are relatively time independent. While there are slight changes observed at early times in ω_0 (Figure 5.5d), they are within the $\sim 2.7 \text{ cm}^{-1}$ resolution of the detector. A small increase in ω_0 of approximately 3 cm^{-1} is observed as the interface is changed from air to pH 13. Such a change is expected as ω_0 is the frequency of the coupled mode, and another continuum is present to couple to once electrolyte is added. The pH 7 interface shows a similar ω_0 as pH 13, and pD 13 lays somewhere in between. The q parameter changes significantly with interface as anticipated, with values as a function of z-distance between -1 and -2.5 in air and near zero (-0.2 to 0.2) in pH 13. Figure B.10 shows q for pD 13 to range between -0.5 and -1 with z-distance, between the values of air and pH 13.

The time dependence of A and Y_0 are given in Figure B.10 for all interfaces. Previous work in air⁷⁹ shows $A(t)$ to have similar growth kinetics as $S(t)$ and $\Gamma(t)$. This behavior agrees across all four interfaces examined here. Some data shows evidence of non-equilibrium transients in $A(t)$

before the kinetics stabilize. In air, with a single continuum present, Y_0 is observed to be small and close to zero with a rise and decay within the first 4 ps. In contrast, a large, positive Y_0 is observed in both pH and pD conditions, as expected with the addition of a second continuum. This Y_0 is similar in magnitude to the Fano A parameter, and shows a similar growth kinetics as S, Γ and A in electrolyte conditions.

The asymmetry parameter q changes markedly with the overlap of the STO/electrolyte interface with the evanescent. Across all interfaces, q (Figure 5.5e) is shown to increase linearly with decreasing z -distance. As the sample is moved closer to the ATR element, the intensity of the evanescent wave reaching into the STO crystal increases exponentially. The mode excitation exists in a single layer at the surface, while the continuum excitations are taken from some volume of the semiconductor where coupling can occur (and of the liquid when present). Thus, as the z -distance gets smaller and more of the electronic excitations in the STO crystal are probed, the contributions from the continua will increase more rapidly than those from the mode, which results in a decrease in the magnitude of q with z -position. Type III ANOVA statistical tests were performed to further quantify the effect z -distance on the equilibrated values of ω_0 , Γ , and q (Figures B.11-B.13). The results, summarized in Tables B.4 and B.5, concurred with the above observations, with correlations for Γ and q with z -distance but not for ω_0 . The smaller change in Γ with z -distance could result from a vibrational coupling constant dependent on the extent of excited continuum.

Time-dependent Fano parameters for data taken at a single z -position for a range of fluences from 0.04-0.5 mJ/cm² are shown in Figure B.14 for each interface. Overall, the growth kinetics do not change with fluence, and the equilibrium values of q , ω_0 , and Γ are consistent across all the data sets (see Tables B.6 and B.7 for a summary of all parameters).

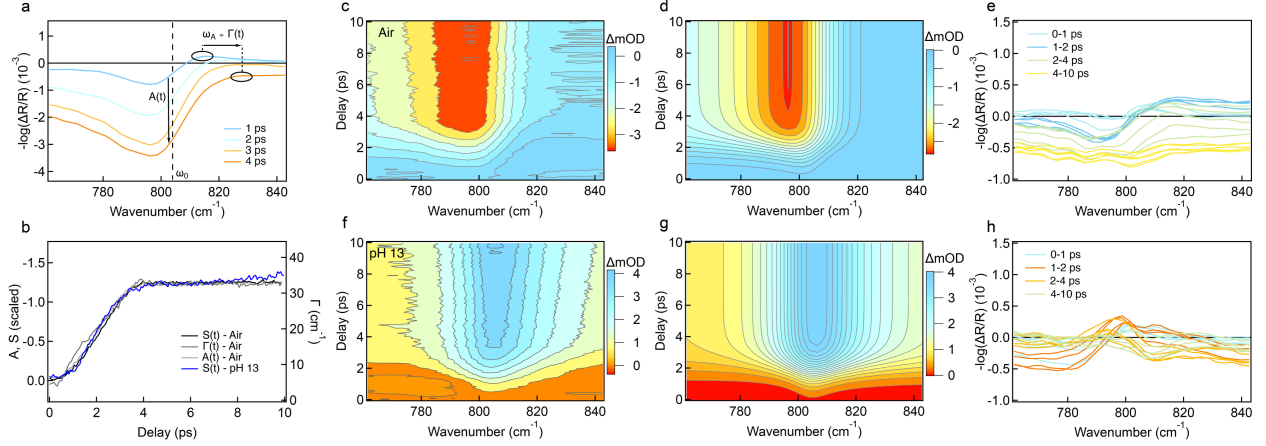


Figure 5.6: Modelling the equilibrated PES of the oxyl and the non-equilibrium transient. (a) illustrates the spectral growth of the vibrational signature at the air interface in the first 4 ps. Depicted is the growth of the signal at the resonant frequency ω_0 used to extract the time evolution of the coupled continuum excitations $A(t)$, and the changing of the anti-resonance frequency ω_A used to extract the growth of the coupling constant $\Gamma(t)$. (b) shows the time evolution of $A(t)$, $\Gamma(t)$, and $S(t)$ in air along with $S(t)$ in pH 13. (c-e) depict the data contour plot (c), model contour plot (d), and difference spectral slices (e) for the n-STO/air interface. (f-h) show the same for the pH 13 interface. The input parameters for the model are defined in the text.

Since $S(t)$, the bare vibrational cross-section, has similar growth kinetics as $A(t)$ and $\Gamma(t)$, the parameters that define the coupling to the continuum, the coupling dynamics do not define the growth. That the q and ω_0 Fano parameters are time-independent also define a vibration that, once present, instantaneously couples to the continuum. Given the time-independence of q and ω_0 observed, one can evaluate the Fano lineshape (Equation 5.2) at the resonant frequency of the coupled mode (ω_0) to extract $A(t)$ separately from the free fits. Similarly, evaluating the Fano equation at the anti-resonant frequency (ω_A) can be used to extract $\Gamma(t)$. A depiction of this process in Figure 5.6a shows $A(t)$ and $\Gamma(t)$ for an air spectrum growing in time from 1 to 4 ps. Further details on this extraction are given in the supplemental (Figure B.15).

The resulting $A(t)$ and $\Gamma(t)$ for air are shown plotted with $S(t)$ in Figure 5.6b. When normalized, the growth of the three parameters has the same sigmoidal shape. The extracted $A(t)$ exhibits less non-equilibrium transient behavior than the free fit A (Figure B.10). $\Gamma(t)$ looks

significantly different in shape than the free fit Γ (Figure B.15). The symmetry of the spectrum at the pH 13 interface complicates the extraction of $A(t)$ and $\Gamma(t)$ by the resonant and anti-resonant frequencies. Since the air data shows such agreement between $S(t)$, $A(t)$, and $\Gamma(t)$, the average logistic parameters found using $S(t)$ for all interfaces will be used to model the full time and spectral dependence of the data.

The same logistic growth parameters $\tau = 0.56$ ps and $t_{1/2} = 1.76$ ps are used to model the full contour plots for all four interfaces in Figure 5.6 air (c,d), pH 13(f,g) (also Figures B.16 and B.17 respectively) and in Figure B.18, B.19 for pD 13, pH 7. Additional time-independent inputs for air include $q = -1.97$ (Figure 5.5e), $\omega_0 = 804$ cm⁻¹ (Figure 5.5d), a maximum for $A(t)$ of -0.58 mOD (Figure B.10d), and a base of 10 cm⁻¹ to a maximum of 30.8 cm⁻¹ for $\Gamma(t)$ (Figure 5.5c). For pH 13, they include $q = -0.15$ (Figure 5.5e), $\omega_0 = 804.1$ cm⁻¹ (Figure 5.5d), a maximum of -4.07 mOD for $A(t)$, (Figure B.10d), and a base of 10 cm⁻¹ to a maximum of 28.2 cm⁻¹ for $\Gamma(t)$ (Figure 5.5c). A Y_0 term is added for pH 13 with the same logistic growth from a zero base to a maximum of 4.0 mOD (Figure B.10e).

Figure 5.6c, 5.6d, and 5.6e show the data contour for the air interface, the model, and resultant difference spectral slices for several time delays. The spectral slices show a small frequency dependent transient with an asymmetric shape that appears in the first picosecond, but that then becomes a frequency independent transient background beyond 4 ps. The resultant difference contour is given in Figure B.16. Figure 5.6f, 5.6g, and 5.6h show the data contour for the pH 13 interface, the model, and difference spectral slices with similar conclusions for the transients. Model results for the pD 13 and pH 7 interfaces at similar z-positions are given in Figures B.18 and B.19 respectively. The transients are somewhat higher at these two interfaces which we attribute to factors such as beam and sample alignment.

The same modeling process was performed at a second sample z-position closer to the ATR element for each interface. The results are shown alongside the first z-position for each interface in Figures B.16-B.19, with essentially the same results as above for the comparison between the model and the data. With all interfaces, the transient increases by a factor comparable to that of the overall signal strength which suggests that the transient originates from the pump excitation of the STO interface. One possibility is that the photoexcitation creates a short-lived excited state continuum that only exists on the order of a few picoseconds. If the vibrational mode couples to this excited state continuum, a short-lived Fano lineshape would be added on top of the longer-lived signal arising from the ground state continuum.

5.3 Discussion

We investigated four different solvent interfaces to 0.7% Nb-STO—air, pD 13, pH 7, and pH 13—for the formation kinetics of the terminal oxyl radical. These interfaces significantly change the ability of the free solvent motion to screen the radical through the number of free solvent layers (comparing air to electrolyte), the protonation of the solvent (comparing pH 7 to pH 13), and the rotational-vibrational energy levels of the solvent (comparing pD 13 to pH 13). Since the q-factor of the Fano resonance between the oxyl vibration and the solvent motion is inversely proportional to the coupled solvent density of states, it is a direct measure of the free solvent motion associated with the high frequency optical dielectric constant; it changes from -1.6 in air, to -0.8 in pD 13, to -0.1 in pH 13. The q-factor also changes with the overlap between the evanescent wave and the interface; as the overlap increases, the importance of the electron plasma continuum in the solid increases while the solvent continuum persists, and the q decreases. While the change

in the free solvent motion available for screening is clear, the same formation kinetics are observed for the oxyl radical: a logistic function rise with a rate of 0.56 ps and half-rise of 1.76 ps.

The following discusses the origin of the kinetic invariance, and thus, negligible outer-sphere reorganizational energy. To do so, we first review the expectations for hole-trapping based on theoretical calculations, including density functional theory and the Marcus phenomenological model, that suggest why the inner-sphere reorganizational energy might predominate for these interfaces. This conclusion is put forward in context of what could change the reorganizational energies across the experimental conditions chosen, which are the hydration layer (inner), the interfacial electric fields (outer), and the librational motion (outer). Then, the discussion is focused on the commonalities across all conditions and the measured formation dynamics by the Fano parameters to present a hypothesis for what—instead of the reorganizational energies—could govern the picosecond formation dynamics of the titanium oxyl.

The expectations for hole-trapping at a semiconductor surface adapt Marcus-Hush theory to a semiconductor bandgap, which can reflect HOMO-LUMO gaps of molecules albeit with continuous energy levels for delocalized carriers that are not present in molecules. An adaptation has been made that incorporates both vertical ionization energies and adiabatic levels⁷¹, with rutile TiO₂ as a prominent example¹⁵. As depicted in Figure 5.1a (adapted from ref.¹⁵), the thermalization of the hole to the valence band edge lowers the reorganizational energy for oxidation (λ_O) compared to reduction (λ_R) such that the two are no longer equal, *i.e.* the non-linear response regime of electron transfer theory. Compared to the OH⁻/OH[•] redox reaction in bulk water for which activation energies are large by both experiments and calculation^{15,71}, the hole transfer from the semiconductor to the surface is barrierless, being located maximum of the Marcus-Hush curves such that $\lambda_O = -\Delta G(U_{VB})$; $\Delta G(U_{VB})$ is the hole-trapping free energy from the valence band edge.

Furthermore, in calculations of ΔG (U_{VB}), often a single adsorbed layer is used, and further layers do not markedly change the estimates, leading to formation free energies of the titanium oxyl of -0.67 eV on SrTiO_3 ¹³ and of -0.71 eV and -0.84 eV on rutile TiO_2 by two separate calculations^{13,15}. Thus, the theoretical calculations suggest that the inner reorganizational energy of the lattice and bound solvent predominates and leads to barrierless hole-transfer. In comparison, the reorganizational energy for the $\text{OH}^-/\text{OH}^\bullet$ reaction in bulk aqueous solutions is 3 eV by similar calculations⁸³. The work here is a test of whether the kinetic description for oxide surfaces is correct, by systematically introducing free solvent motion that could change the outer sphere reorganizational energy.

While the interfaces differ by the availability of solvent librational motion, they are more alike in their first couple of adsorbed water layers that determine the inner reorganizational energy of adsorbed water species. For the 0.7% Nb STO interface with gas phase water, ambient pressure x-ray photoemission spectroscopy (AP-XPS) measured two adsorbed layers by 2% RH¹⁷. That same study also found that the water fully dissociates in the first layer, leading to a surface monolayer of hydroxyls¹⁷. Under pH 13 conditions, there could be a propensity to dissociate these hydroxyls to bare oxygen but that has not been quantified. Nonetheless, the AP-XPS characterization suggests that the air, pH 7, and pH 13 interfaces are alike in terms of a large degree of de-protonation, and that at least two layers of water are adsorbed across all conditions in the optical laboratory.

The interfaces do change in their ability to support an interfacial electric field through a Helmholtz layer, which can affect the static dielectric constant of water and therefore the outer-sphere reorganizational energy. All the interfaces are highly doped and so support a Helmholtz layer at equilibrium. As described previously²⁷, the Helmholtz fields have been derived from

photo-electrochemical measurements for the pH 7 and pH 13 interfaces. In open circuit conditions, the floating potential at the back of the electrode equilibrates to redox potential of OER (U_{redox}), such that the voltage applied across the interface is $U_{\text{redox}} - U_{\text{FB}}$ where U_{FB} is the flatband potential. Since U_{redox} of OER and U_{FB} change equivalently with pH due to proton transfers to solution (−59 mV/pH), the potential drop across the interface is then understood to be constant with pH⁷³. However, the proportion dropped across the semiconductor (V_{SC}), the inner Helmholtz layer ($V_{\text{H, IN}}$), and the outer Helmholtz layer ($V_{\text{H, OUT}}$) can change with pH. If the hydroxylation changes, there is a pH dependence of $V_{\text{SC}} + V_{\text{H, IN}}$ that is presumed to be compensated at $V_{\text{H, OUT}}$. One way to measure $V_{\text{SC}} + V_{\text{H, IN}}$ is by the open-circuit photo-voltage V_{OC} . As shown previously, V_{OC} increases from −0.85 V at pH 13 to −0.5 V at pH 7. With $U_{\text{redox}} - U_{\text{FB}} = 1.73$ and the measured V_{OC} , one obtains $V_{\text{H, OUT}} = 0.88$ V at pH 13 and $V_{\text{H, OUT}} = 1.23$ V at pH 7. Therefore, the inner and outer Helmholtz fields range across interfacial conditions. They are also large ($V_{\text{H, OUT}} \sim 1$ V) across all interfacial conditions which limits the ability of water to polarize freely around electron transfer.

The equilibrium conditions suggest that the inner sphere reorganization is similar across the interfaces, while the outer-sphere reorganization is likely impeded by the strong electric fields in the Helmholtz layer. Because these are the equilibrium conditions, they most readily report on the static dielectric constant. We now turn to changes the Fano resonance that measures the density of states for high frequency, librational motion. In the Fano resonance, the off-diagonal term (V) in the Hamiltonian couples the vibrational dipole to the dipolar solvent motion. Usually, dipolar coupling is associated with a nanometer scale from the interface, which incorporates a couple of layers of water. The width of the Fano lineshape is determined $\Gamma = \pi V^2$ and across the interfaces measured here and with lower doping³⁹, amounts to a range of 30-45 cm^{−1}. Thus, what changes

the q across the interfaces is the density of states, which may be more water layers within the spatial scale of the coupling, the density of those water layers, or changes in water motion within the H-bonded network. The pD 13 case shows explicitly that when the librational motion is of lower energy, less couple to the vibrational dipole.

Another conclusion can be drawn from the formation dynamics captured by the Fano resonance. Since the continuum density of states $A(t)$, background $Y_0(t)$, and dipolar coupling $\Gamma(t)$ all have essentially the same rise as the bare vibrational cross-section measured by $S(t)$ and q is time-independent, the rise then is not due to the coupling time of the vibration to the solvent. Moreover, the width parameter Γ suggests a coupling time of ~ 100 fs, which is much faster than the couple of picoseconds rise. Thus, once the vibrational cross-section is formed, it couples to the continuum instantaneously. Given that $\Gamma(t)$ rises with the same dynamics as $A(t)$ and $S(t)$ this also suggests that the strength of the vibrational coupling to the excited continuum is dependent on the degree to which the bare vibrational dipole is present.

One way to understand how the static and high frequency dielectric constants for these systems leads to a low outer sphere reorganization energy is the phenomenological description given by Marcus²² for which the solvent reorganization energy is proportional to $(\frac{1}{D_\infty} - \frac{1}{D_s})$; optical is D_∞ and static is D_s . If D_∞ of bulk water drops from 80 to 2-3 at an interface⁷⁴, then it would be in the range of D_∞ near 2 at 800 cm^{-1} . In addition to needing to know the change in the dielectric constant at the interface, such phenomenology can obscure molecular details, especially for the first hydration layer⁶⁷. So, while such effects need to be measured, the results show that the phenomenological description can rationalize the lack of solvent reorganization energy for oxygen radicals trapped within the first 1-2 hydration layers.

We now turn to a hypothesis as to the origin of the formation dynamics given that the solvent does not play a role and that the Fano resonance reports on the vibrational cross-section of the mode, rather than any coupling dynamics. This hypothesis utilizes instead the global conditions under which the vibration for the titanium oxyl forms, the couple picosecond formation kinetics, and the detailed fit of the kinetics by a logistic function. The vibrational cross-section of the oxyl radical is only seen in p-polarization (shown in Figure 5.2a)², which means it only has a moment perpendicular to the sample plane. The samples are all n-doped, which means that there is a planar electric field also perpendicular to the sample plane; the vibration is not seen for undoped samples². For all the electrolyte conditions, the outer Helmholtz plane is measured to contain a strong electric field²⁷. The same could be anticipated for the air interface, if at least two layers of water form. The hole-trapping is expected to occur in the first adsorbed layer and that first layer is likely to be quite de-protonated across all conditions, given the strong water dissociation of the 0.7% Nb STO surface measured by AP-XPS¹⁷.

Given these common global conditions and the high free energies for surface hole trapping, we can suggest that while the hole-trapping is spontaneous, it takes time for the titanium oxyl to orient its dipole according to the static electric field that exists prior to excitation in the Helmholtz layer. At the earliest timescales, the hole-trapping event is barrierless, as one would expect for Marcus-Hush theory at a semiconductor surface^{15,71} and measured here by a rising exponential (e^{rt}) that describes a logistic function at $t \sim 0$. The reorganizational energy associated with this hole-transfer event is then the inner reorganizational energy associated with the titanium oxide and the first, adsorbed layer. After hole-trapping, the titanium-oxyl encounters the field in the Helmholtz plane and starts to orient itself to it. The vibration is then also created with a polarization perpendicular to the surface. Since the vibrational cross-section is of a surface coverage of

titanium oxyl's, a net-polarization of the oxyl's is also a planar field perpendicular to the surface. The saturation in the vibrational cross-section $S(t)$ (shown in Figure 5.4d) could be related to a saturation in the induced polarization within the Helmholtz field. This would be consistent with a logistic function in which the exponential rate slows down as the population increases and eventually becomes zero as a limiting coverage is reached, as anticipated by the Clausius-Mossotti phenomenology. So, while the polarization that dominates the (inner) reorganizational energy is a matter of modifying bonding, another polarization exists associated with the planar, static Helmholtz field prior to hole-trapping and the polarization of the titanium oxyl and its infrared dipole to it could explain the observed formation dynamics. The orientation time for molecular dipoles in water is suggested to be picoseconds, with one molecular dynamics and analytic calculation for a generic dipole inside of a capacitor with a dielectric of water showing timescales up to 5 ps⁸⁴.

5.4 Conclusions

Here, the solvent dynamics are tracked spectroscopically by a Fano resonance of the titanium oxyl's vibration with the librational modes of water while simultaneously measuring constant ultrafast formation kinetics. The well-defined growth kinetics of a logistic function—with a rate of 0.56 +/- 0.08 ps and a half rise of 1.76 +/- 0.39 ps—are all within the standard deviation of data sets tracked across four interfaces (air, pH 7, pH 13, pD 13) and using both fluence and overlap between the interface and the evanescent probe to quantitatively define the kinetics. That the growth kinetics are unchanged shows that the photo-driven formation of titanium oxyis is truly within the regime dictated by the energetics of surface adsorption. This is an important finding justifying the methods for calculating adsorption energies of OER

intermediates and more generally, the stability of surface hole polarons on semiconducting oxides. Rather than the reorganizational energies associated with the formation of the hole-polarons, the picosecond rise is suggested to be related instead to the orientation of the titanium oxyl and its vibration to the static electric field within the Helmholtz layer that exists prior to excitation. Therefore, the quantitative nature of the growth kinetics recorded here also motivate ab-initio molecular dynamics simulations of infrared dipoles of reactive oxygen intermediates at aqueous and electrified interfaces.

5.5 Experimental Methods

Sample and ATR Cell: 0.7% Nb-doped by weight SrTiO₃ single crystal samples with a (100) crystallographic orientation were acquired from MTI. The crystals measured 10 mm x 10 mm x 0.5 mm in size, with the front side of the sample polished to an arithmetic mean roughness of 0.5 Å.

For each measurement a custom-built ATR cell made of PEEK plastic was employed, shown in Figure S1. The internal reflection element (IRE) used was a single-bounce 45° trapezoidal diamond (GladiATR plate, PikeTech) with a 1 mm front facet and 1.4 mm side facets. The STO samples were mounted within the cell using epoxy (Loctite 615). While the epoxy was still wet, the sample was lightly pressed against the IRE using a Thorlabs Polaris P20 actuator and allowed to fully dry, ensuring the crystals' alignment was parallel with the IRE.

The pH 7 and pH 13 solutions were created by dissolving appropriate amounts of Na₂SO₄ and NaOH respectively in deionized water to create 0.1 M solutions. The pD 13 solution was produced by dilution of concentrated NaOD solution to 0.1 M with purified D₂O.

Transient Infrared Setup: The pump and probe beams were generated using a Legend Coherent Elite amplifier Ti:sapphire laser, emitting 800 nm pulses with a temporal width of 150 fs and a repetition rate of 1 kHz. A portion of the light was directed through a 0.5 kHz chopper and then converted through third harmonic generation to a 266 nm pump beam. The pump was directed through the front facet of the IRE at normal incidence to excite the STO sample. Before reaching the IRE, the pump was focused and attenuated using a focusing lens and variable OD filters, resulting in a beam size of 665 μm FWHM with a fluence of 0.1 mJ/cm^2 at the sample position. With a 400 fs pulse beam width determined by a cross-correlation (IRF in Figure S3a), this results in a peak fluence in the diamond of 1.14 GW/cm^2 .

Another portion of the 800 nm pulse was directed into an optical parametric amplifier (Opera Solo) to convert the light to infrared pulses with a center wavelength of 800 cm^{-1} and a 150 cm^{-1} bandwidth with P polarization. This polarization has a component perpendicular to sample and allows for exciting the oxyl vibrational mode that is likewise perpendicular to the sample surface. The IR beam was then split using a 50/50 beam splitter to create a probe and reference line. The probe, with a beam size of 350 μm FWHM, was sent through the IRE in the ATR cell at an incidence angle of 60° using a focusing lens. This resulted in an evanescent wave penetration depth of 1.1 μm at the diamond/air interface (1.26 μm at the diamond/aqueous interface) used for measurements.

After passing through the IRE, the probe was collimated and focused into an entrance slit for an Acton SP-2300 spectrograph (Princeton Instruments), where it was dispersed onto the top row of a dual-array 64-element detector (MCT-12-64, Infrared Associates). The reference beam was directed to the bottom array of the detector. The signal was amplified using a boxcar amplifier (FPAS boxcar integrator) and sent to a computer. The delay between pump and probe pulses was

controlled by a delay stage (MTM 250CC1, Newport). The probe was normalized using the reference line to account for shot-by-shot differences.

Transient IR ATR measurements: During the experiments, the sample was pressed into the evanescent wave at the diamond/air (or diamond/electrolyte) interface using the actuator. The sample was photoactivated by the 266 nm 0.5 kHz pump and probed with the IR 800 cm^{-1} 1 kHz probe. The absorbance was calculated using Beer's Law with $\Delta A = -\log(\Delta R/R)$, where ΔR is the change in reflectivity before and after exciting with the pump, and R is the initial reflection before excitation, measuring the change in reflectance of the sample before and after being pumped. Spectra were collected with a 67 fs step across the desired time range. Following each experiment, the sample was removed from the evanescent wave and a transient background was recorded under the same experimental conditions.

Chapter 6: Investigation of surface phonon polaritons in SrTiO₃ and rutile TiO₂

6.1 Introduction

Surface phonon polaritons (SPhPs) are hybrid modes that couple light to vibrational optical phonon modes in crystalline materials^{85–87}. Phonon polaritons enable the spatial confinement of light enabling applications in molecular sensing, waveguiding, and nano-electronics and optics^{29,88,89}. Attenuated total reflection (ATR) spectroscopy has been used to measure SPhPs experimentally for decades^{37,86,90,91}. The evanescent field produced upon total internal reflection in the ATR prism is able to couple to surface modes whose wavevectors are higher than that of light in free-space^{86,91}. In a normal reflectivity geometry without the presence of the ATR prism, SPhPs are not observed. SPhPs exist in specific spectral windows known as Reststrahlen bands, an area of high material reflectivity between the transverse optical (TO) and longitudinal optical (LO) phonon frequencies where the real part of the permittivity is negative^{91–93}.

Metal-oxide materials have previously been observed to support SPhPs in the mid-infrared region^{37,90}. These materials exhibit multiple Reststrahlen bands across a broad range of frequency, each of which can support an SPhP. Such signals have been characterized in metal-oxides such as BaTiO₃, KTaO₃, and SrTiO₃ (STO)^{37,94,95}. Rutile TiO₂ exhibits many of the same dielectric properties as STO including multiple Reststrahlen bands in the mid-infrared region^{37,96}. However, although the existence of an SPhP in this region would be anticipated, no such signal has been reported. This work will report on a surface phonon polariton observed in rutile TiO₂ (100) between the LO and TO phonons at 500 cm⁻¹ and 830 cm⁻¹ respectively⁹⁶. The existence of an associated excited state signal following UV excitation of the sample surface, which modifies the real and imaginary parts of the material dielectric^{27,97}, will also be reported. A comparison will be made

between the signals in STO and TiO₂ in terms of the location along the frequency axis and the lifetimes of the excited state signals. The location and response of the photoexcited signal in both samples is also compared to the signal of the oxyl in n-doped STO, which appears in a similar frequency region in on STO but does not appear in the rutile TiO₂ samples.

6.2 Ground state surface phonon polariton in STO and rutile TiO₂

SPhPs exhibit several characteristic responses to the coupling of light in the ATR geometry that can be used to define the existence of the vibrational mode. First, they exhibit a dispersion curve relating the frequency of the observed mode to changes in the wavevector of the coupled light^{37,90}. Second, they exhibit a polarization dependence due to the coupling of light to the TO phonon where only P-polarized light can couple⁹². Finally, a critical coupling position of the sample relative to the ATR element can be observed where the coupling of the light to the phonon mode is maximized^{29,91,92}. As such, a dependence of the spectra on the distance between the sample and ATR element is anticipated. Here, we will attempt to observe these characteristics and compare data taken for rutile TiO₂ to the known polariton signal observed on STO within our ultrafast ATR geometry.

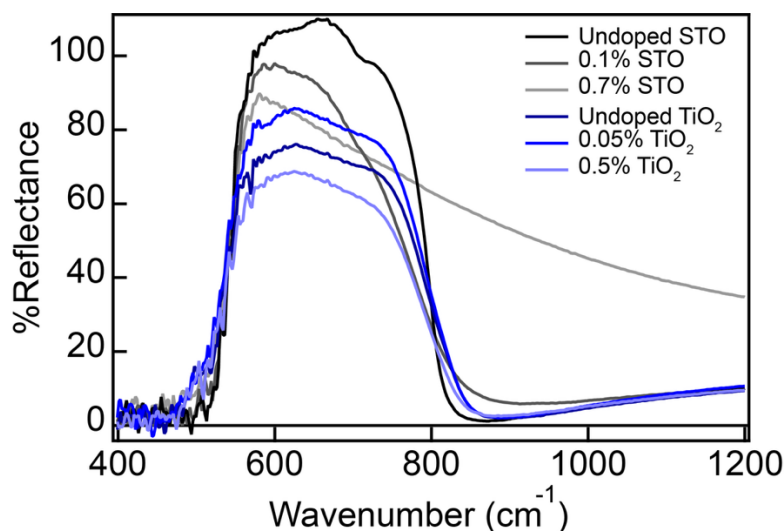


Figure 6.1: Infrared reflectance measurements of STO and Rutile TiO₂. The high reflectivity between 500-800 cm⁻¹ is indicative of a Reststrahlen band of the material. This reflectivity is observed to decrease with increased Nb doping of the samples. The percentages in the legend represent Nb doping levels.

Figure 6.1 shows infrared reflectance spectra of STO and rutile TiO₂ in the mid-infrared regions from 400-1200 cm⁻¹ as a function of Nb doping. The spectra show the area of high reflectivity between the TO (~500 cm⁻¹) and LO (~830 cm⁻¹) modes in both the STO and TiO₂ materials, indicating the Reststrahlen region for the material^{37,96}. The similar material properties for the two titanium oxide materials results in a similar spectral region of high reflectivity. The maximum reflectance changes with Nb doping, where the dopant plasma can result in more absorbance. The highest doping of STO (0.7% Nb) exhibits a significantly broadened reflectance, likely due to a coupling of the LO phonon to the high plasma density⁹⁸. The instrument resolution is poor as you approach the lower frequency limit, so other optical phonon modes below 500 cm⁻¹ are not visible here.

Unfortunately, two experimental limitations prevent the measurement of the polariton dispersion curve with our ultrafast ATR setup. First, the power output of the OPA used to convert light into the mid-infrared beam drops off significantly below 800 cm⁻¹, resulting in an inability to measure below ~700 cm⁻¹. The reported dispersion curve for STO spans from the TO phonon

frequency near 500 cm^{-1} to very near the LO phonon mode³⁷, so we are only able to observe the upper third of the curve. Second, the optical setup and 45° cut of the diamond crystal make changing the wavevector of the incoming light through the input angle extremely difficult. Use of a hemispherical prism could reduce this issue, but that was not implemented here. Instead, we will compare spectra measured on STO to the known dispersion curve. Spectra measured on TiO_2 will then be compared to those of STO. For a full characterization of the polariton signal, the dispersion curve should be measured in its entirety.

Ground state ATR spectra for undoped STO and rutile TiO_2 (100) in air are shown in Figure 6.2 as a function of the sample z-position relative to the diamond ATR element. All spectra here are measured with P-polarized light, no peak is observed in S-polarized light. While STO is an isotropic crystal, TiO_2 is anisotropic with a tetrahedral crystal lattice. As such, TiO_2 is shown for data taken along both the a=b and c crystal axes, which will have different dielectric and absorptive properties⁹⁶.

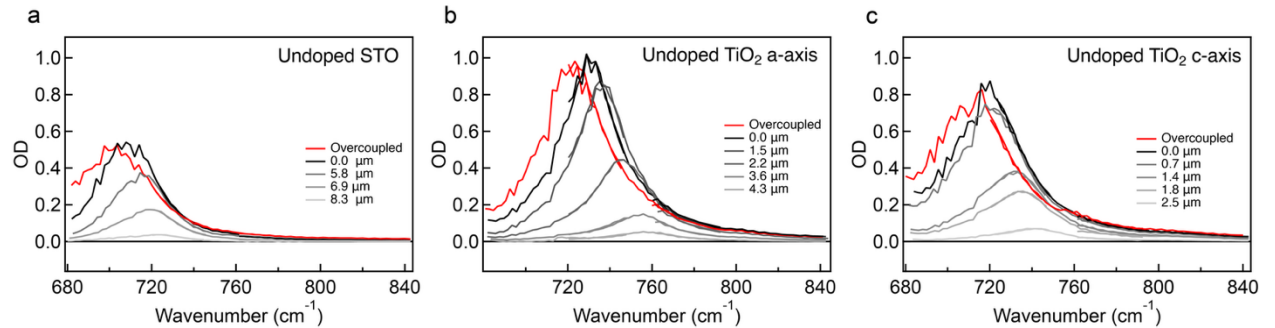


Figure 6.2: Ground state ATR spectra of undoped STO (a) and undoped rutile TiO_2 a-axis (b), and c-axis (c) as a function of z-position relative to the ATR element. The maximum absorbance is given as the zero position in μm , while the red spectrum for each sample indicates the overcoupled regime where the sample is too close to the crystal and absorption drops.

In Figure 6.2a, the frequencies of the spectra measured for STO agree well with the dispersion curve reported by Fischer et al³⁷. For our system, the wavevector of our light is quite high, with $k \sim 1250 \text{ cm}^{-1}$ for an input beam of 750 cm^{-1} into the diamond. Thus, we are in the upper

portion of the dispersion curve where the polariton frequencies appear between 700-730 cm^{-1} , which is what we observe for the peak frequencies in our spectra appearing around $\sim 720 \text{ cm}^{-1}$. The frequency of the signal shifts to lower wavenumber as the z-distance between the sample and crystal is lowered. We also observe that the maximum absorption is not at the smallest distances. This behavior is indicative of a critical coupling regime, where the coupling of the evanescent wave to the SPhP is maximized. If the gap size is smaller than the critical coupling distance, i.e. the sample is too close to the crystal, radiative losses can occur that prevent efficient excitation of the mode^{91,92}. This is indicated by the red “overcoupled” curves in Figure 6.2. On the other side, if the gap size is much larger than the critical distance, you will have less overlap with the evanescent wave, and the coupling is less efficient. This behavior has been reported previously for SPhPs in silicon carbide crystals^{91,99}.

Moving to TiO_2 , in both the a-axis (Figure 6.2b) and the c-axis (Figure 6.2c) the peak frequencies for similar coupling regimes (z-distances) are shifted to slightly higher frequencies relative to STO. Both axes display the same type of critical coupling behavior as STO. Along the two different crystal axes, differences can be observed in the frequencies of the SPhP with the critical coupling appearing $\sim 15 \text{ cm}^{-1}$ higher in the axis. This is attributed to the effect of propagation direction on the frequencies of the phonon modes in anisotropic crystals⁹⁹.

6.3 Excited state signal associated with SPhPs in STO and TiO_2

Figure 6.3 displays excited state spectra for undoped STO and TiO_2 taken following UV excitation with a 266 nm pump pulse. The spectra are shown as difference spectra between the excited and ground state surfaces based on a change in reflectance in ΔmOD as $-\log(R_{\text{on}}/R_{\text{off}})$. Spectra are shown at $\sim 10 \text{ ps}$ following photoexcitation, at which time the signal has equilibrated

to a steady shape and magnitude, and are given as a function of z-distance between the sample and diamond.

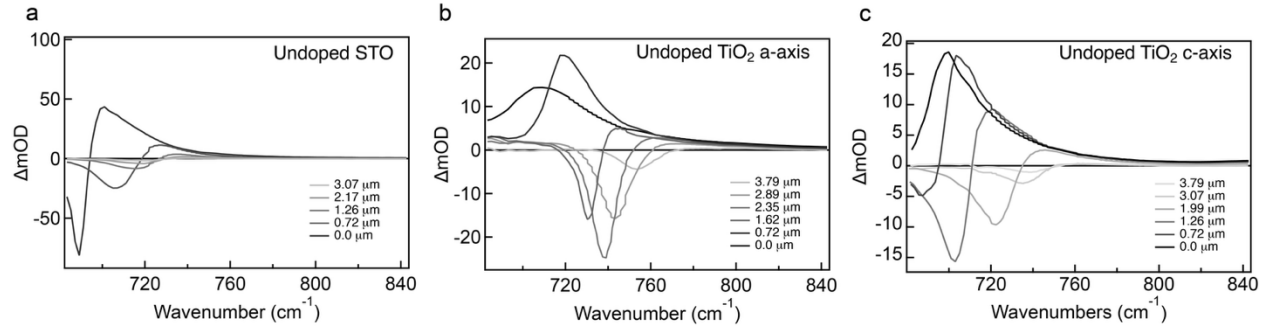


Figure 6.3: Photoexcited ATR spectra of undoped STO (a) and undoped rutile TiO_2 a-axis (b), and c-axis (c) as a function of z-position relative to the ATR element.

At larger z-positions, the undoped STO/air interface (Figure 6.3a) shows spectra with a positive peak on the higher frequency side and a relatively symmetric negative dip in optical density on the lower frequency side. As the z-distance gets smaller, the intensity increases while the entire spectrum shifts toward lower frequencies, mirroring the behavior of the ground state spectra observed above. At the smallest z-distances, the observed spectrum changes shape considerably to a broader peak with only positive optical density. These behaviors are likely due to the critical coupling regime discussed with the ground state spectra above. The center frequencies of the photoexcited spectra, in this case represented by the midpoint between the positive and negative peak optical densities, align closely with the peak frequencies of the ground state spectra in Figure 6.2a.

The photoexcited spectra of both the a and c-axes of TiO_2 , given in Figures 6.3b and 6.3c respectively, show a similar up-down asymmetric lineshape as STO. The a-axis spectra appear at slightly higher frequencies than those taken along the c-axis, reflective of the ground state data. They also show less symmetry across the zero of the y-axis than STO, with the negative optical density being much stronger in intensity than the positive peak. The same z-dependence is

observed in both axes, with spectra shifting to lower frequencies with smaller z-distances. At very small z-distances, the lineshape changes to a broad, positive peak as observed in STO. Figure C.1 and C.2 provide examples of ground and excited state spectra taken at the same z-positions plotted together for undoped TiO₂ (c-axis) and STO respectively to illustrate the consistency in the z-dependent trends. These z-dependent trends, along with the frequency location of the signal, serve to associate the observed excited state signature with the ground state SPhP.

Excited state spectra from ~10 ps after photoexcitation for a single z-position for undoped and doped STO and TiO₂ materials are shown in Figure 6.4. The spectral range extends through the region of the titanium oxyl's vibrational signature on 0.7% Nb STO, discussed in depth in previous chapters, centered at 800 cm⁻¹. Figure 6.4a shows spectra taken in air, where only n-doped STO exhibits the oxyl signature at higher frequencies. This signal does not appear on any TiO₂ samples, even the higher doped 0.5% Nb material.

In terms of the excited state signal associated with the SPhP between 700 cm⁻¹ and 750 cm⁻¹, all materials except the 0.7% Nb STO exhibit a photoexcited response. Although the oxyl's lineshape is quite broad and extending over SPhP region, no additional lineshape is observed. The n-doped TiO₂ signal is weaker and more broad than those of the undoped but still present in the excited state spectra. Z-dependent ground and excited state spectra for 0.5% Nb TiO₂ can be found in Appendix Figure C.3, and exhibits similar behaviors as the undoped samples.

Figure 6.4b shows excited state spectra taken for the same samples at an electrolyte interface (pH 13). Here, the SPhP associated signal consistently disappears across all samples, while the oxyl signal in 0.7% Nb STO remains present with a modified lineshape (discussed previously in Chapters 3 and 5). This serves to differentiate the two photoexcited signals. The disappearance of the SPhP signal can be accounted for by the change in the refractive indices of

the medium⁸⁶. As described previously, a SPhP signal will change frequency with the wavevector of the coupling light^{37,90}. This will change with the refractive index of the medium⁸⁶, in this case air vs water (refractive indices of 1 and 1.33 respectively). Thus, the signal should shift to lower frequencies in an aqueous environment, likely beyond the resolution of the spectra collected here (below the 700 cm^{-1} limitation of our OPA). So, although the signal is not observed here, it may be present at lower frequencies beyond our ability to collect. The oxyl signal in comparison is not dependent on the wavevector of the incoming light, and thus the resonant frequency of the peak does not change from air to electrolyte (see Table 3.2).

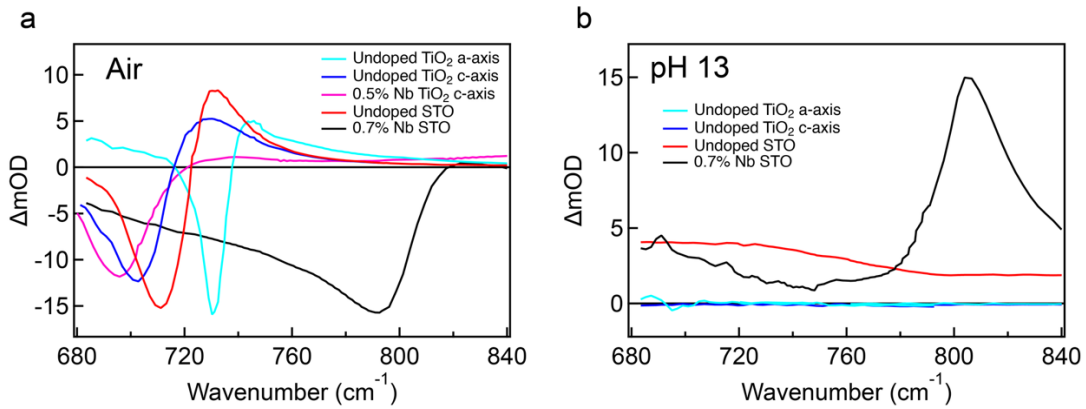


Figure 6.4: Photoexcited spectra for STO and TiO_2 interfaces with (a) air and (b) pH 13. Only 0.7% Nb STO exhibits the oxyl signal around 800 cm^{-1} , but does not exhibit any other feature at lower frequencies. The SPhP associated signal disappears for all samples in pH 13. The broad signal at low frequencies on STO in pH 13 is not consistently repeatable and is attributed to a background absorption.

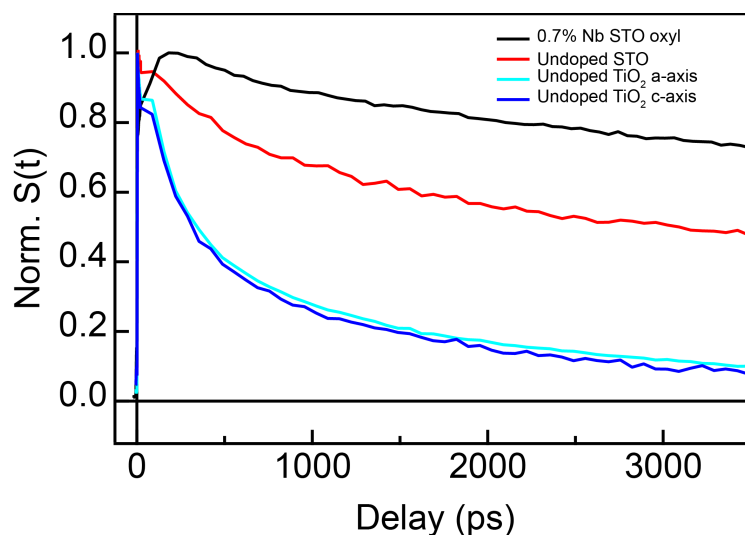


Figure 6.5: Time-dependent spectral integration (S) of photoexcited signal on undoped STO and rutile TiO_2 materials compared to the signal of the oxyl on 0.7% Nb STO (black) for the first 4 ns after photoexcitation. Kinetics are normalized to the maximum signal strength.

Kinetics of the excited state spectra are given in Figure 6.5 for the STO and TiO_2 samples for the first 3.5 ns following photoexcitation. Across all the undoped samples, a very fast ps rise is observed, after which the signal immediately begins to decay exponentially over the ns timescale shown. The rate of decay appears consistent across z-position for each sample. For undoped STO, the signal decays by approximately 40% over the 3.5 ns shown. On the hand, both axes of TiO_2 decay more quickly, by approximately 90% over the same time regime, with the same dynamics observed for both crystal axes. This is a much more rapid decay compared to the signal decay of the hole-trapped oxyl radical observed on n-doped STO in Figure 6.5, which is relatively steady over the course of the 3.5 ns timescale ($\sim 15\%$ decay in air conditions). The longer lifetime of the oxyl can be attributed to the lifetime of the hole-trapped intermediate species formed⁹⁷. In comparison, the observed faster decay of the SPhP signal could be indicative of faster charge recombination dynamics in the materials without the oxyl¹⁰⁰.

6.4 Future work

Although the observed spectra for the photoexcited STO and TiO₂ surfaces have been associated with the ground state SPhP, an exact understanding of the source of those spectra has yet to be defined. Future work will attempt to define the excited state observations through an understanding of the changes in the dielectric properties of the semiconductor materials induced upon UV photoexcitation and formation of electron/hole charge carriers. The spectral shapes observed and the mirroring of behaviors between the ground and excited states could be indicative of a ground state shift of the SPhP on the photoexcited surface. Modelling of the ground state and photoexcited spectra will be explored to test this theory, introducing a photoinduced plasma frequency to the ground state before calculating difference spectra based on any induced changes. One could then make use of this knowledge to interpret the observed ps kinetics growth and ns decay in terms of the photoexcited charge carrier dynamics and how they differ across the different titanium oxide materials.

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<https://doi.org/10.1021/jz500770c>.

Appendix A

Supplemental Transient ATR Data for the Formation of the Oxyl's PES in Air

A.1 Processing Methods for Transient ATR Data

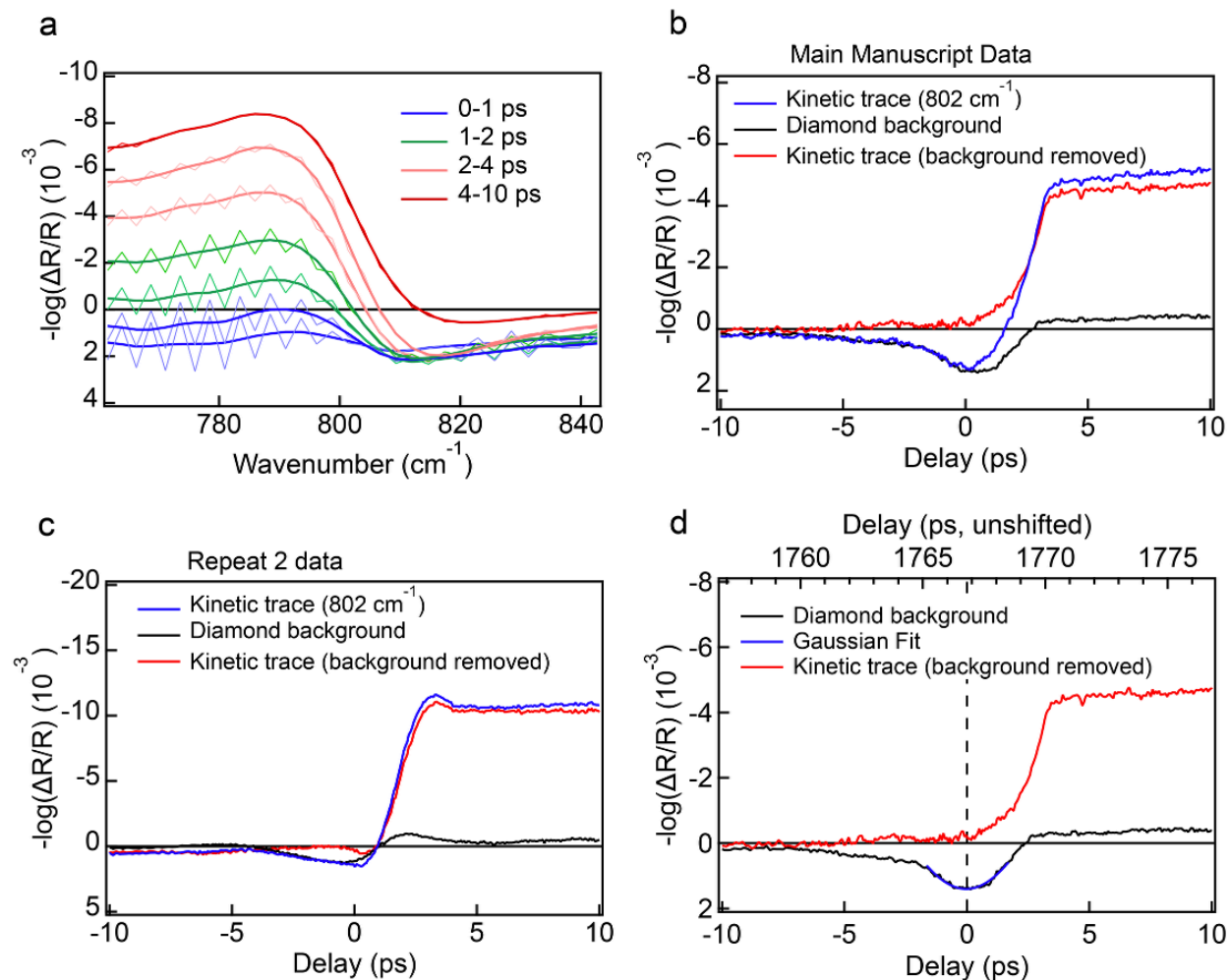


Figure A.1: Raw data processing and time zero determination. Unfiltered (faded) and filtered (solid) spectra (a). Raw, background, and background subtracted kinetics for the main manuscript data (b) and for Repeat 2 data (c). Time zero determination by fit of background kinetics with a gaussian (d).

The raw spectra contain oscillations around time zero with and without a sample present. These oscillations have a constant frequency in time and are highest in magnitude at time zero. As they are additive to the signal of the observed vibration, they can be removed by a FFT filter to

produce smooth spectra. Each spectrum is treated with the low pass FIR filter in Igor Pro 8 (0.25 Hz end of pass band, 0.35 Hz start of rejection band) to produce filtered spectra (Figure A.1a).

A transient background, present in the absence of any sample, is collected under the same experimental conditions following each data set (Figure A.1b). Following filtration, the background is subtracted from the spectrum at each time delay to produce the final spectra and kinetics used for further analysis. The magnitude of the background is constant even with differing signal strength, as illustrated by Figure A.1c which shows the subtraction for the repeat 2 data that has a significantly stronger signal.

The background is attributed to a pump-probe response of the diamond ATR element. The bandgap of the diamond is higher than the pump beam (5.5 eV vs 4.7 eV), however, it has been shown that two photon absorption of diamond occurs at similar pump wavelengths and fluences. The shape of the background kinetics is generally a narrow and reasonably symmetric peak that has been used as a beam autocorrelation measurement and thus can be used to determine time zero. This peak can be fit with a gaussian (Equation A.1) and the resulting x_0 is determined to be time zero for that background and the corresponding data set (Figure A.1d). The spectral kinetics are shifted appropriately.

$$f(x) = Ae^{-\left(\frac{x-x_0}{width}\right)^2} + y_0 \quad \text{Equation A.1}$$

A.2 Time Resolution of the UV Pump

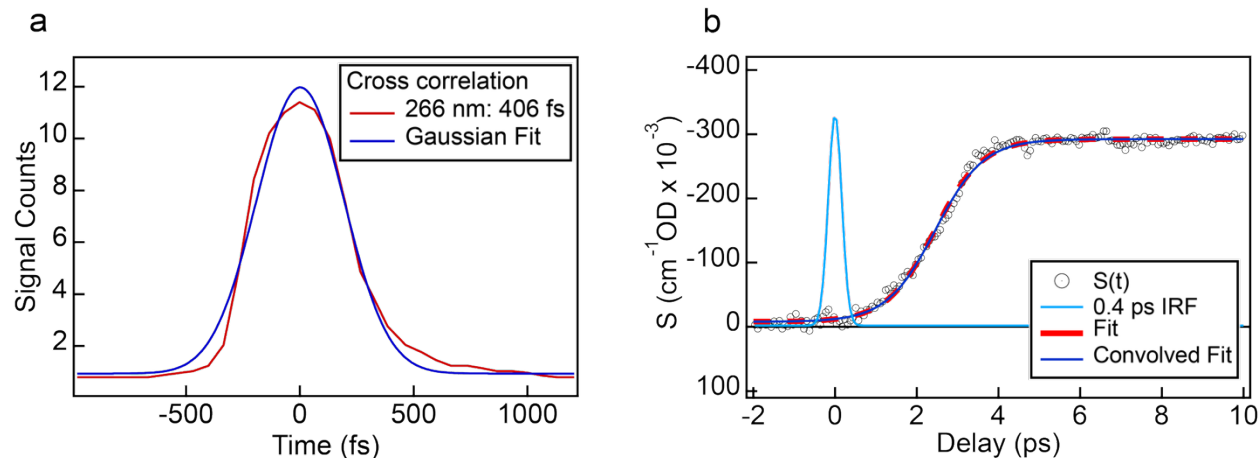


Figure A.2: Determination of the time resolution of the 266 nm pump (a) and the instrument response function (IRF) convoluted with logistic fit of oxyl rise (b).

A cross correlation of the 266 nm pump was performed to calculate the time resolution and resultant IRF (Figure A.2a). The measured IRF with a 0.4 ps width convoluted with a logistic function produces a fit that is not noticeably different from the non-convoluted logistic fit (Figure A.2b). Thus, it is concluded that the IRF does not affect the reaction kinetics and the data is treated with the logistic function for simplicity.

A.3 Repeat Trials of Transient ATR Data in Air

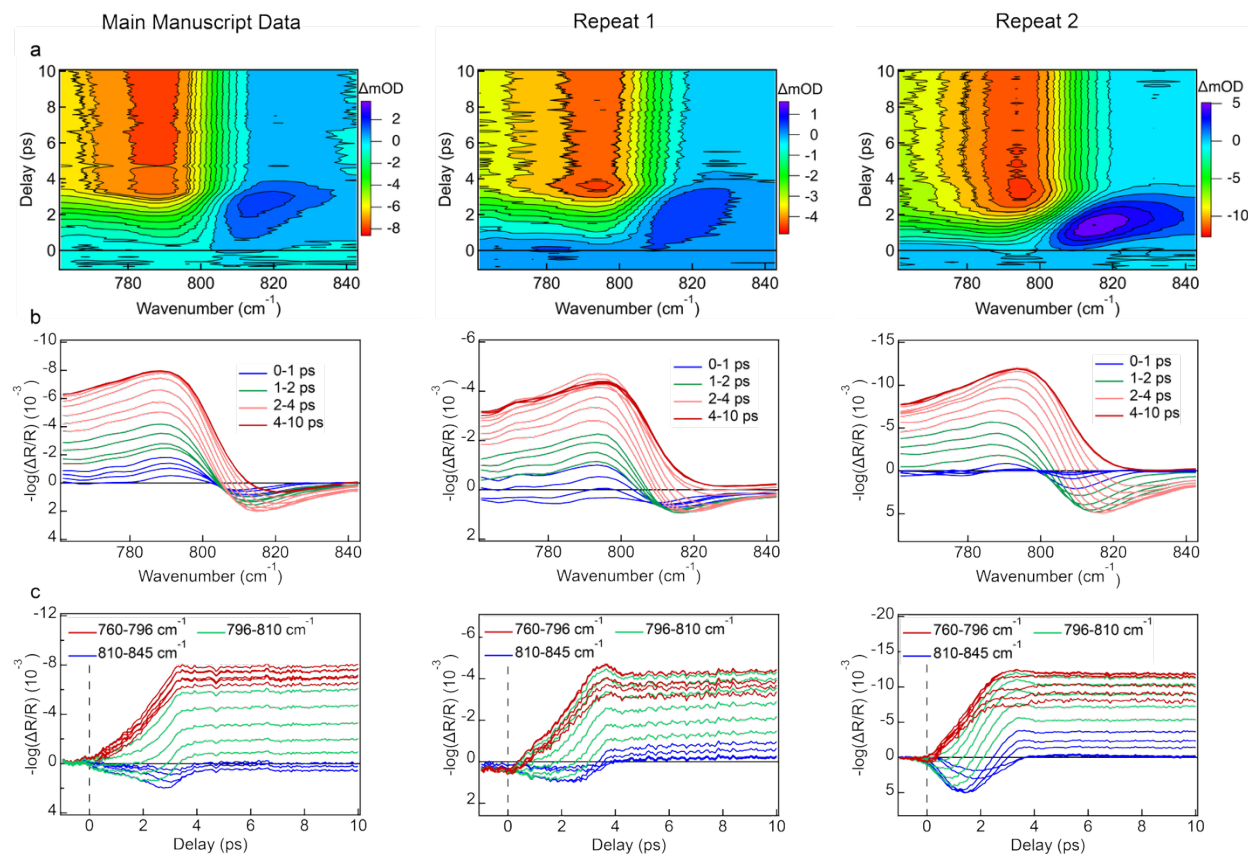


Figure A.3: Contour maps (a), spectra at specific time delays (b), and kinetics at specific wavenumbers (c) for three separate data sets.

Figure A.3 displays the dataset used in the main text (first column) compared with two other experimental trials taken under the same experimental conditions (0.7% Nb STO in air). While slight variations exist within the data sets, the results are similar and looked at more in depth by analyzing the Fano fits of each data set in Figures A.5 and A.7. The contour plots in Figure A.3a all show a similar signal growth in red at lower wavenumbers in the first 4 ps to some equilibrium value along with a transient background in blue at higher wavenumbers that grows in and decays within that same 4 ps. The spectral slices in Figure A.3b reflect this growth and background shift seen in the contours. The peak maximum in the red region appears to be at slightly different wavenumbers across the three trials, which is attributed to the detector resolution which

has a frequency difference of $\sim 2.6 \text{ cm}^{-1}$ between pixels in this range. The kinetic traces in A.3c similarly show the transient background that decays away by 4 ps in the blue traces and appears consistent across trials. Differences in overall signal intensity are a result of sample proximity and orientation to the diamond due to the nature of the decaying evanescent wave in the ATR configuration. When changing the distance of the STO sample from the diamond with the actuator the signal intensity changes, but the kinetics of the signal remains the same.

A.4 Fano Fitting of O₂'s Vibrational Signal in Air

Figure A.4 shows spectral slices from specific times following UV excitation fit with the Fano equation (Equation 4.1). During the 0-1 ps time regime, the fits have some deviation from the data with a slightly too narrow width and missing the peaks in the spectral intensity. The quality of the fits improves with time, matching the data better after 1 ps and almost perfectly by 4 ps when the system has equilibrated.

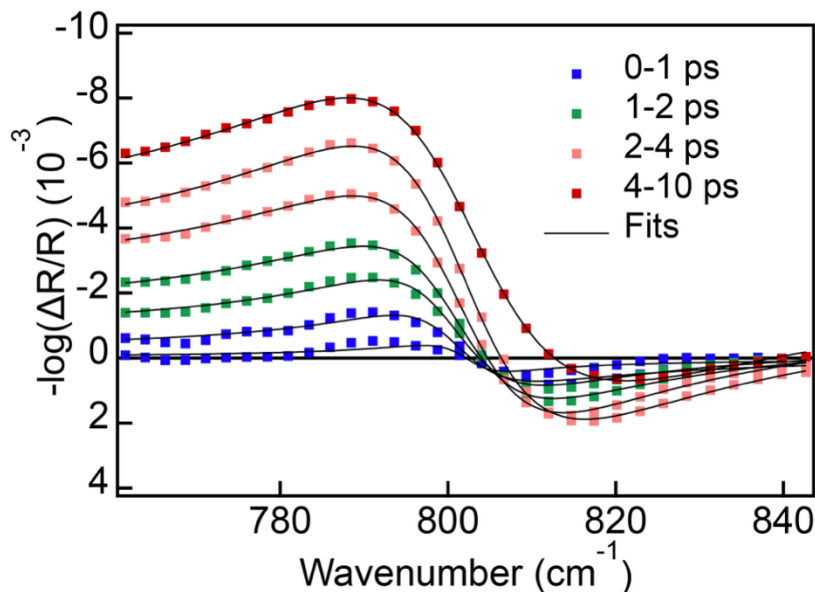


Figure A.4: Spectra and corresponding Fano free fits of main manuscript data at specific time delays during signal growth. Fits were performed using Equation 4.1.

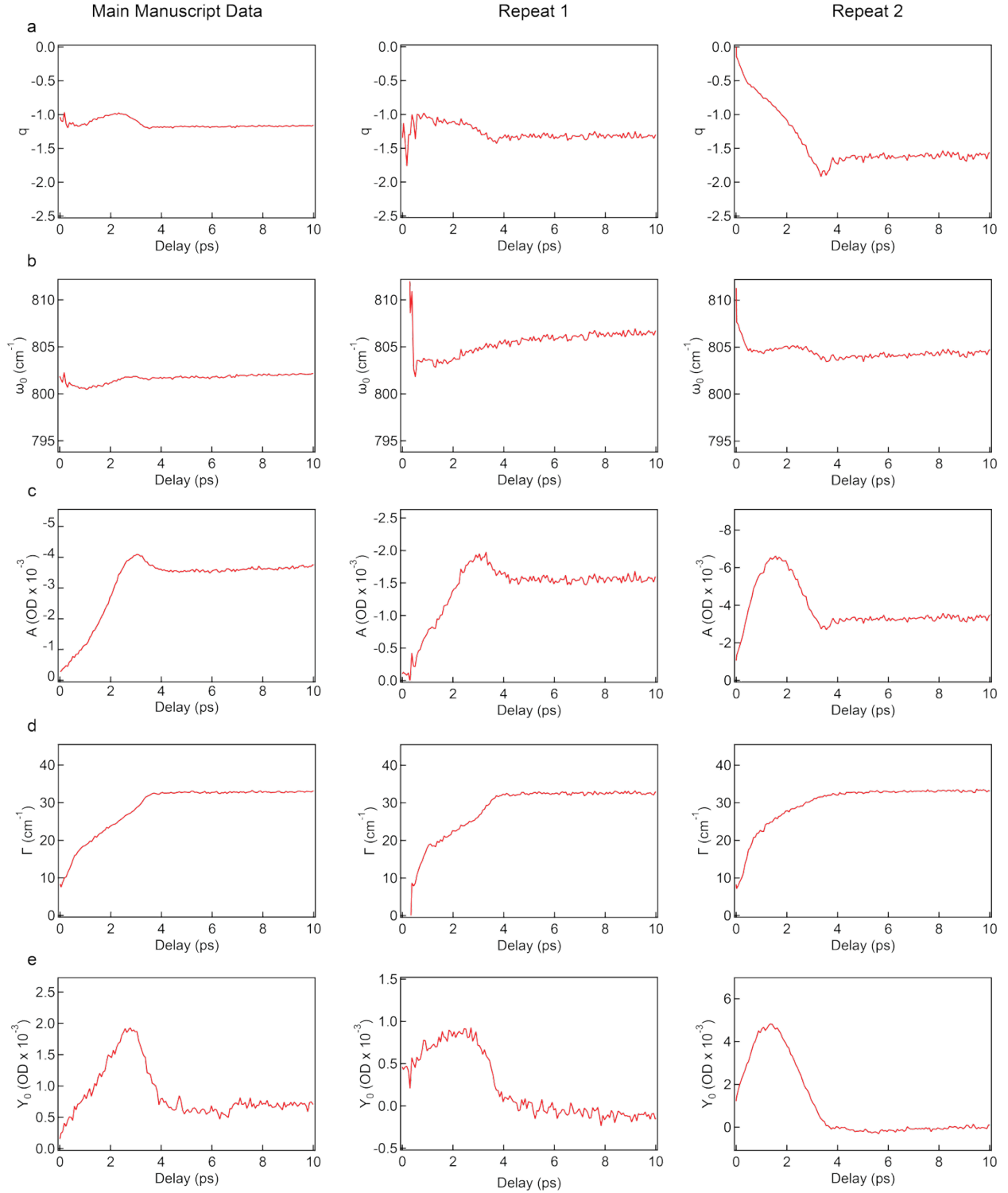


Figure A.5: A comparison of Fano free fit parameters is shown for three data sets. q : asymmetry constant (a); ω_0 : resonant frequency (b); A : continuum excitations coupled to the mode (c); Γ : Fano coupling constant (d); Y_0 : background shift (e).

Time-dependent free fit Fano parameters for all three datasets are given in Figure A.5. All five parameters are largely similar across the three data sets. The largest noticeable difference is found in the q and A parameters of repeat 2 when compared to the other data. Repeat 2 shows a time dependence of q in the early times rather than a constant value while A shows a much sharper early growth followed by a large decay not seen elsewhere. These differences are attributed to interplay between the two parameters in the Fano equation (Equation 4.1) where variation in one parameter can be accommodated by changing the other. In the case of repeat 2, an increase in the magnitude of q can be compensated by a decrease in the value of A to achieve the same spectral weight at a given frequency. The variation in the resonant frequency ω_0 across data sets between 802 cm^{-1} and 806 cm^{-1} is attributed to the resolution of the detector which has a frequency difference of $\sim 2.6 \text{ cm}^{-1}$ between pixels in this range. Differences in the overall magnitude of A and Y_0 are due to the different signal strengths seen and discussed in Figure A.3.

A.5 Extraction of $\Gamma(t)$ via the Anti-Resonance Frequency ω_A

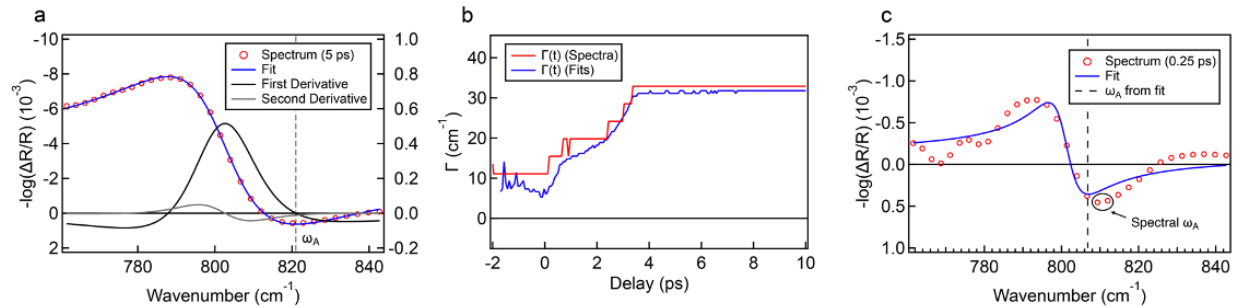


Figure A.6: Determination of the Fano continuum coupling constant (Γ) from the anti-resonance frequency (ω_A). (a) Representative spectrum and corresponding Fano fit (left axis) along with the first two derivatives of the fit (right axis) used to determine the anti-resonance frequency. (b) The calculated $\Gamma(t)$ determined from both the spectral data and the Fano fits of the spectra. (c) Sample spectrum immediately following time zero and the corresponding Fano fit illustrating the inaccuracy of the very early time fits.

The anti-resonance frequency (ω_A) of the Fano lineshape is defined where $|\langle \psi | T | i \rangle|^2 = Y_0$ (Equation 4.1). For a pure Fano without a Y_0 background, this occurs where the spectrum touches

zero. With a Y_0 present, this point occurs at the minimum in the spectra (Figure A.6a). The value of the anti-resonance frequency can be determined from the first and second derivatives of the spectrum, where the first derivative equals zero and the second derivative is negative. The value of Γ for the spectrum can then be calculated using Equation 4.4, which applies at the anti-resonance. Doing so at each time delay yields $\Gamma(t)$ (Figure A.6b, blue curve). Due to the resolution of the detector, with pixels being $\sim 2.6 \text{ cm}^{-1}$ apart, this results in a $\Gamma(t)$ that steps in value from pixel to pixel. Applying the same process instead to the Fano fits of the spectra yields a much smoother time evolution (Figure A.6b, red curve) as the fits contain approximately six points to every one in a spectrum. The fits are used to calculate $\Gamma(t)$ seen in Figure 4.4 and Figure A.7c.

At very early time delays (below $\sim 1 \text{ ps}$), the spectra do not appear to be a pure Fano shape (Figure A.6c) compared to spectra at later time points like in A.6a. In particular, the anti-resonance given by the Fano fit in the early times is shifted slightly to a lower frequency than in the spectrum because the fit does not perfectly capture the shape. As such, Γ would be calculated as a lower value based on the fits than from the actual spectrum. These points can be extracted manually from the spectra at early times where the fits are not as accurate a description of a spectrum, as seen in Figure A.7c.

A.6 Time-Dependent Growth of the Oxyl's PES using a Logistic Fit

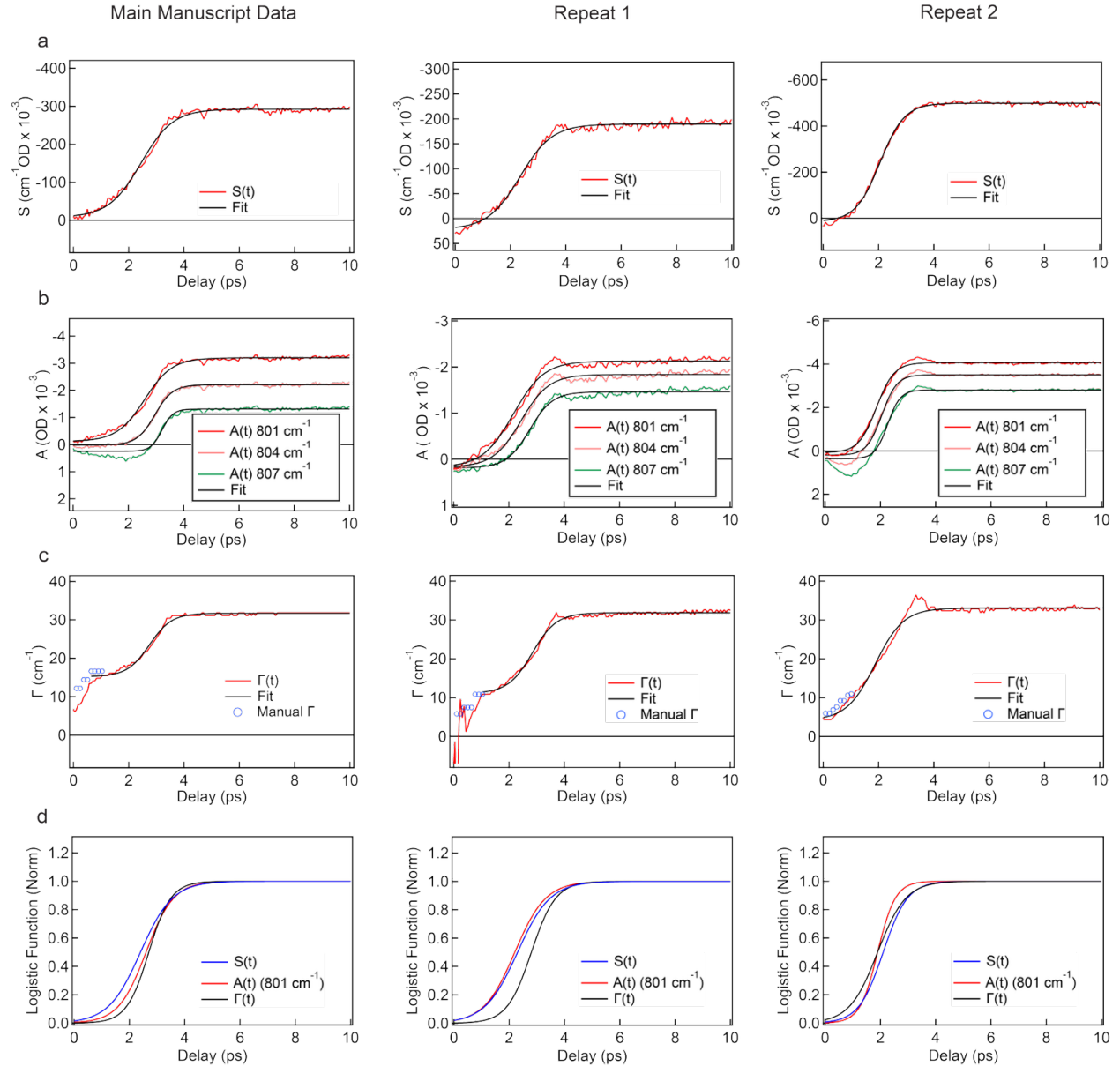


Figure A.7: (a) Integrated spectral weight S , (b) coupled continuum excitations A at and near resonance, and (c) continuum coupling constant Γ determined from the anti-resonance as function of delay for three data sets. (d) shows the resulting logistic fits from (a), (b) and (c) in one graph to allow for a better comparison.

Figure A.7 shows the extracted $S(t)$, $A(t)$ and $\Gamma(t)$ for each of the three datasets. All three quantities are fit with a logistic function and show similar behavior across parameters. $A(t)$ is shown for three frequencies due to variance in the resonant frequency (ω_0) from the Fano free fits in Figure A.5. There are slight changes to the logistic fit parameters as the frequency increases

(see Table A.1) but the overall shape is consistent. The lower signal intensity in data set two results in a noisy value of Γ in the first picosecond preventing the fit from extending further. This could explain the differences in the fit of Γ compared to those of S and A for that data set. Such noise appears less prominent as overall signal strength is increased, as in repeat 2. The normalized logistic functions with no base offset are shown for each data set to illustrate the similarities given by the fits of each parameter (Figure A.7d). The logistic fit values for all parameters are given in Table A.1 below. The overall average logistic fit from all data sets is shown in Figure A.8a along with the range of the data expressed plus/minus one standard deviation of both relevant time parameters. Figure A.8b shows the effect of changing each time parameter by one standard deviation individually.

Data Set	Parameter	τ (ps)	$t_{1/2}$ (ps)
Set 1	S(t)	0.58	2.4
	A(t) (801 cm^{-1})	0.50	2.6
	A(t) (804 cm^{-1})	0.32	2.9
	A(t) (807 cm^{-1})	0.20	3.2
	Γ (t)	0.40	2.7
Set 2	S(t)	0.59	2.3
	A(t) (801 cm^{-1})	0.56	2.2
	A(t) (804 cm^{-1})	0.51	2.4
	A(t) (807 cm^{-1})	0.42	2.7
	Γ (t)	0.44	2.8
Set 3	S(t)	0.44	2.1
	A(t) (801 cm^{-1})	0.32	1.9
	A(t) (804 cm^{-1})	0.28	2.0
	A(t) (807 cm^{-1})	0.23	2.3
	Γ (t)	0.51	1.9
Average		0.48	2.3
σ		0.09	0.3

Table A.1: Logistic fit values for S(t), A(t), and Γ (t) for all three data sets. The average values were taken using only the resonance A(t) (801 cm^{-1}) for each data set along with S(t) and Γ (t).

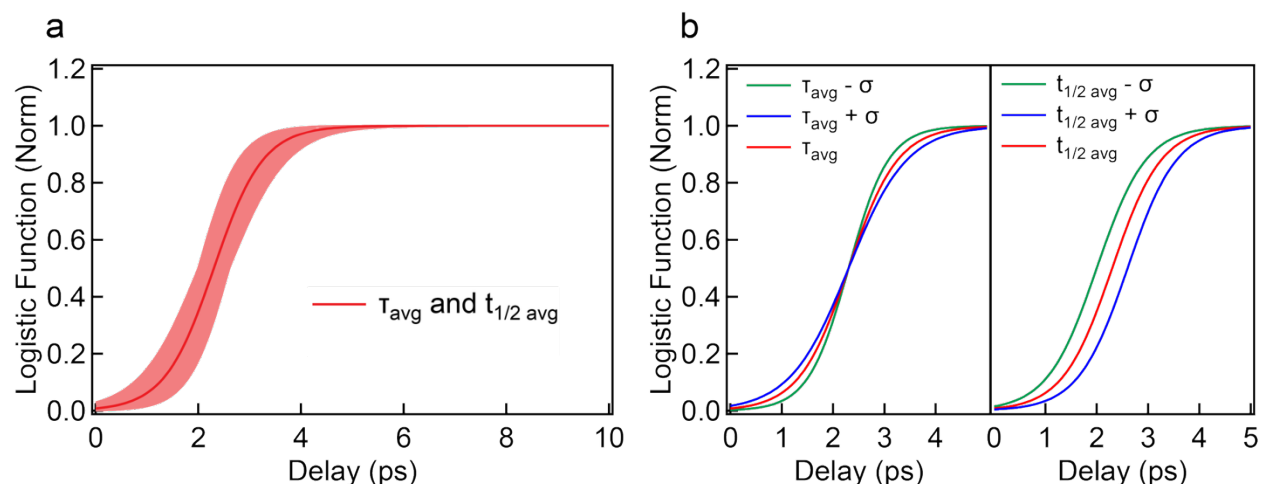


Figure A.8: (a) A normalized logistic function (red curve) plotted using the average logistic fit parameters of all three data sets (Table A.1). The shaded region represents the area around the average fit within a single standard deviation of each parameter to illustrate the variation of the observed signal rises across all parameters around the average. (b) Normalized logistic functions $\pm$ a standard deviation of the average. The left half uses $t_{1/2 \text{ avg}}$ for all curves with varying τ while the right half uses τ_{avg} for all curves with $t_{1/2}$ varied to show the effects of changing the two logistic parameters individually.

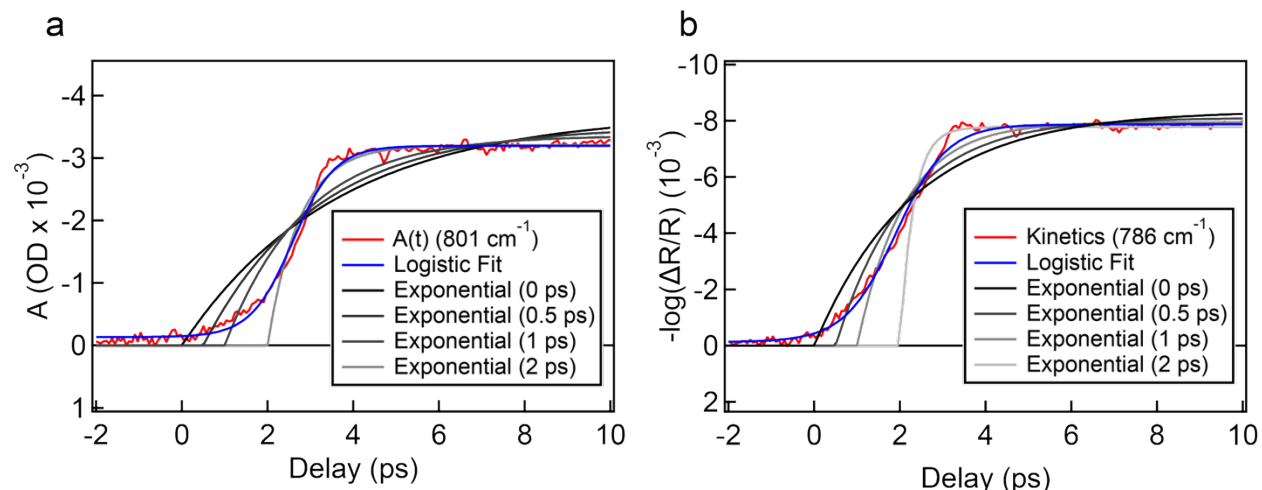


Figure A.9: Comparison of logistic and exponential fits for the Fano A constant at resonance (a) and the kinetics at the peak maximum (b).

A rising exponential decay (Equation A.2) is a common fit for transient absorption measurements in similar systems. Figure A.9 illustrates the failure of such a fit to capture the early signal growth described here, as shown by fitting of $A(t)$ at the resonance frequency (Figure A.9a) and the time trace at the peak frequency (Figure A.9b). The fit was initiated at multiple time delays after the determined time zero to illustrate the failure to capture the shape of the rise. Starting at

earlier time delays (0 ps) fails to capture any part of the rise. Starting at later time delays (1-2 ps) begins to capture the upper half of the signal but fails to capture the slow early rise. The logistic fit used throughout this work, able to capture all aspects of the growth, is shown for comparison.

$$f(x) = A \left(1 - e^{-\frac{t}{\tau}} \right) \quad \text{Equation A.2}$$

Appendix B

Supplementary Transient ATR data for the Formation of the Oxyl at the 0.7% Nb STO interfaces with Air, pD 13, pH 7, and pH 13

B.1 Data Processing and Time Resolution

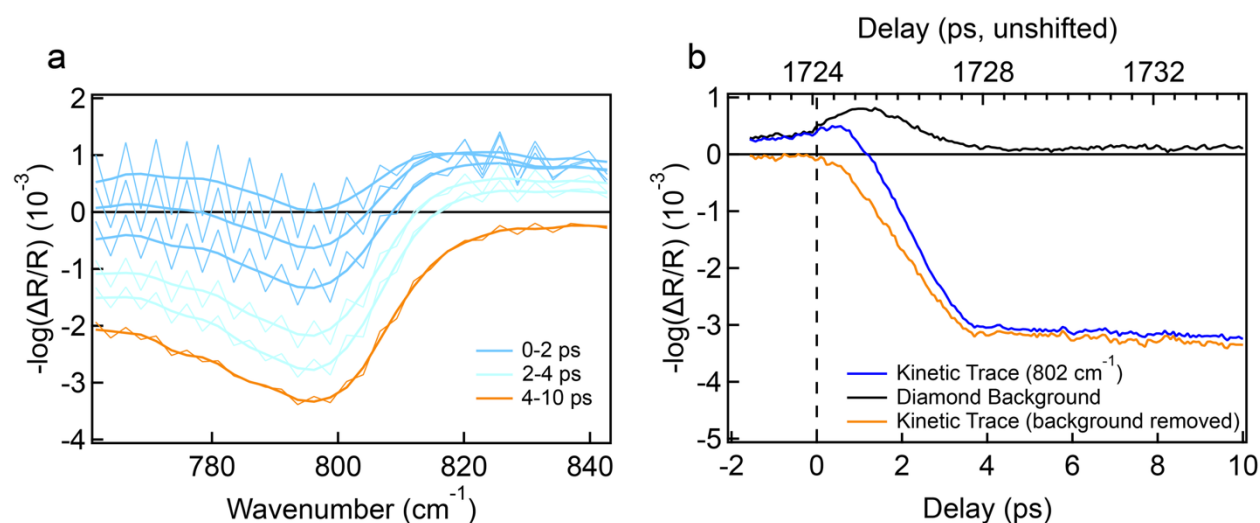


Figure B.1: Raw data processing methods for representative dataset for the n-STO/air interface. (a) Unfiltered (faded) and filtered (solid) spectra. (b) Raw, background, and background subtracted kinetics with time zero correction.

The raw spectra contain oscillations around time zero with and without a sample present. These oscillations have a constant frequency in time and are highest in magnitude at time zero. As they are additive to the signal of the observed vibration, they can be removed by a FFT filter to produce smooth spectra. Each spectrum is treated with the low pass FIR filter in Igor Pro 8 (0.25 Hz end of pass band, 0.35 Hz start of rejection band) to produce filtered spectra (Figure B.1a).

A transient background, present in the absence of any sample, is collected under the same experimental conditions following each data set (Figure B.1b). Following filtration, the background is subtracted from the spectrum at each time delay to produce the final spectra and

kinetics used for further analysis. This background is attributed to a pump-probe response of the diamond ATR element. Following background subtraction, time zero is determined according to the onset of signal growth and the spectral kinetics are shifted appropriately, as shown in Figure B.1b.

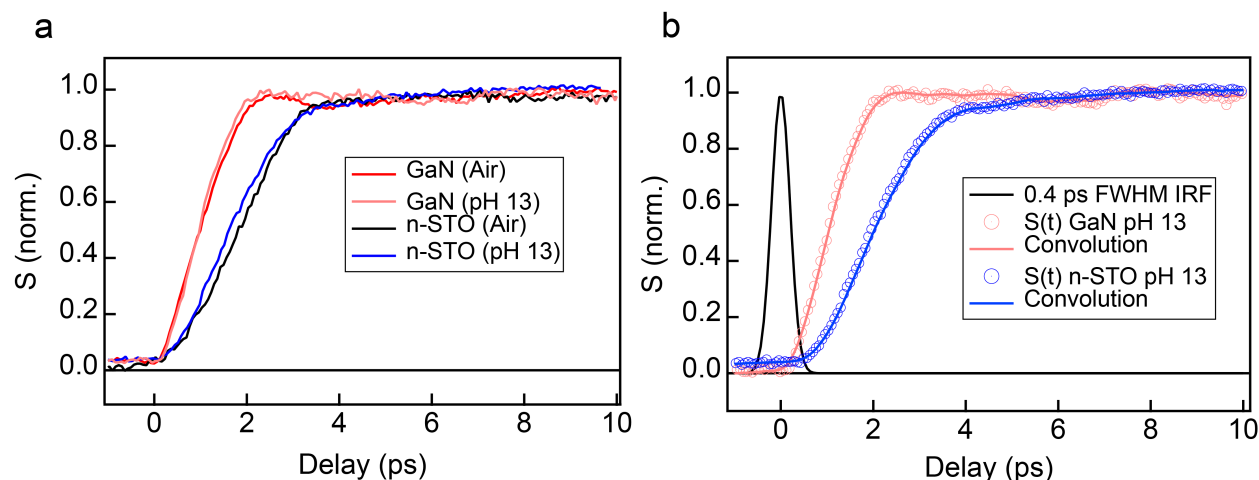


Figure B.2: Time resolution of the 266 nm pump. (a) Normalized spectral weight of 0.7% Nb STO and GaN at air and pH 13 interfaces following UV excitation. (b) Convolution of the instrument response function (IRF) with the spectral response of both GaN and STO.

GaN and STO responses were measured under the same experimental conditions with the 800 cm^{-1} probe, with the results shown in Figure B.2. In both air and pH 13, both sample responses begin to rise at the same time immediately after time zero. The initial rate of growth is faster in GaN, and the signal reaches saturation approximately 2 ps earlier than STO. This demonstrates the experimental capability of measuring a faster response than that of STO under these conditions. Both sample responses convoluted with the IRF of 0.4 ps width producing a convolution that is not noticeably different from the data for both samples. Thus, it is concluded that the IRF does not affect the measured reaction kinetics and the data is treated with the logistic function for simplicity.

B.2 Z-dependent Contour Plots and Spectra

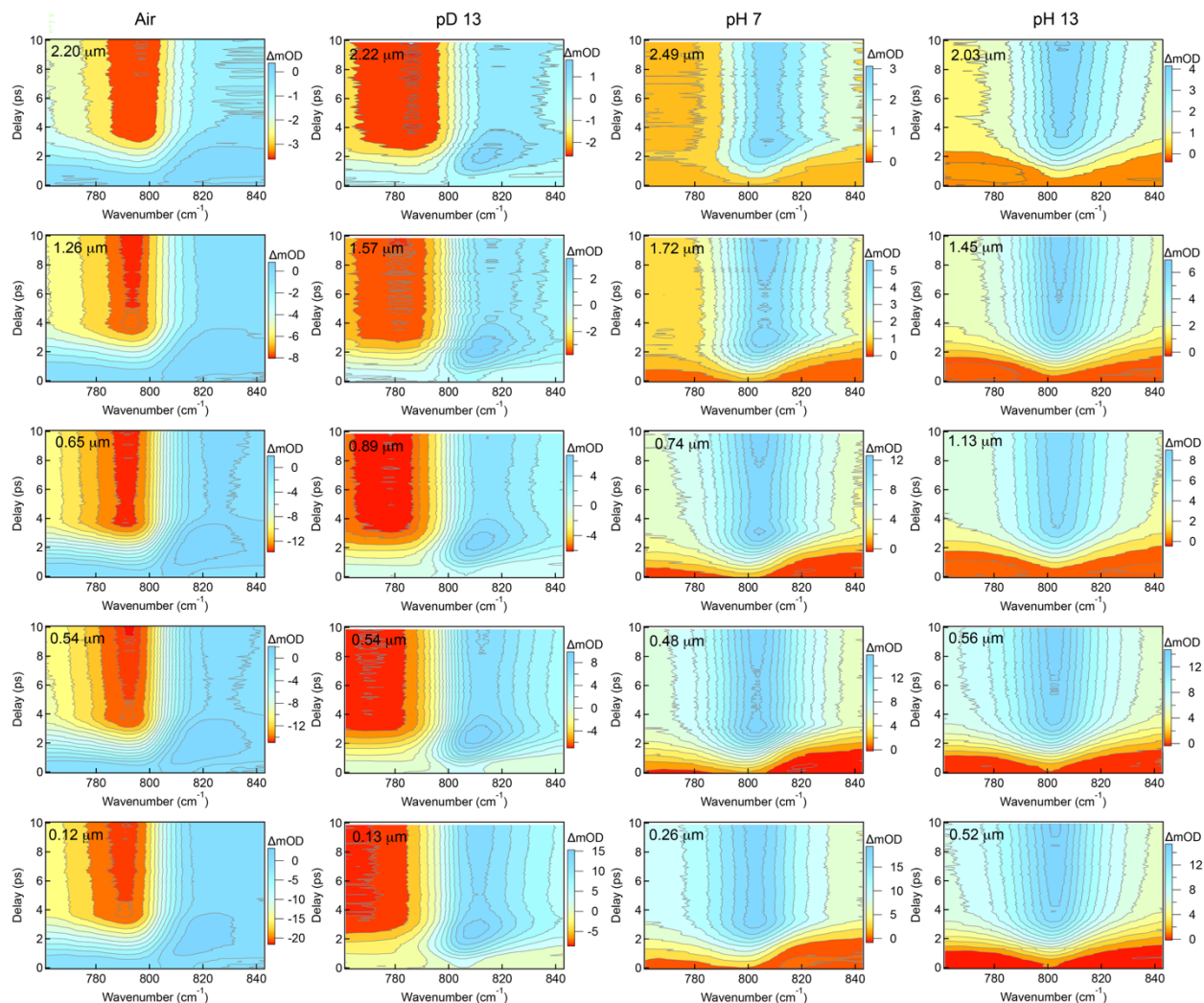


Figure B.3: Z-Dependent contour plots for air, pD 13, pH 7, and pH 13 interfaces with 0.7% Nb STO.

Figure B.3 provides contour plots for the four measured interfaces with 0.7% Nb STO. Each column shows a z-dependence of the oxyl signal for a given interface with larger gap sizes at the top, the smallest gap sizes at the bottom. All data within a column was taken on the same day by starting at the largest gap size and gradually moving the sample forward. In all conditions, the signal growth is consistent with z-position showing a gradual growth in the first four picoseconds before reaching a steady, equilibrated signal. The contour plots for the air interface show a very asymmetric lineshape with a strong negative optical density peaking near 790 cm^{-1} .

The pD 13 interface also shows a very asymmetric shape with a negative peak at slightly lower frequencies than air along with a much stronger positive component at higher frequencies. Both pH interfaces show comparable shapes that are entirely positive and with only very slight asymmetry that varies with z-position, switching from more positive density on the high frequency side at larger gap sizes to the lower frequency side at the smallest gaps. There is a small shift of the peak optical density toward lower frequencies as the z-distance gets smaller at all interfaces, most visible in red for air and pD 13 but still present in blue for the pH interfaces. The overall signal strength increases with decreasing gap size, as expected for an ATR geometry as the sample moves farther into the evanescent wave.

Each row shows comparable z-positions for the interfaces, with some variation due to the lack of precise z control in the experimental setup. Moving right to left across a row illustrates the change in spectral shape with condition, from the most asymmetric shape in air to the nearly symmetric shape in the pH conditions. Similar z-positions have comparable signal strengths in all conditions.

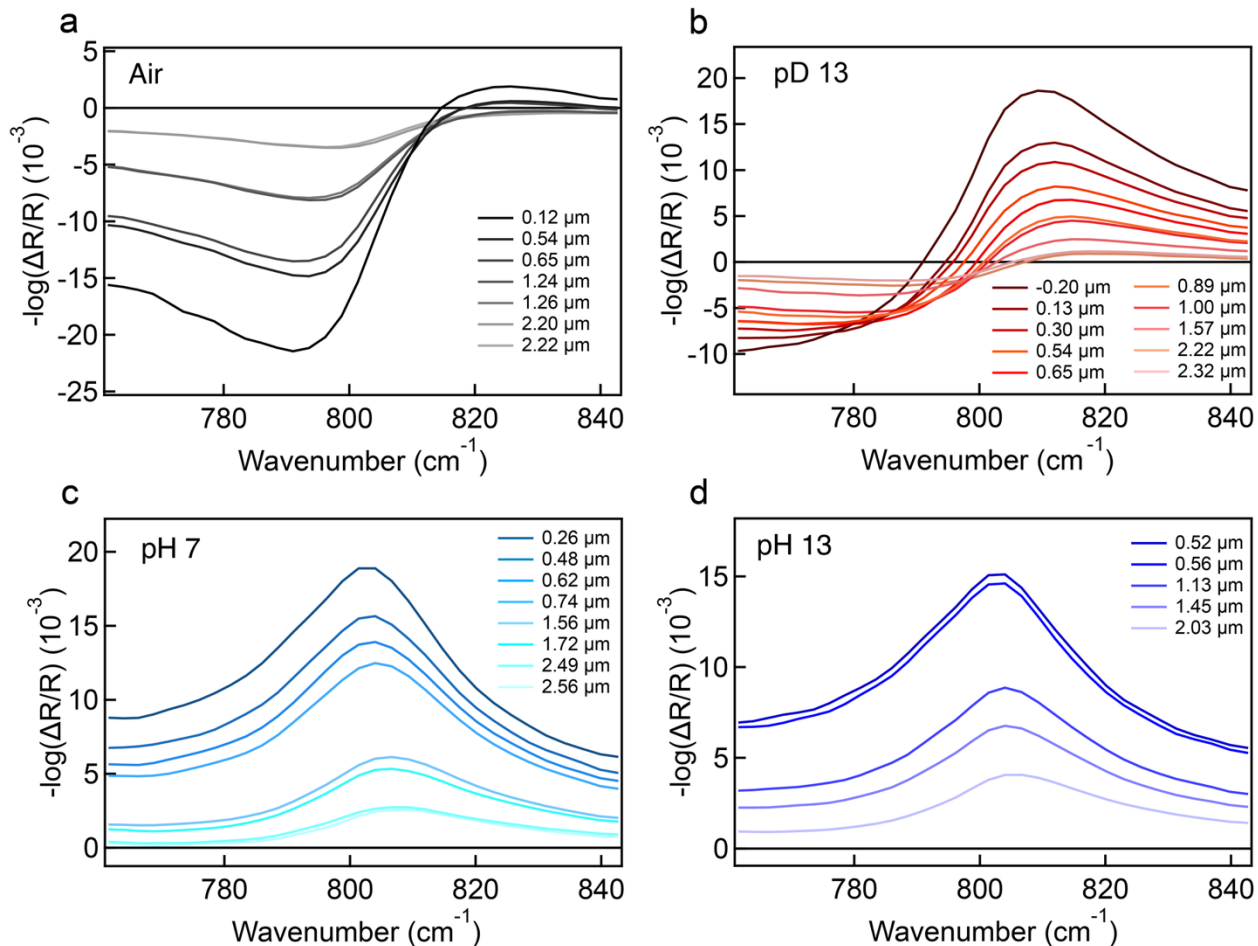


Figure B.4: Z-dependent spectra for air (a), pD 13 (b), pH 7 (c), and pH13 (d).

Spectra are taken from an equilibrium time delay (~ 10 ps) from the data contours shown in Figure B.3 are given in Figure B.4, with additional z-positions for some datasets. The overall magnitude of the spectra grows with decreasing z-distance as expected for an ATR geometry. The air spectra are very asymmetric, consistent at all z-positions. A positive transient appears to grow in at smaller gap sizes around 820 cm^{-1} . The pD 13 spectra are also highly asymmetric but have a much larger positive optical density above 800 cm^{-1} than air at all z-positions. The ratio of positive optical density at higher frequencies to negative optical density at lower frequencies appears to change with z-position, with the positive side growing more rapidly as the gap size decreases. This along with the positive and negative peak frequencies both redshifting toward lower frequencies

as gap size decreases indicates a change in the asymmetry of the spectra with z-distance. A similar trend appears in the more symmetric pH 7 and pH 13 spectra. In both cases, optical density decays more rapidly from the peak on the lower frequency side at smaller gaps. This switches to a more rapid decay on the higher frequency side as the gap size gets smaller. The peak frequency similarly redshifts as the z-distance decreases.

B.3 Growth Kinetics of the Oxyl's Vibrational Cross-Section

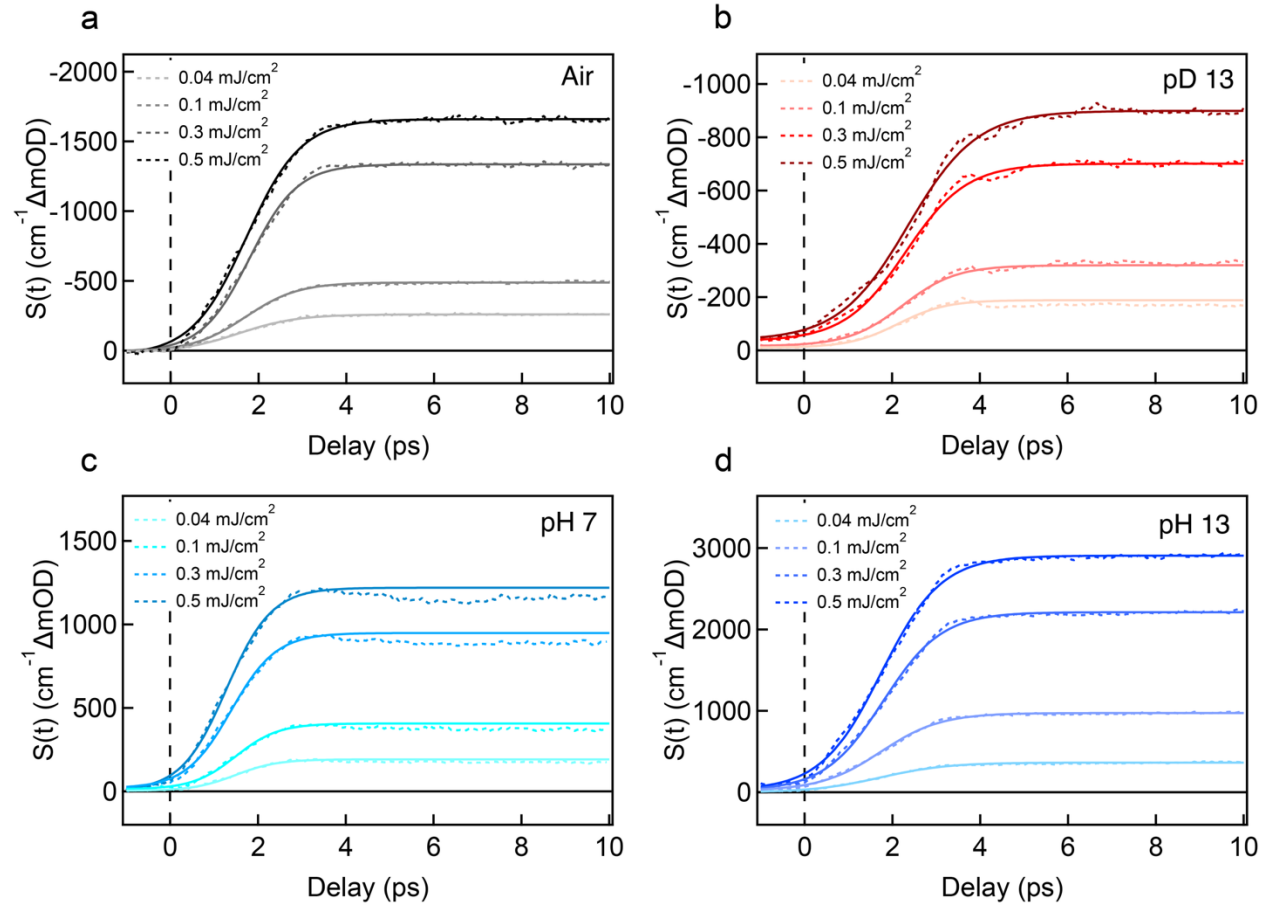


Figure B.5: Fluence Dependent $S(t)$ and corresponding logistic fits for air (a), pD 13 (b), pH 7 (c), and pH 13 (d) interfaces with 0.7% Nb STO.

Figure B.5 shows fluence dependent spectral weights for the four different n-STO interfaces. At all interfaces, $S(t)$ begins to rise immediately following time zero and grows to an

equilibrated state by 4 ps. All interfaces show the same s-shaped growth. As fluence is increased from 0.04 mJ/cm² to 0.5 mJ/cm², overall signal strength increases, as expected with increased electron/hole pair formation, while the growth kinetics remain unchanged. Each S(t) was fit with the logistic function given in Equation 5.1. The relevant fit parameters, given in Table B.1 are the same across the measured range of fluences for each condition.

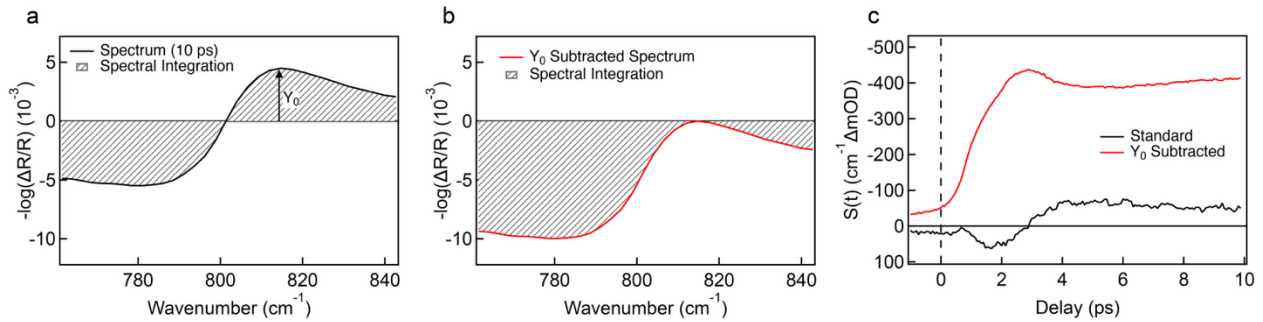


Figure B.6: S(t) extraction for 0.7% Nb STO/pD 13 interface. (a) The spectral integration of an equilibrated spectrum. (b) Spectral integration of the same spectrum after the background Y_0 has been subtracted. (c) Resulting S(t) from integrating all time delays from 0-10 ps for each method.

Figure B.6a depicts the integration of a spectrum at the 0.7% Nb STO interface with pD 13 solution. Also depicted on the spectrum is the Fano Y_0 parameter, which is defined as a background superimposed on the spectrum due to excitations of the continua, as discussed in more detail elsewhere in the main text. By the Fano theory, without the presence of this background there exists a frequency, the anti-resonant frequency, where the spectrum touches zero. Figure B.6b shows the same spectrum after the Y_0 background has been subtracted such that the maximum is zero. The results of integrating the n-STO/pD 13 spectra with and without subtraction at every time delay for a representative data set are shown in Figure B.6c. The standard method without Y_0 subtraction results in an S(t) near zero at all delays that does not accurately capture the spectral growth. This is a result of the background creating a symmetry of the spectrum around zero on the y-axis such that integration is zero despite a large spectral signal. By removing that background,

the extracted $S(t)$ shows a large, s-shaped growth that equilibrates by 4 ps after excitation. This growth aligns with that of the other three interfaces defined here.

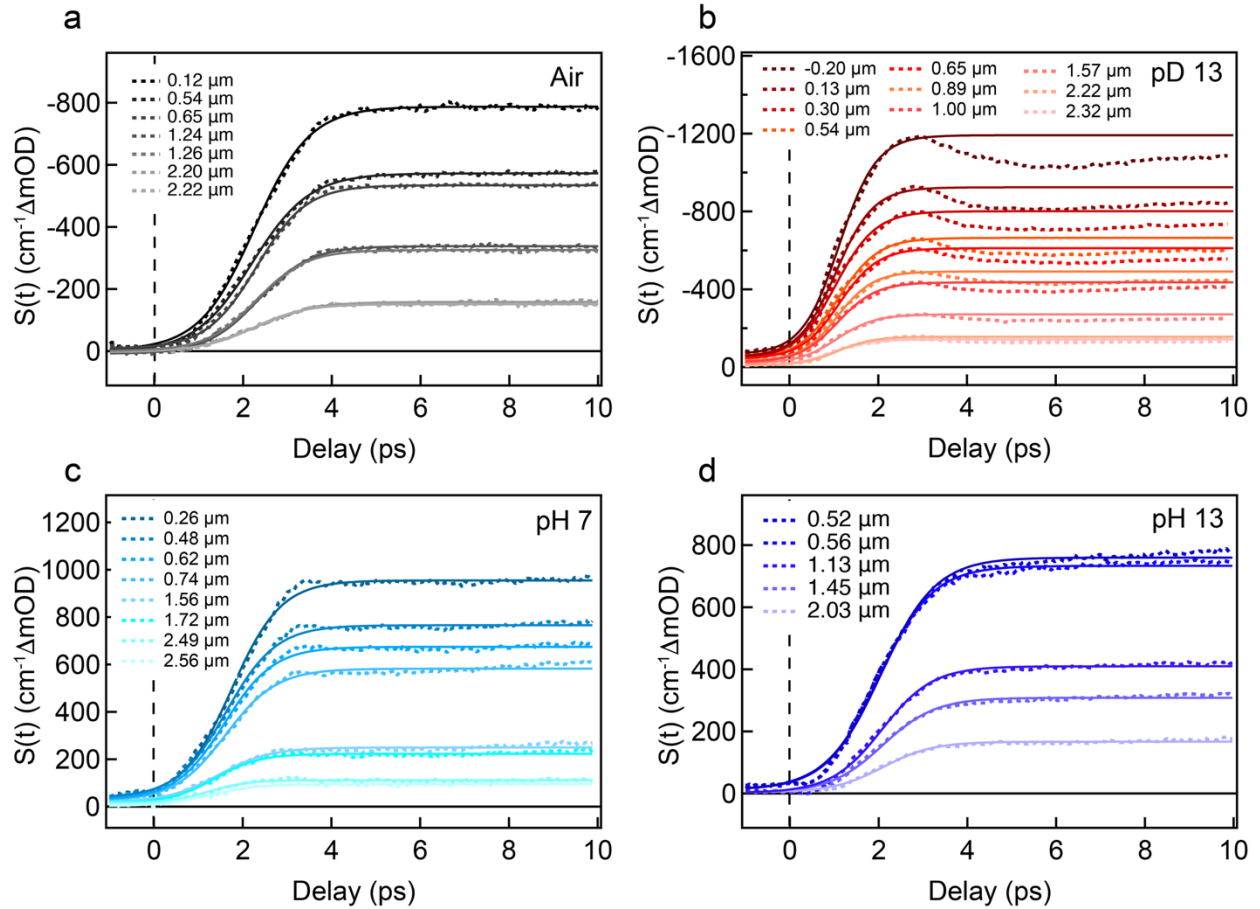


Figure B.7: Z-dependent $S(t)$ and corresponding logistic fits for air (a), pD 13 (b), pH 7 (c), pH 13 (d) interfaces with 0.7% Nb STO.

Figure B.7 shows z-dependent spectral weights for the four different n-STO interfaces. For all conditions, the magnitude of $S(t)$ grows as the z-distance between the sample and ATR element gets smaller, as expected for the experiment geometry. The time dynamics remain consistent with z-position and across conditions. The signal begins to grow immediately following time zero. After a slow initial growth period, the signal grows rapidly before reaching a saturation by 4 ps. The pD 13 data in (b) appears to grow slightly faster following time zero compared to the other conditions,

and contains a small decay in signal from 3-4 ps. These differences are attributed to non-equilibrium transient effects that vary in strength between data sets. They are observed in other data sets to varying extents. The extraction and attribution of these transients is discussed in more detail in Figure 5.6 of the main text and in Figures B.16-B.19. Logistic fits using Equation 5.1 are shown for all z-positions. The resulting fit parameters are consistent for all z-positions and conditions. They are summarized in Table B.2.

	Fluence (mJ/cm ²)	τ (ps)	$t_{1/2}$ (ps)
Air	0.04	0.67	1.54
	0.10	0.60	1.70
	0.30	0.55	1.80
	0.50	0.62	1.72
pD 13	0.04	0.55	2.13
	0.10	0.61	2.23
	0.30	0.70	2.30
	0.50	0.79	2.37
pH 7	0.04	0.48	1.49
	0.10	0.49	1.49
	0.30	0.52	1.39
	0.50	0.51	1.28
pH 13	0.04	0.77	1.72
	0.10	0.68	1.73
	0.30	0.67	1.79
	0.50	0.68	1.74

Table B.1: Logistic fit parameters for fluence dependent $S(t)$ data shown in Figure B.5.

	Z-position (μm)	τ (ps)	$t_{1/2}$ (ps)
Air	2.22	0.65	2.27
	2.20	0.58	2.23
	1.26	0.58	2.34
	1.24	0.56	2.29
	0.65	0.65	2.20
	0.54	0.57	2.30
	0.12	0.62	2.25
pD 13	2.32	0.41	1.00
	2.22	0.40	1.10
	1.57	0.43	1.07
	1.00	0.43	1.08
	0.89	0.41	1.08
	0.65	0.43	1.12
	0.54	0.45	1.09
	0.30	0.45	1.03
	0.13	0.42	1.04
	-0.20	0.42	1.12
pH 7	2.56	0.55	1.26
	2.49	0.45	1.21
	1.72	0.50	1.37
	1.56	0.58	1.45
	0.74	0.58	1.61
	0.62	0.55	1.58
	0.48	0.56	1.62
	0.26	0.56	1.75
pH 13	2.03	0.56	2.11
	1.45	0.59	2.09
	1.13	0.57	2.07
	0.56	0.60	2.01
	0.52	0.62	2.05

Table B.2: Logistic fit parameters for z-dependent $S(t)$ data shown in Figure B.7.

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Air	3	1.784314	0.594771	0.000322
pD 13	3	1.6394	0.546467	0.014115
pH 7	3	1.583125	0.527708	0.000665
pH 13	3	1.72645	0.575483	0.017396

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.008009	3	0.00267	0.328603	0.805041	4.066181
Within Groups	0.064997	8	0.008125			
Total	0.073006	11				

Table B.3: One way ANOVA test for logistic rate (τ) across the four measured conditions. The P-value of 0.8 indicates not variance across the four conditions.

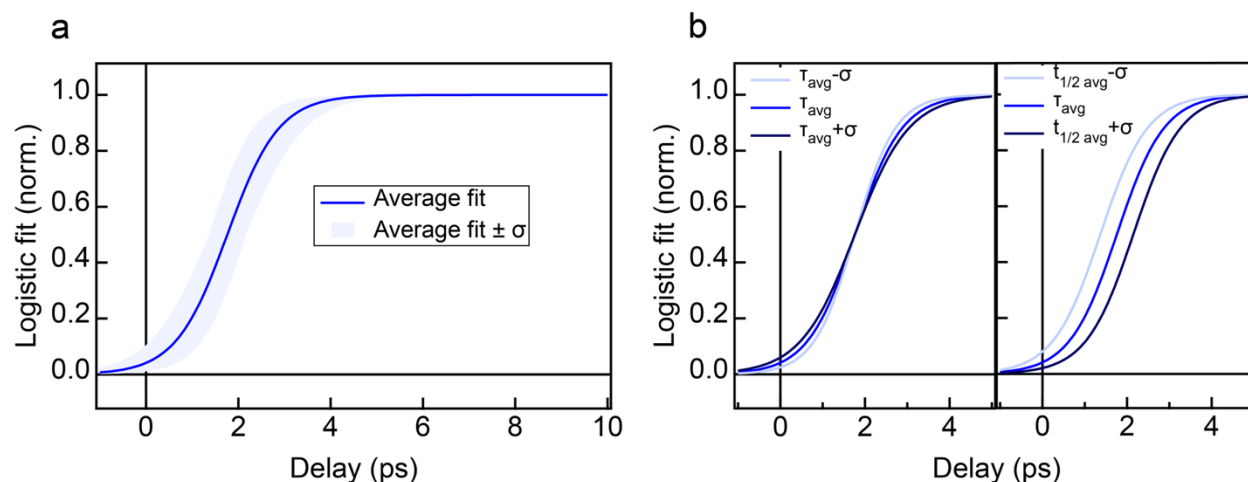


Figure B.8: Normalized logistic curves with average fit parameters. (a) The normalized logistic plotted using the average rate (τ) and x-half ($t_{1/2}$) from all data for all conditions (blue curve). The shaded region represents the area around the average fit within a single standard deviation of each parameter to illustrate the variation of the data around the average. (b) Normalized logistic functions +/- one standard deviation of the average for t (left) and $t_{1/2}$ (right). The left half uses $t_{1/2 avg}$ for all curves while varying τ while the right does the opposite, using τ_{avg} for all curves while varying $t_{1/2}$ to show the effects of changing the logistic time parameters individually.

B.4 Fano Fitting of the Oxyl's Vibrational Lineshape

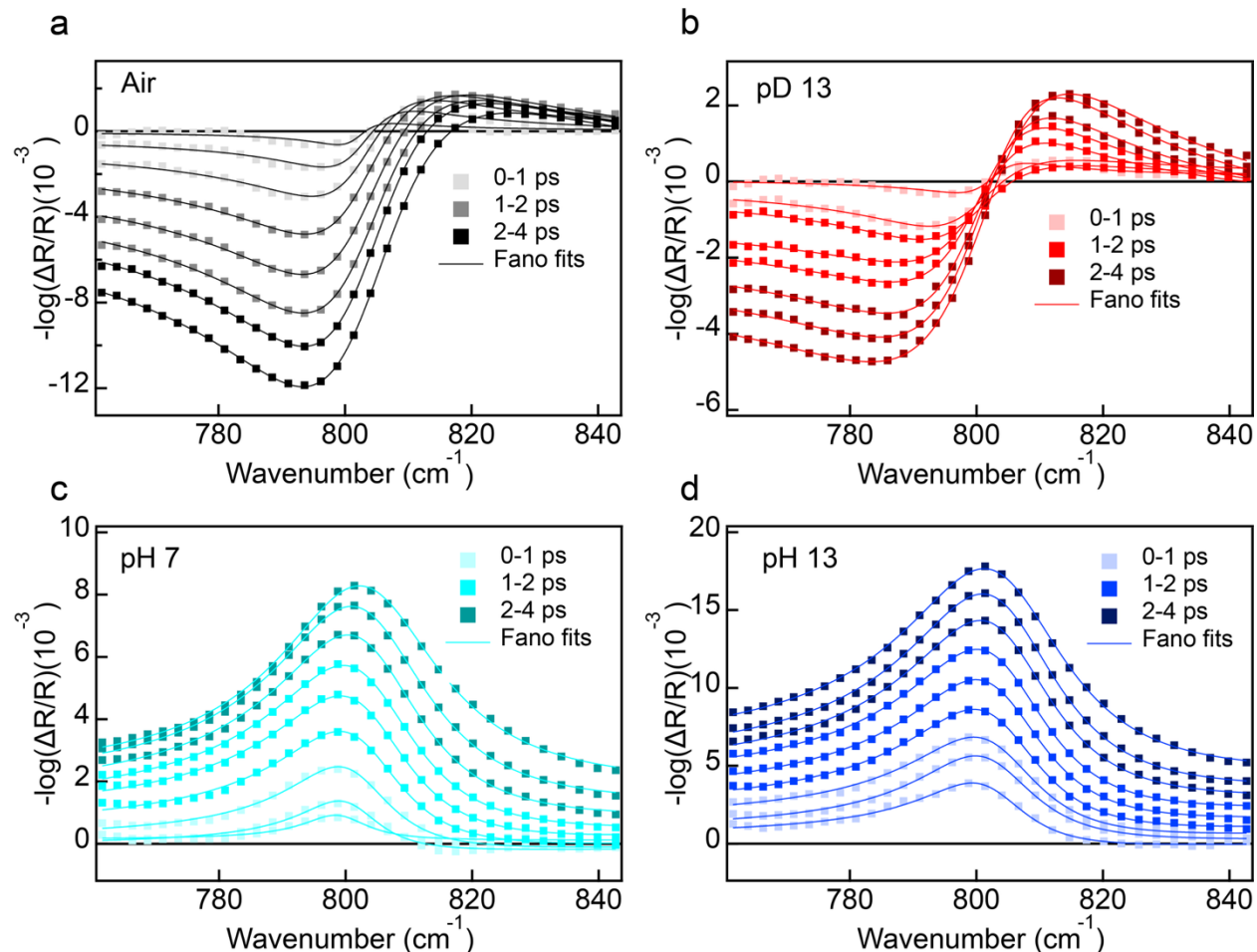


Figure B.9: Spectra and corresponding Fano fits at specific time delays for representative datasets at the air (a), pD 13 (b), pH 7 (c), and pH 13 (d) interfaces.

Sample Fano fits for each of the four interfaces with n-STO are given in Figure B.9. The different line shapes exhibited at each interface, from highly asymmetric in air and pD13 to nearly symmetric in pH conditions, are all well fit by the Fano equation (Equation 5.2). During the 0-1 ps range, the fits have some deviations from the data, particularly near the peaks in the more asymmetric shapes. The quality of the fits improves with time, more accurately capturing the spectral shape after 1 ps and perfectly matching the data once an equilibrium state is reached (after

4 ps). These deviations are likely due to the presence of other, non-Fano transients at early times, which is explored in more detail elsewhere.

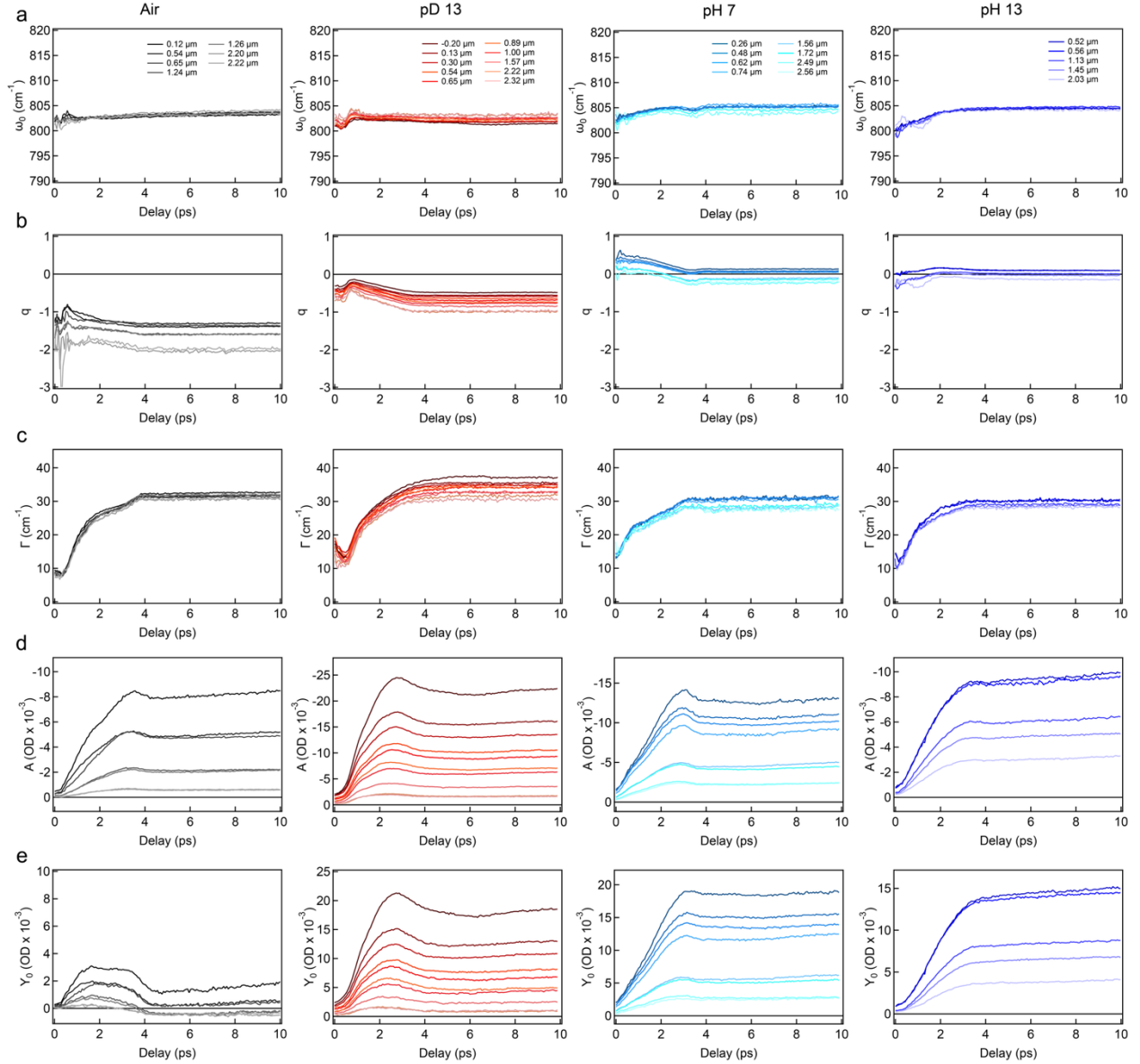


Figure B.10: A comparison of the time-dynamics of the Fano free fit parameters for the four interfaces with 0.7% Nb STO: Air, pD 13, pH 7, and pH 13. Each row displays a different parameter: the resonant frequency ω_0 (a), the asymmetry constant q (b), the coupling constant Γ (c) coupled continuum excitations A (d), and the background shift Y_0 (e).

Figure B.10 provides time-dependent Fano parameters for the four different n-STO interfaces as a function of z -position. The time-dependence of each parameter is largely consistent

across the four conditions, with ω_0 and q time-independent while Γ and A show rapid growth following time zero that reaches an equilibrated value by 4 ps. The growth of Y_0 matches that of A in all liquid conditions but not in air. There, it shows an initial growth, small in comparison to that of the other interfaces, that rapidly decays away to a small, near-zero value. Deviations from the overall trends in the time-dependence do occur to varying degrees. For example, if we examine $q(t)$ for the pH 7 data, there does appear to be a small growth in the parameter at early times not present in the pH 13 data. Examining the A parameter for the same data, early times in pH 7 shows an initial rapid growth that slows after approximately 1 ps, along with a small decay in the 3-4 ps regime. In comparison, pH 13 has a steadier growth throughout the 0-4 ps range with little to no apparent decay. Such behavior is attributed to two factors. First, that these free fits allow for interplay between parameters. As such, a growth in one parameter, such as q , can be accommodated by a change in another parameter, A , in the Fano equation. Thus, one set of fits is not necessarily unique. Second, the presence of non-equilibrium transients at early times can appear in these parameters to varying degrees. Such transients can appear in different magnitudes under similar conditions due to factors such as alignment. The extraction of these transients is explored elsewhere.

Turning to the equilibrated Fano parameters, we can examine both changes with z -distance for a given interface as well as across conditions. For the resonant frequency ω_0 , it is unchanging with z -distance across all conditions. There is some variation in the pD 13 and pH 7 data, shifting approximately 2 cm^{-1} from largest to smallest gap size. This is within the resolution of the detector in this regime ($\sim 2.7 \text{ cm}^{-1}$ between pixels) and is attributed to experimental fluctuations.

The largest change with both gap size and condition occurs with q , the asymmetry constant. Across all conditions, q is observed to increase as the gap size decreases. In absolute value, air has

the largest asymmetry with q ranging from -2.3 to -1.2 . This decreases with the addition of pD 13, which has a q ranging from -1 at the largest gaps to -0.5 at the smallest gaps. In both pH 7 and pH 13, the q value begins at approximately -0.25 , moving across zero to reach a positive 0.25 at the smallest gap size. The change in value across condition is expected for the Fano lineshape as we move from a single continuum present in air, the electronic continuum of the semiconductor, to two in solution with the addition of the water librational continuum. The difference between the value of q in pD and pH can be explained by the location of the librational peak, which is shifted to lower frequencies farther from the mode in D_2O compared to H_2O .

The spectral width, Γ , shows some change with z -position, the degree of change varying across condition. The largest change occurs in pD 13, with a nearly 8 cm^{-1} difference between the smallest and largest gap size. While the other conditions change less, in all cases Γ grows larger as the gap size decreases. There is some variation in the equilibrium value across condition, but all range between 28 and 32 cm^{-1} at the largest gap sizes. Given the detector resolution discussed with w_0 , it is difficult to draw conclusions on differences with condition based on such variations.

Both A and Y_0 show the anticipated behavior for an ATR geometry across conditions, increasing in magnitude as the gap size gets smaller and the sample is moved farther into the evanescent wave. The overall magnitude of Y_0 in air is smaller, as expected where only a single continuum is present. It decays to near zero at equilibrium, but is still present to some degree, particularly with the smallest gap sizes. Differences in overall magnitude of A and Y_0 across conditions are attributed to the dependence of signal strength on gap size.

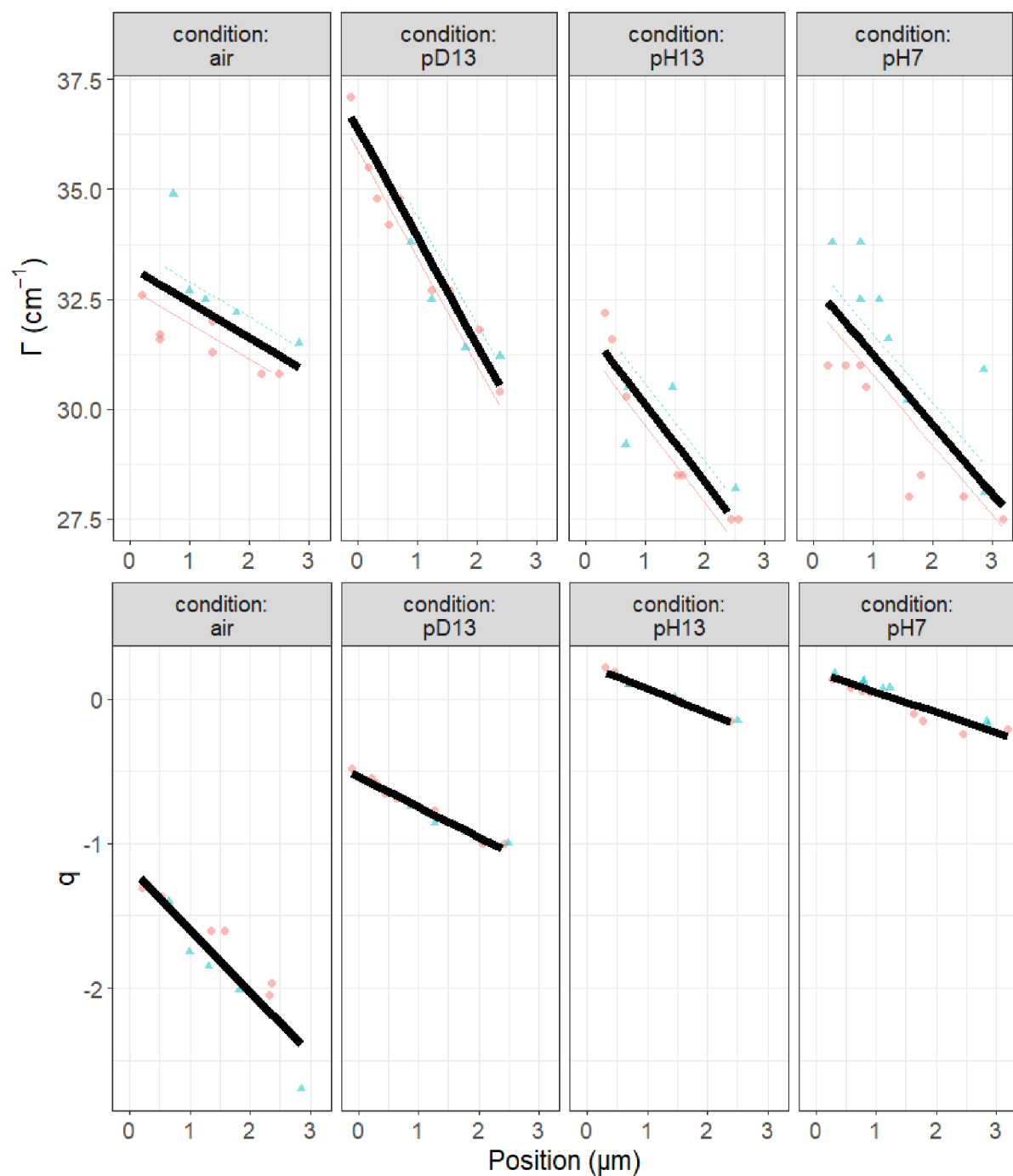


Figure B.11: Linear mixed-effects models (LMM) with both free slopes and intercepts for the Fano parameters Γ and q across the four measured conditions as a function of sample z-position.

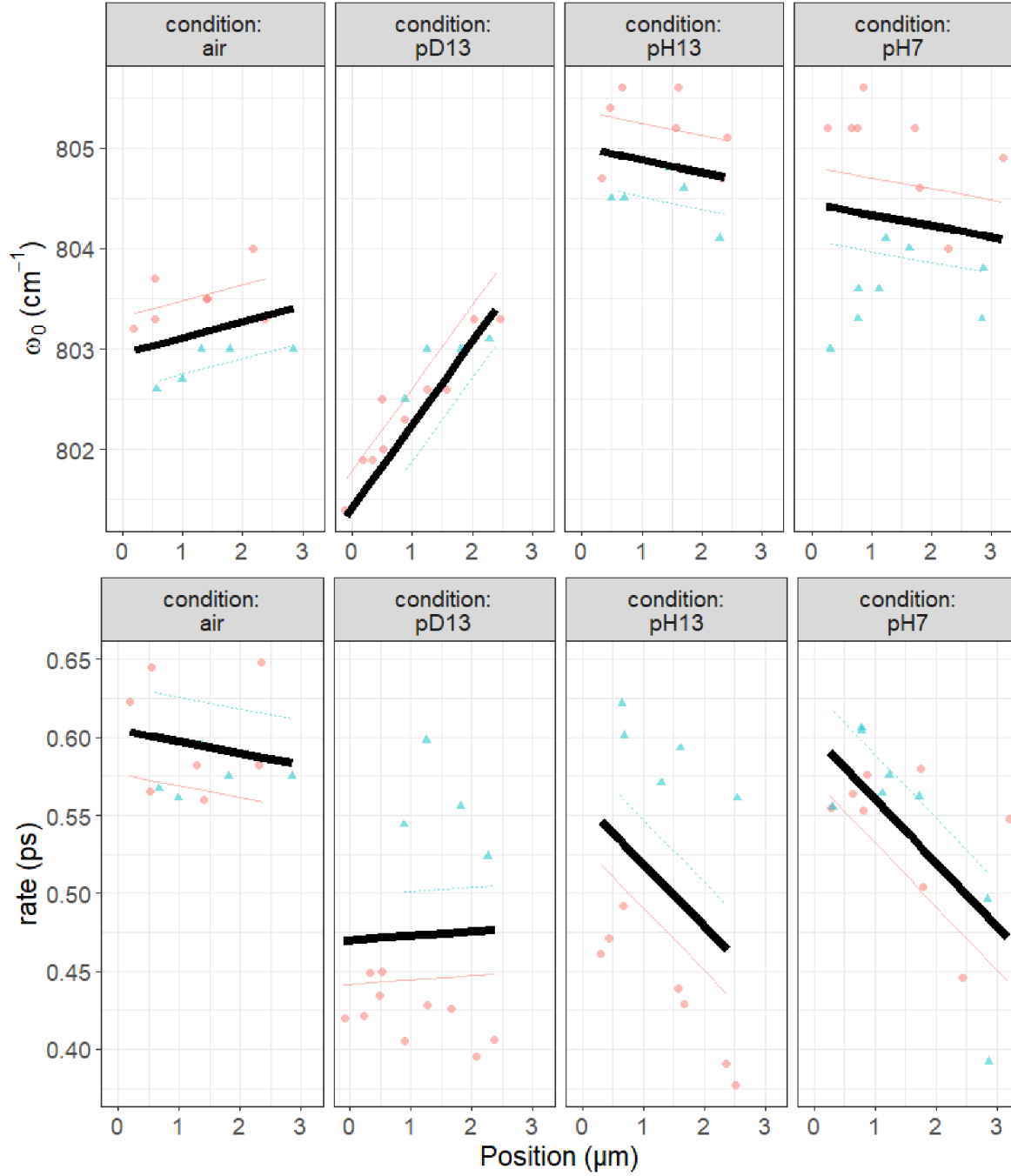


Figure B.12: Linear mixed-effects models (LMM) with both free slopes and intercepts for Fano ω_0 and the logistic rate τ across the four measured conditions as a function of sample z-position.

Z-dependence of the logistic rise and Fano fit parameters was analyzed using linear mixed-effects models (LMM) with both free slopes and intercepts. Experimental condition and z-position were treated as fixed effects, while experimental trial was included as random intercept to account

for between trial variability. In this model, each condition was allowed to have an independent linear dependence on z .

For the Fano parameters Γ and q (a, b), both show a clear negative linear dependence on z , with larger values observed at smaller gap sizes across all conditions. This contrasts with the resonance frequency ω_0 (c) and logistic rise rate (d) which showed larger scatter in individual fits and less consistent trends across conditions.

To quantify these effects, Type III analyses of variance (ANOVA) using Satterthwaite's approximation for degrees of freedom were performed for each model (Table B.4). This analysis tests the contribution of each fixed effect by comparing variance between groups to the variance within the groups using the F – test statistic and distribution.

For this full model, strong evidence for an environmental condition effect was observed for Γ , q , and ω_0 ($P < 10^{-6}$), while the logistic rise rate also showed a significant but less strong condition dependence ($p = 2 \times 10^{-4}$). With respect to z -dependence, Γ and q showed extremely strong evidence for a non-zero slope ($P < 10^{-16}$), while ω_0 and the logistic rise rate showed a weaker but still significant z dependence ($p = 0.027, 0.0042$ respectively).

Given the weaker and inconsistent z -trends observed for ω_0 and the logistic rise rate in this model, a reduced LMM was also performed for these parameters. In this reduced model, the slope with respect to z was constrained to be the same across all conditions, while allowing for condition specific intercepts (Figure B.13). This model was again analyzed using ANOVA with the results shown in Table B.5.

Under the new constraints of the reduced model, the z -dependence of ω_0 was no longer statistically significant ($P = 0.10$), while the effect of experimental condition remained highly significant ($P = 1.1 \times 10^{-15}$). This suggests that changes in ω_0 are primarily driven by experimental

condition rather than changes in z . For the logistic rise rate, both z -position and condition effects remained statistically significant in the reduced model ($P=0.0026$ and $P = 10^{-6}$, respectively).

Looking at the random effects shows a large variability between experimental trials, especially for the logistic rise rate. Large differences were observed between the pH 13, pD 13, and pH 7 datasets. Due to only having two trials for the z -dependence measurements and having prior work showing air to have a similar rise rates as the other conditions, an additional one-way ANOVA test was performed using the rate values from a single z -position with an additional data set from the fluence dependence measurements (with the same fluence and similar position). This showed no statistically significant difference in the rise rate between conditions ($P=0.8$), supporting the interpretation that trial variability dominates over any condition dependence for the logistic rise rate (see Table B.3).

	Sum sq	Mean sq	NumDF	denDF	F value	P value
Γ						
position	85.37	85.37	1	45.076	95.87	9.84E-13
condition	45.6	15.2	3	45.087	17.07	1.51E-07
position:condition	8.37	2.79	3	45.058	3.13	0.035
q						
position	1.92	1.92	1	45.46	271.9	2.20E-16
condition	4.35	1.45	3	45.472	205.42	2.20E-16
position:condition	0.51	0.17	3	45.331	24.2	1.69E-09
ω_0						
position	0.88	0.89	1	45.026	5.24	0.027
condition	31.02	10.34	3	45.031	61.72	5.45E-16
position:condition	5.8	1.93	3	45.02	11.52	9.93E-06
rate						
position	0.0211	0.0211	1	45.059	9.12	0.0042
condition	0.0563	0.0188	3	45.068	8.11	0.0002
position:condition	0.0206	0.0069	3	45.045	2.96	0.0421

Table B.4: Full model (free intercept, slope), Type III Analysis of Variance (ANOVA) using Satterthwaite's method.

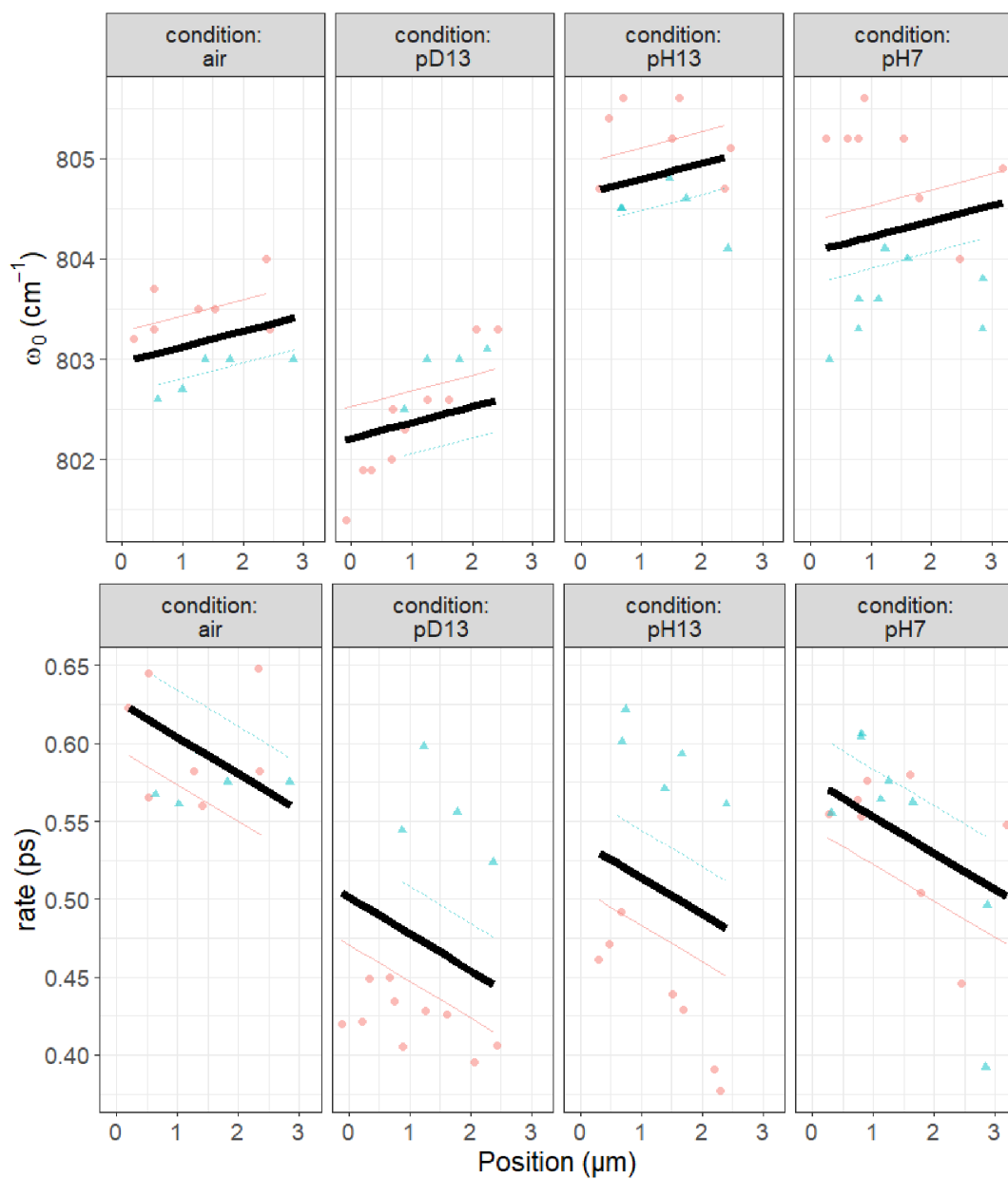


Figure B.13: Z-dependent free intercept linear mixed model for logistic rise and Fano ω_0 . This model is reduced by assuming that the z-dependent slope across samples should be the same, while still allowing for condition specific intercepts.

	Sum sq	Mean sq	NumDF	denDF	F value	P value
ω_0						
position	0.78	0.78	1	48.079	2.793	0.101
condition	46.62	15.54	3	48.036	55.789	1.11E-15
rate						
position	0.026	0.0261	1	48.074	10.089	0.00261
condition	0.109	0.0364	3	48.034	14.083	1.03E-06

Table B.5: Reduced model (free intercept), Type III Analysis of Variance (ANOVA) using Satterthwaite's method.

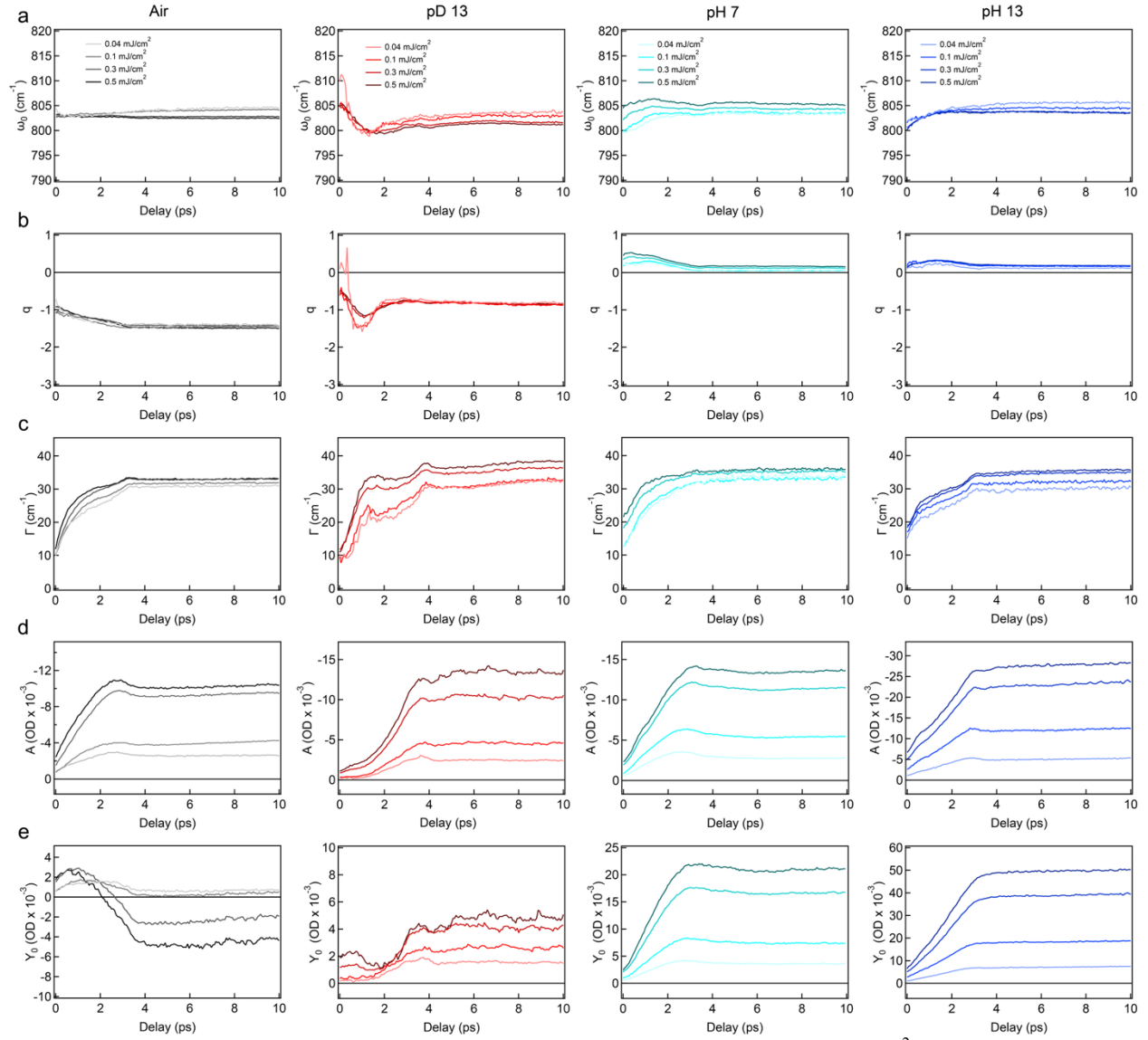


Figure B.14: Time-dynamics of Fano parameters at a range of fluences from 0.04-0.5 mJ/cm² for four interfaces with 0.7% Nb STO: air, pD13, pH 7, and pH 13. Each row displays a different parameter: the resonant frequency ω_0 (a), the asymmetry constant q (b), the coupling constant G (c) coupled continuum excitations A (d), and the background shift Y_0 (e).

Time-dependent Fano parameters are shown for specific pump fluences from 0.04-0.5 mJ/cm² in Figure B.14 for four different interfaces with n-STO. The resonant frequency ω_0 is shown in row a. No trend with increasing fluence is observed in ω_0 . There is some variation in the equilibrium values for each interface, but the change is not consistent across all conditions (ω_0 gets smaller with increasing fluence in air, pD 13, and pH 13, while getting larger with fluence in pH 7). These changes are attributed to experimental variation and are within the $\sim 3 \text{ cm}^{-1}$ resolution of the detector. Similarly, the Fano q shows no change with fluence at any interface. Both ω_0 and q are time-independent across all fluences, as observed in the z -dependent data in Figure B.10.

The time-dependence of Γ (Figure B.14c), A (Figure B.14d), and Y_0 (Figure B.14e) is the same at all fluences and consistent with the growth observed in the z -dependent data. At equilibrium, there is some variation observed in Γ with values differing by a maximum of $\sim 3 \text{ cm}^{-1}$ in air and as high as $\sim 6 \text{ cm}^{-1}$ in pD 13. While the highest fluences tend to have the largest values of Γ , there is no clear trend of increasing Γ with fluence across all data. The spread in values is largely attributed to experimental variation and interdependence of the free fit parameters.

Both A and Y_0 increase in value at equilibrium with increasing fluence at all interfaces. As these values represent a measure of signal strength and are defined by excitations of the continuum as discussed elsewhere, this is expected with increasing the number of electron/hole pairs created with fluence.

	Z-position (μm)	ω_0 (cm^{-1})	Γ (cm^{-1})	A (DmOD)	Y_0 (DmOD)	q
Air	2.22	804.0	30.80	-0.58	-0.50	-1.97
	2.20	803.3	30.80	-0.63	-0.36	-2.05
	1.26	803.5	31.30	-2.10	-0.25	-1.60
	1.24	803.5	32.00	-2.20	-0.25	-1.60
	0.65	803.3	31.70	-4.80	0.40	-1.36
	0.54	803.7	31.60	-5.20	0.54	-1.39
	0.12	803.2	32.60	-8.36	1.70	-1.31
pD 13	2.32	803.3	30.40	-1.60	1.00	-1.00
	2.22	803.3	31.80	-1.60	0.90	-1.00
	1.57	802.6	32.70	-3.57	2.50	-0.86
	1.00	802.6	32.70	-6.20	4.40	-0.77
	0.89	802.3	34.20	-7.00	4.90	-0.73
	0.65	802.5	34.20	-9.20	6.70	-0.69
	0.54	802.0	34.80	-10.50	8.10	-0.65
	0.30	801.9	34.80	-13.40	10.70	-0.58
	0.13	801.9	35.50	-16.10	12.90	-0.55
	-0.20	801.4	37.10	-22.20	18.20	-0.48
pH 7	2.56	804.9	27.50	-2.20	2.60	-0.21
	2.49	804.0	28.00	-2.30	2.80	-0.24
	1.72	804.6	28.50	-4.30	5.30	-0.15
	1.56	805.2	28.00	-4.70	6.00	-0.10
	0.74	805.6	30.50	-8.80	12.00	0.05
	0.62	805.2	31.00	-9.90	13.60	0.05
	0.48	805.2	31.00	-10.70	15.30	0.08
	0.26	805.2	31.00	-12.80	18.50	0.14
pH 13	2.03	804.1	28.20	-3.20	4.00	-0.15
	1.45	804.6	28.80	-5.00	6.80	-0.03
	1.13	804.8	30.50	-6.30	8.60	0.01
	0.56	804.5	29.20	-9.30	14.40	0.10
	0.52	804.5	30.50	-9.60	14.90	0.10

Table B.6: Equilibrated Fano fit parameters for z-dependent data shown in Figure B.10.

	Fluence (mJ/cm ²)	ω_0 (cm ⁻¹)	Γ (cm ⁻¹)	A (Δ mOD)	Y_0 (Δ mOD)	q
Air	0.04	804.55	30.90	-2.67	0.72	-1.40
	0.10	804.29	32.00	-4.43	0.56	-1.42
	0.30	802.75	33.00	-9.56	-1.96	-1.44
	0.50	802.50	33.00	-10.44	-4.24	-1.49
pD 13	0.04	803.88	32.50	-2.40	1.63	-0.81
	0.10	802.71	32.86	-4.56	2.67	-0.84
	0.30	801.62	36.38	-10.32	4.06	-0.84
	0.50	801.26	38.19	-13.38	4.77	-0.87
pH 7	0.04	803.15	33.72	-2.75	3.56	0.04
	0.10	803.57	32.70	-5.48	8.40	0.05
	0.30	804.27	35.08	-11.39	16.60	0.13
	0.50	805.28	35.65	-13.44	20.86	0.16
pH 13	0.04	805.70	30.28	-5.37	7.53	0.12
	0.10	804.51	32.00	-12.50	18.58	0.17
	0.30	803.64	34.67	-23.77	39.14	0.18
	0.50	803.52	35.76	-28.47	49.95	0.18

Table B.7: Equilibrated Fano fit parameters for fluence dependent data shown in Figure B.14.

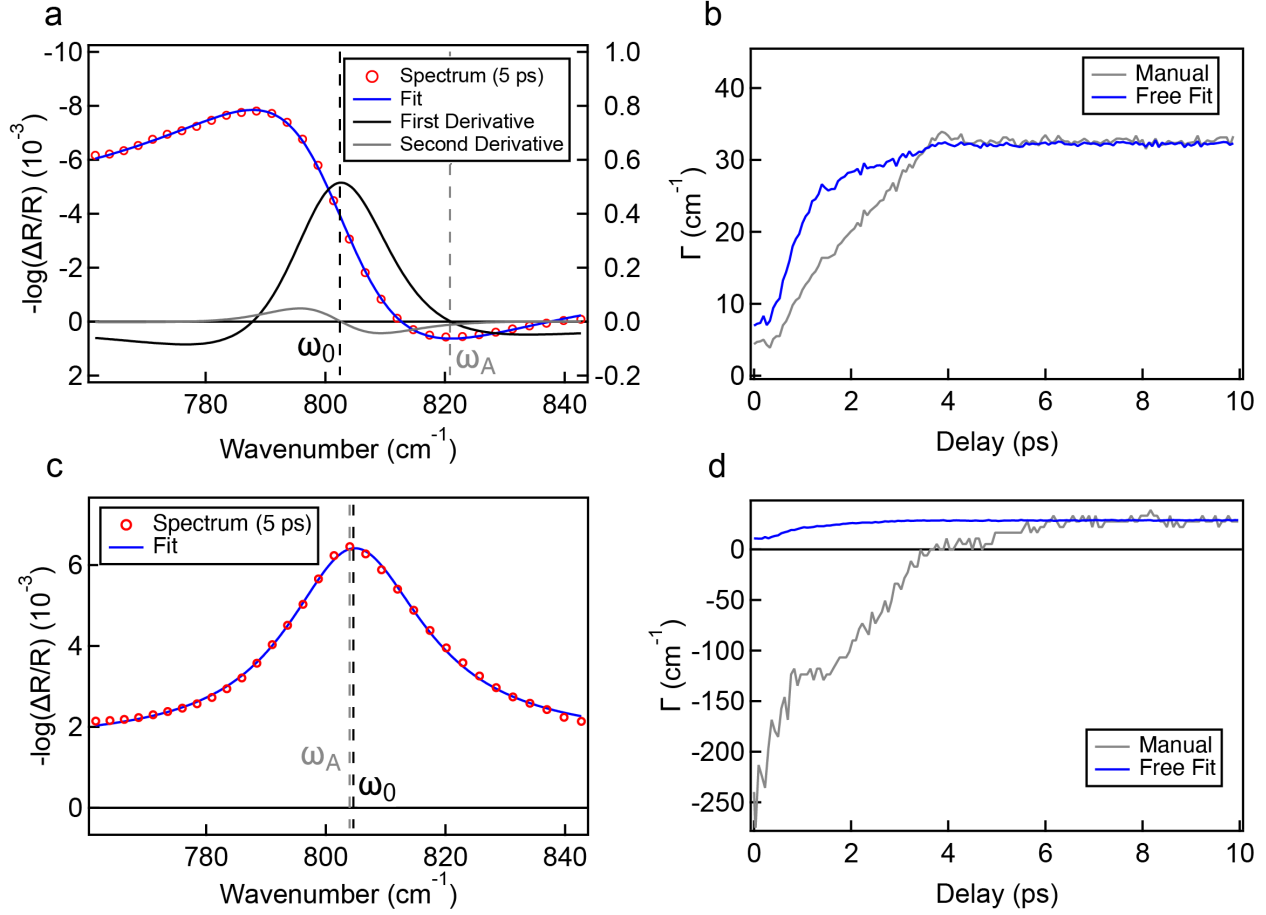


Figure B.15: Extraction of the Fano continuum coupling constant $\Gamma(t)$ via the anti-resonant frequency (ω_A). (a) Representative spectrum at the n-STO/air interface and corresponding Fano fit (left axis) along with the first two derivatives of the fit (right axis) used to determine the anti-resonant frequency. (b) The calculated $\Gamma(t)$ plotted with the free fit time dependence of Γ . (c) and (d) show the same for the pH 13 interface respectively, without the two derivatives of the pH 13 fit.

By evaluating the Fano lineshape at specific frequencies, the time evolution of the coupled continuum excitations, $A(t)$, and the coupling constant, $\Gamma(t)$, can be uniquely extracted. To do so, q and ω_0 are treated as time-independent, as supported by the free fits in Figure B.10. In air, the Y_0 offset is considered a transient that decays to near zero by 4 ps. Thus, at the resonant frequency with $Y_0 = 0$, the Fano lineshape given in Equation 5.2 simplifies to

$$|\langle \Psi | T | i \rangle|^2 = A(t) \cdot q^2 \quad \text{Equation B.1}$$

The value of q and ω_0 are determined from the free fits. A representative air spectrum is shown in Figure B.15a, where ω_0 is depicted near the half-rise of the peak. Using equation B.1,

$A(t)$ is calculated using the kinetics at the resonant frequency. An example is plotted in Figure 5.6 and shows an S-shaped growth similar to that of $S(t)$ with no noticeable transients.

Similarly, the anti-resonance frequency ω_A can be used to determine calculate $\Gamma(t)$. The anti-resonance frequency is located at the minimum of the concavity in the Fano lineshape, as labeled in Figure B.15a. In the absence of a Y_0 offset, ω_A occurs at the frequency for which the Fano lineshape is zero. Assuming a nonzero $A(t)$, the frequency that zeros the numerator of Equation 5.2 obtains ω_A in terms of Γ , q , and ω_0 :

$$\omega_A = \frac{-q\Gamma(t)}{2} + \omega_0 \quad \text{Equation B.2}$$

Given the presence of an offset, ω_A is extracted from the data by taking the first and second derivatives of the spectrum to find the frequency at which the first derivative is zero and the second derivative is negative (Figure B.15a). Once this frequency is extracted for each time delay, $\Gamma(t)$ is calculated from equation B.2 with the determined q and ω_0 from the free fits. An example of the resulting time evolution is plotted in Figure 5.6b and exhibits the same S-shaped growth as $A(t)$ and $S(t)$ that saturates by 4 ps. Figure B.15b compares the extracted $\Gamma(t)$ to the free fit time evolution. The free fit Γ rises much faster following time zero with a more exponential shape, indicating the variation that can arise from free fitting with variables that can compensate for each other.

A representative pH 13 spectrum is shown in Figure B.15c with the resonance and anti-resonance frequencies labeled. In comparison to air, the anti-resonant frequency moves to the peak of the spectrum, and the two frequencies are within 2 cm^{-1} of each other. The time-dependence of the coupled continuum excitation $A(t)$ can be extracted by the same logic as in air, with the additional factor of the large Y_0 term in solution. If you subtract Y_0 from the spectrum, $A(t)$ is still extracted from the kinetics at the resonant frequency using Equation B.1. However, once Y_0 is

subtracted, the peak of the spectrum touches zero. The proximity of the resonant frequency to this peak means that the kinetics at that frequency are also near zero. Also, due to ω_A and ω_0 being within the resolution of the detector ($\sim 2.7 \text{ cm}^{-1}$ between pixels), some time delays have the resonant frequency at zero after Y_0 subtraction. Thus, the calculation of $A(t)$ results in a time dependence with very poor signal:noise that does not accurately reflect the signal kinetics.

A similar argument is true for the extraction of $\Gamma(t)$. Equation B.2 calculates $\Gamma(t)$ using the difference between the resonant and anti-resonant frequencies, along with the equilibrium value of q . If these two frequencies exist within the resolution of the detector, the result is a $\Gamma(t)$ with a large amount of noise. An example is shown in Figure B.15d, which plots the free fit Γ with the $\Gamma(t)$ extracted from the anti-resonant frequency. Although the same equilibrium value is eventually reached, the two curves do not align at all. The extracted $\Gamma(t)$ contains a lot of noise even at equilibrium, and begins at a large negative value, which does not make physical sense for a coupling constant. This is attributed to the resolution issues, along with the presence of non-equilibrium transients. Such transients may have a small effect in air where the two frequencies have large separation but exhibit a large effect when they are so close together at a solution interface.

B.5 Modelling the Growth of the Oxyl's Vibrational Cross-Section

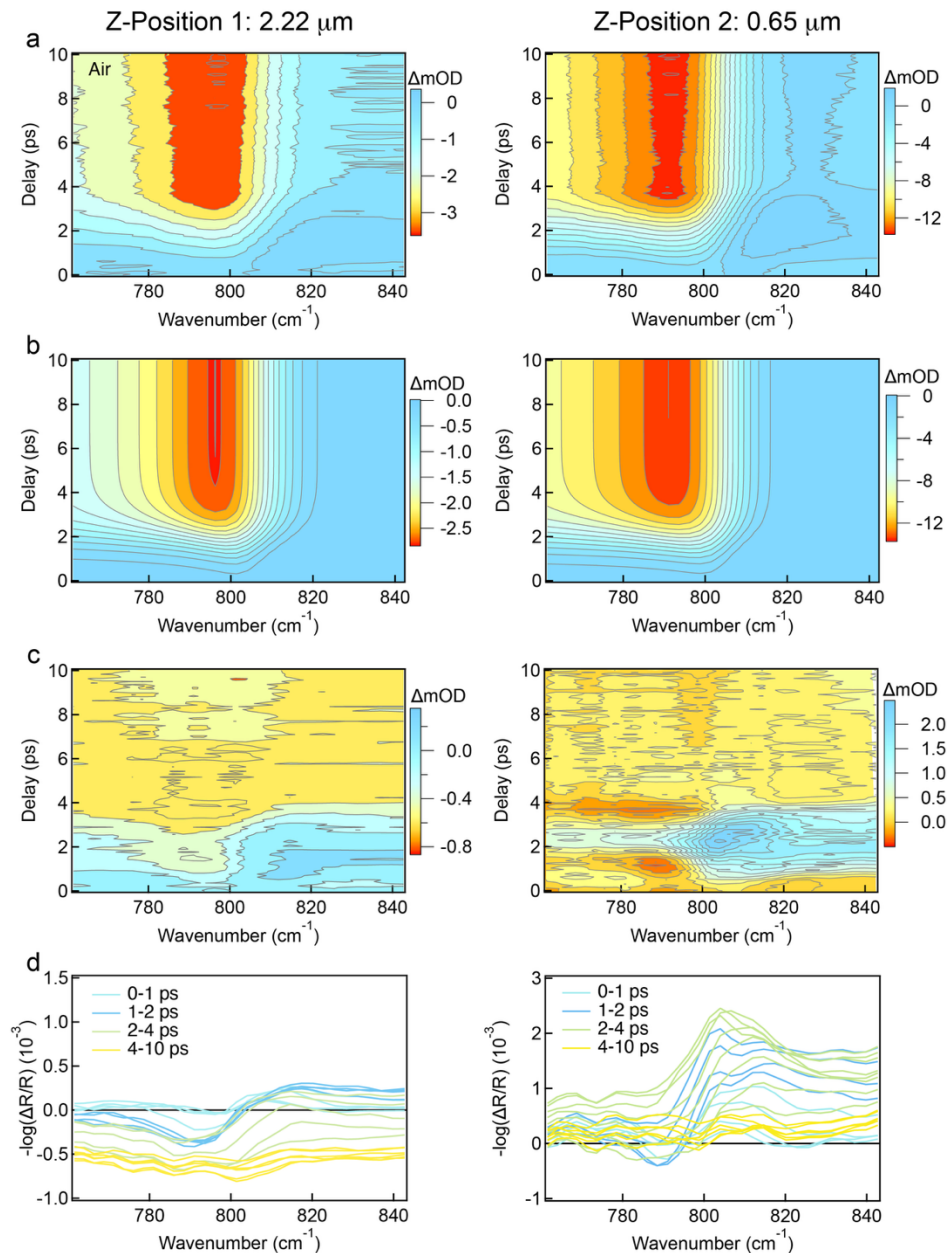


Figure B.16: Model of the equilibrated PES of the oxyl and the non-equilibrium transient at the n-STO/air interface. The two columns represent two z-positions with (a) data contour plot, (b) model contour plot, (c) difference contour plot, and (d) difference spectral slices at specific time delays. The details of the modeling are discussed in the main text. All equilibrated Fano parameters input to the model were determined from Figure B.10.

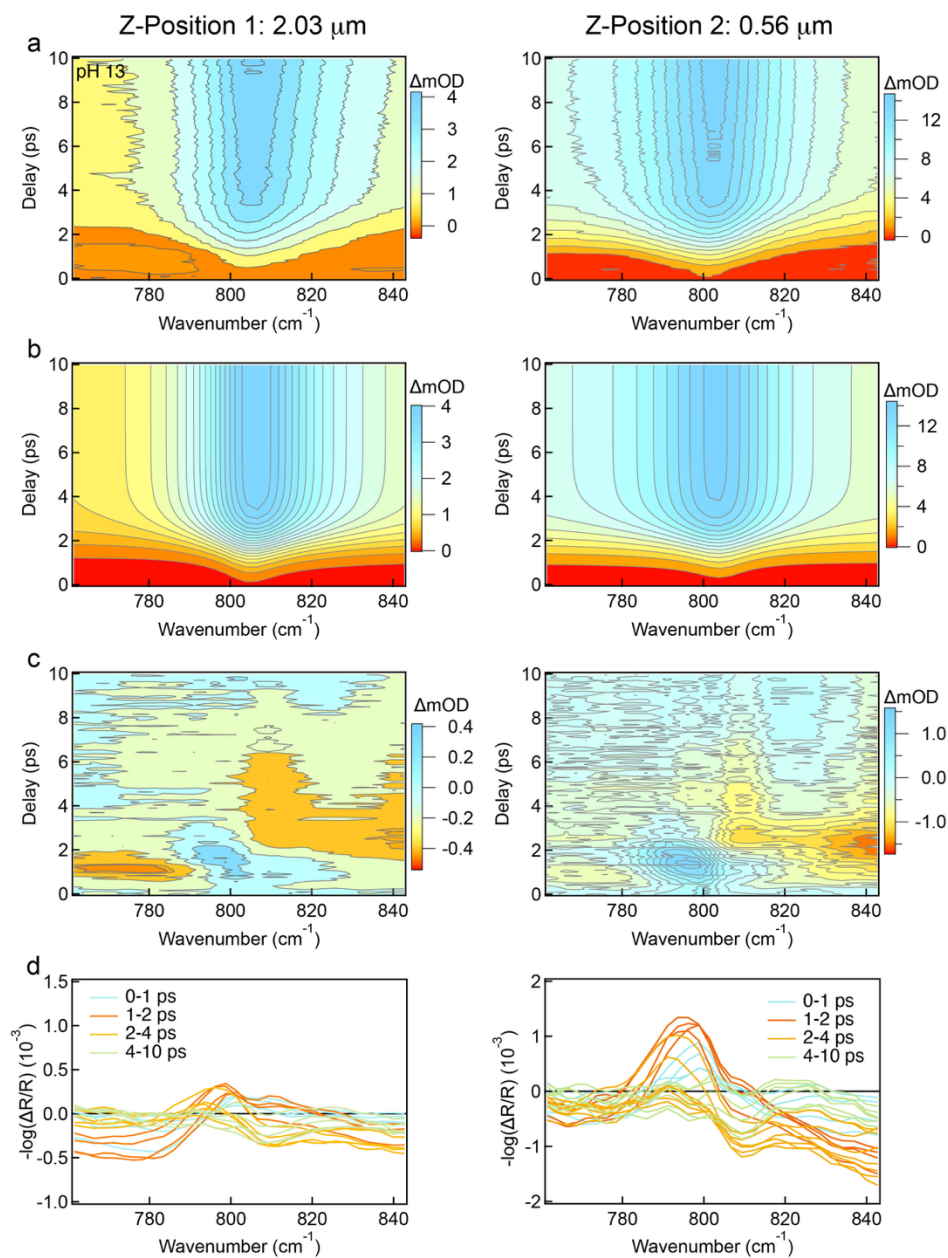


Figure B.17: Model of the equilibrated PES of the oxyl and the non-equilibrium transient at the n-STO/pH 13 interface. The two columns represent two z-positions with (a) data contour plot, (b) model contour plot, (c) difference contour plot, and (d) difference spectral slices at specific time delays. The details of the modeling are discussed in the main text. All equilibrated Fano parameters input to the model were determined from Figure B.10.

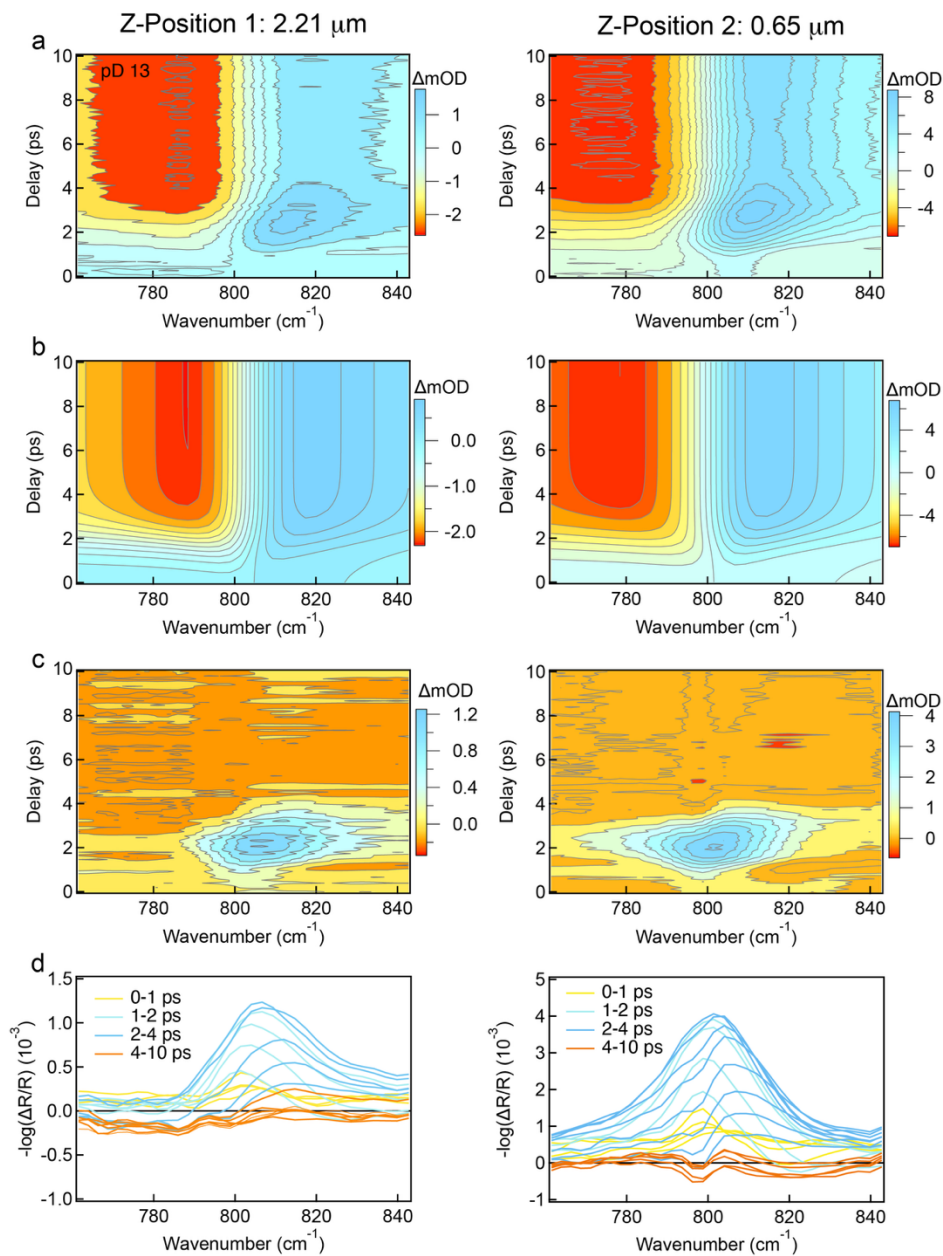


Figure B.18: Model of the equilibrated PES of the oxyI and the non-equilibrium transient at the n-STO/pD 13 interface. The two columns represent two z-positions with (a) data contour plot, (b) model contour plot, (c) difference contour plot, and (d) difference spectral slices at specific time delays. The details of the modeling are discussed in the main text. All equilibrated Fano parameters input to the model were determined from Figure B.10.

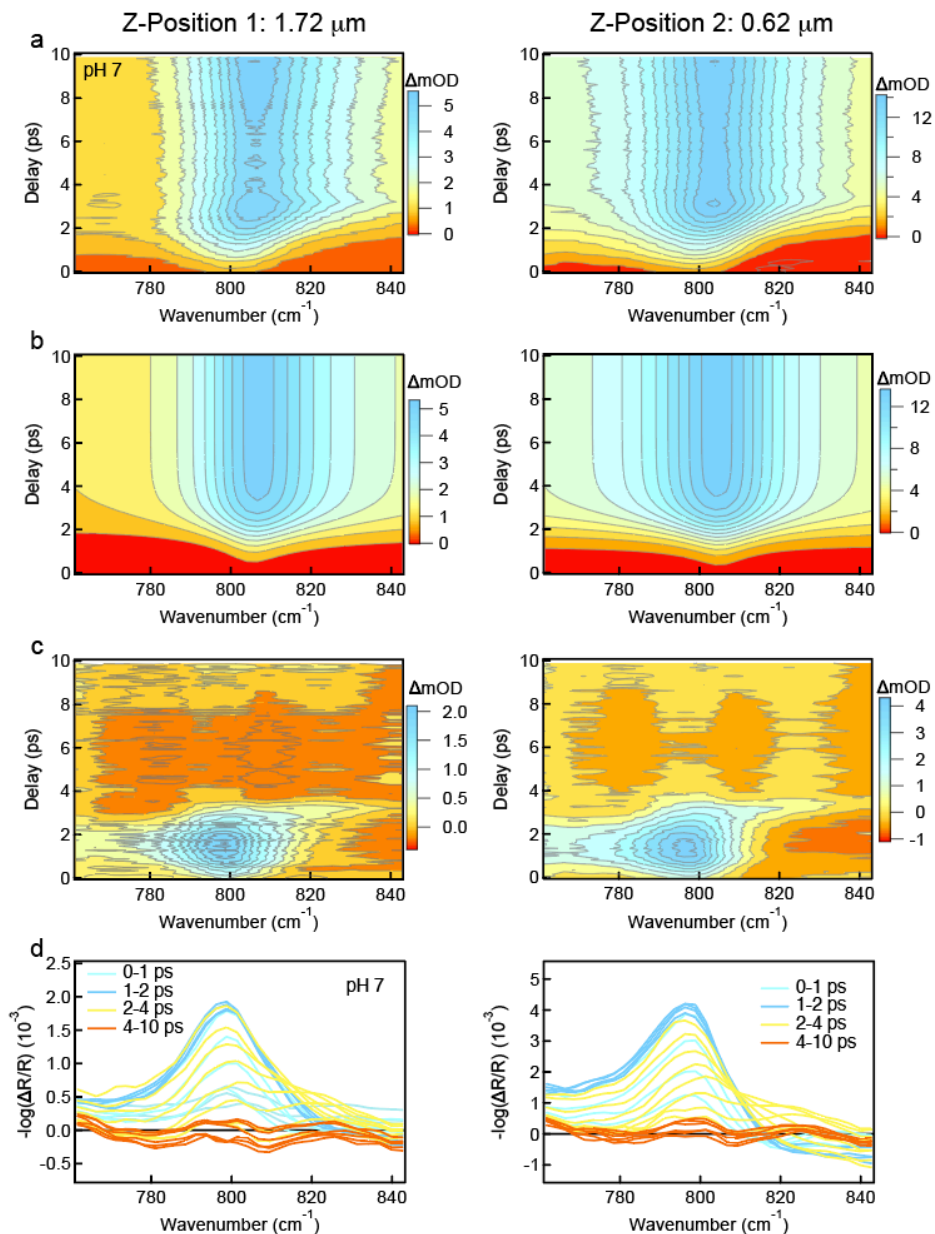


Figure B.19: Model of the equilibrated PES of the oxyl and the non-equilibrium transient at the n-STO/pH 7 interface. The two columns represent two z-positions with (a) data contour plot, (b) model contour plot, (c) difference contour plot, and (d) difference spectral slices at specific time delays. The details of the modeling are discussed in the main text. All equilibrated Fano parameters input to the model were determined from Figure B.10.

Appendix C

Supplemental data for the study of SPhPs on STO and TiO₂

C.1: Z-dependent ground and excited state spectra

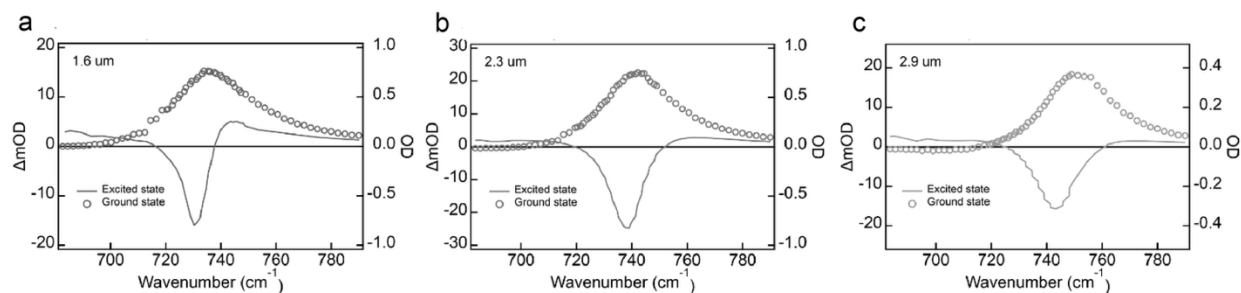


Figure C.1: Ground and excited state spectra for undoped TiO₂ c-axis plotted together for three sample z-positions. The excited state is plotted on the left axis, ground state on the right.

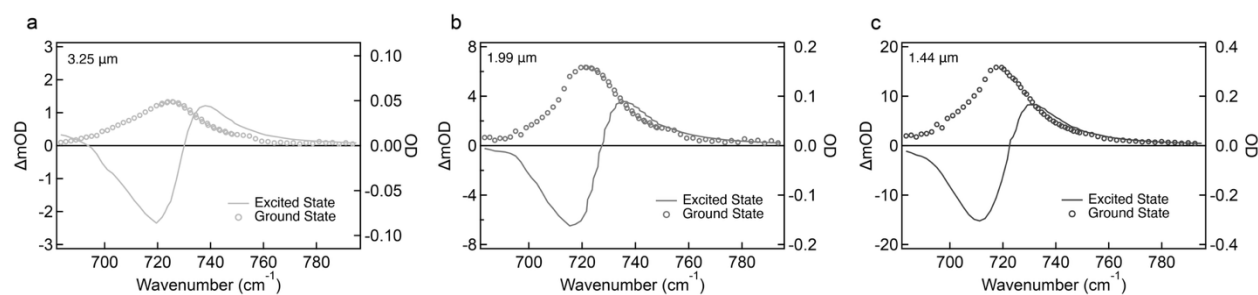


Figure C.2: Ground and excited state spectra for undoped STO plotted together for three sample z-positions. The excited state is plotted on the left axis, ground state on the right.

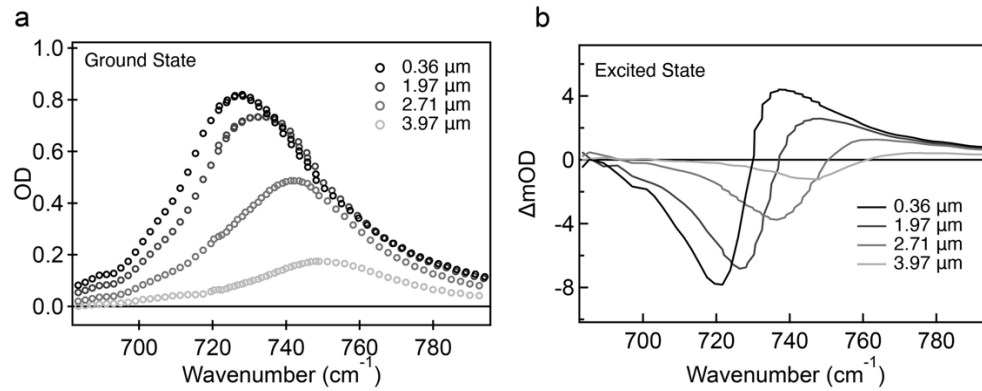


Figure C.3: (a) ground and (b) photoexcited spectra for 0.5% Nb TiO₂ along the c-axis as a function of z-position. Both the ground and excited states exhibit a shifting behavior to lower frequencies with smaller z-positions.