

**Hot Electron Dynamics at Semiconductor Surfaces:
Implications for Quantum Dot Photovoltaics**

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Abstract

Finding a viable supply of clean, renewable energy is one of the most daunting challenges facing the world today. Solar cells have had limited impact in meeting this challenge because of their high cost and low power conversion efficiencies. Semiconductor nanocrystals, or quantum dots, are promising materials for use in novel solar cells because they can be processed with potentially inexpensive solution-based techniques and because they are predicted to have novel optoelectronic properties that could enable the realization of ultra-efficient solar power converters. However, there is a lack of fundamental understanding regarding the behavior of highly-excited, or “hot,” charge carriers near quantum-dot and semiconductor interfaces, which is of paramount importance to the rational design of high-efficiency devices. The elucidation of these ultrafast hot electron dynamics is the central aim of this Dissertation.

I present a theoretical framework for treating the electronic interactions between quantum dots and bulk semiconductor surfaces and propose a novel experimental technique, time-resolved surface second harmonic generation (TR-SHG), for probing these interactions. I then describe a series of experimental investigations into hot electron dynamics in specific quantum-dot/semiconductor systems. A two-photon photoelectron spectroscopy (2PPE) study of the technologically-relevant ZnO(10 $\bar{1}$ 0) surface reveals ultrafast (sub-30fs) cooling of hot electrons in the bulk conduction band, which is due to strong electron-phonon coupling in this highly polar material. The presence of a continuum of defect states near the conduction band edge results in Fermi-level pinning and upward (*n*-type) band-bending at the (10 $\bar{1}$ 0) surface and provides an alternate route for electronic relaxation. In monolayer films of colloidal PbSe quantum dots, chemical treatment with either hydrazine or 1,2-ethanedithiol results in strong and tunable electronic coupling between neighboring quantum dots. A TR-SHG study of these electronically-coupled quantum-dot films reveals temperature-activated cooling of hot charge carriers and coherent excitation of a previously-unidentified surface optical phonon. Finally, I report the first experimental observation of ultrafast electron transfer from the higher excited states of a colloidal quantum dot (PbSe) to delocalized conduction band states of a widely-used electron acceptor (TiO₂). The electric field resulting from ultrafast (<50fs) separation of charge carriers across the PbSe/TiO₂(110) interface excites coherent vibration of the TiO₂ surface atoms, whose collective motions can be followed in real time.

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Chapter 1

Introduction

A study released recently by the Department of Energy (1) notes that world demand for energy is projected to more than double by 2050. The same report states that, “Finding sufficient supplies of clean energy for the future is one of society’s most daunting challenges.” The research presented in this Dissertation is motivated by this challenge. With the dawning reality of global warming, it is imperative that these new energy sources not contribute to already rising levels of atmospheric CO₂. Solar energy is the most fundamental and ubiquitous of all carbon-neutral energy sources. Almost as much energy from sunlight strikes the earth’s surface in one hour ($4.3 \cdot 10^{20}$ J) as the world currently consumes in one year ($4.7 \cdot 10^{20}$ J in 2008) (1, 2). Yet, in 2008, solar energy provided less than 0.1% of the world’s energy (2). The major barrier for widespread solar energy use is its high cost. Currently, the average cost of solar energy is above \$4/W (3), which is much higher than the targeted \$0.33/W needed to be competitive with conventional fossil fuel-derived energy sources (4).

The two major factors that keep the price of solar energy high are low power-conversion efficiencies and expensive high-temperature vacuum manufacturing methods. Traditional photovoltaic cells are based on the *p-n* junction diode, where incident photons with energy greater than that of the semiconductor’s band gap ($h\nu > E_g$) create electron-hole pairs, which are subsequently separated by the electric field at the *p-n* junction. Since charge recombination limits device performance, high temperatures and vacuum

are necessary to manufacture semiconductor materials that are defect free. Consequently, alternative photovoltaic device architectures that are more defect-tolerant and capable of converting more incident solar power to usable energy have the potential to drive down cost considerably.

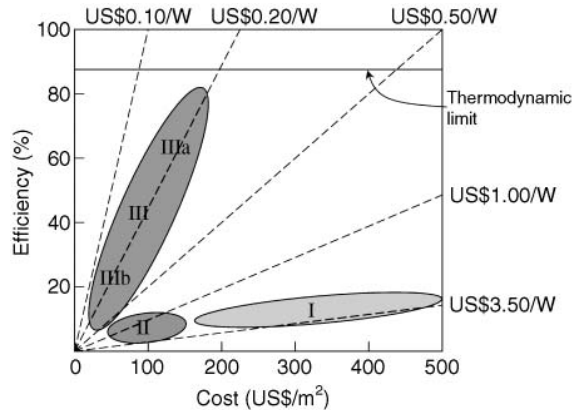


Figure 1.1 Cost-efficiency comparison of the three generations of solar cell technology: (I) silicon wafer-based, (II) thin-film, and (III) emerging technologies. Generation III technology is still in its infancy and the shaded area in this figure is meant to represent the potential of optimized devices. From (4), originally adapted from (5).

Solar cells are commonly classified into three generations of photovoltaic technology according to the material platform on which they are based (6). A comparison of cost and efficiency among these types of devices is shown in Figure 1.1. The “first generation” is based on silicon wafers, and is characterized by high material costs and current industry-leading efficiencies. Increasingly, “second generation” *thin-film* technology is threatening to supplant silicon wafer technology as the industry standard. Second generation devices are based on low-cost large-area deposition of a variety of semiconductor materials, including CdTe, amorphous silicon (a-Si), and copper indium gallium diselenide (CIGS). These devices offer a significant cost savings by eliminating the Si wafer, but suffer from reduced efficiency due to poorer material quality. The net result is only a marginal improvement in the cost-per-watt performance as module price savings are offset by lower power production. A “third generation” in solar cell technology has been anticipated for many years now, but the form of this revolution has yet to take shape. Such a revolution is expected because there is no fundamentally

limiting reason why solar cells need to be as expensive or as inefficient as they are. Terrestrial solar cells converting more than 68% of the sun’s energy to electric power are allowed within the laws of thermodynamics. However, in order to achieve these efficiencies at reasonable costs, device architectures that deviate from the traditional p - n junction diode will be necessary.

1.1. Efficiency limits for solar-to-electric energy conversion

As with any thermodynamic engine designed to transform a flow of energy into useful work, the conversion of energy among different forms is bound by the constraints of the Second Law of Thermodynamics. The Carnot efficiency, $\eta = 1 - T_C/T_H$, gives the upper bound for any device converting the flow of heat between two reservoirs to usable work. If we take the sun to be a heat source at $T_H = 6000\text{K}$ and a solar cell on the surface of the earth to be a heat sink at $T_C = 300\text{K}$, then the corresponding Carnot limit for a terrestrial photovoltaic device is $\eta = 95\%$. The Carnot efficiency corresponds to the limiting case where there is no entropy generation during the energy conversion process. Planck showed, however, that the emission and absorption of radiation involves unavoidable production of entropy (7). Consequently, a more reasonable estimate of the maximum theoretical efficiency for a terrestrial solar cell is obtained by considering the sun and the cell to be two black bodies absorbing and re-emitting radiation reciprocally. The corresponding “black-body limit” is $\eta = 86.8\%$ (6).^{*} The black-body limit assumes that the flow of energy is completely contained within the solid angle of the terrestrial solar cell subtended by the sun. Or, in other words, all black body radiation emitted by the cell is directed toward the sun. This is possible with collection optics and solar tracking and is referred to as the *direct* cell efficiency. However, because of the cost and complexity associated with collection optics and solar tracking, and because only about 75% of sunlight passes through the Earth’s atmosphere unscattered (5), the *diffuse*

^{*} Note that non-reciprocal systems (i.e. systems that do not possess time-reversal symmetry, such as solar cells employing Faraday rotators to selectively channel light re-emitted by the cell) are capable of higher efficiencies. This is the so-called Landsberg limit and corresponds to $\eta = 93.3\%$ (6).

efficiency is the more relevant number to compare among solar cell designs. In this limit, the maximum theoretical efficiency for terrestrial solar cells reduces from $\eta_{dir} = 86.8\%$ to $\eta_{diff} = 68.2\%$ (6). The difference in efficiency reflects the loss of energy by radiative heat transfer to the surrounding environment.

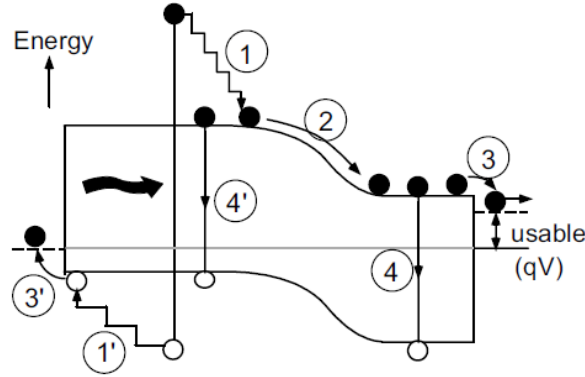


Figure 1.2 Energy conversion loss processes in a standard single-junction solar cell: (1) hot carrier relaxation, or thermalization; (2) junction loss; (3) contact loss; (4) recombination loss. A fifth energy loss process arises from photons with energy less than the semiconductor band gap that are not absorbed. From (8).

Clearly, there is room for improvement beyond the $\sim 15\%$ efficiency typical of commercial p - n junction solar cells available today. The major efficiency loss pathways in a single-junction solar cell are illustrated in Figure 1.2. These include hot carrier relaxation, junction losses, contact losses, recombination losses, and absorption losses because the material cannot absorb photons with energy less than the semiconductor band gap, $h\nu < E_g$. Of these processes, hot carrier relaxation and omission of photons with $h\nu < E_g$ result in the greatest efficiency losses and are fundamental limitations of the single-junction design. Shockley & Queisser (9) showed that the maximum efficiency a standard single-junction solar cell can achieve is 31.0% (40.8% under direct sunlight) with an optimal band gap of 1.3eV. The limitations of the single-junction design are clearly illustrated in Figure 1.3. At shorter wavelengths, any excess photon energy ($E_{excess} = h\nu - E_g$) is lost as heat due to hot carrier thermalization, while longer wavelength photons are not absorbed by the cell at all. The solar cell only operates near the black-body thermodynamic limit when it absorbs photons equal to the band gap, $h\nu = E_g$.

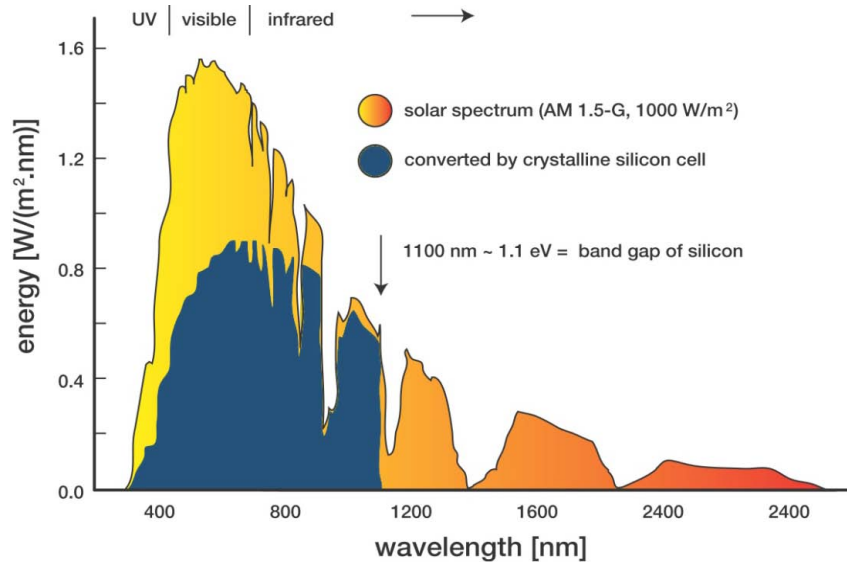


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The overall spectral conversion of the p - n junction design can be improved if the single-junction cell is replaced by a stacked series of p - n junction devices with different band gaps. In this design, each cell operates nearer to its thermodynamic limit and there are fewer absorption and hot carrier thermalization losses. For instance, a stack of two cells with optimized band gaps (1.87eV and 0.98eV) has a maximum efficiency of 42.9%, compared to 31.0% for the single-junction cell (6). For an infinite stack of ideal p - n junction cells, the efficiency is equal to the thermodynamic black-body limit of 68.2%. Tandem cells represent the state-of-the-art in current solar cell technology and efficiencies above 42% (for a three-cell stack) have been claimed. However, the cost of manufacturing tandem cells is prohibitive for widespread solar cell deployment. Consequently, their use has been limited to aerospace or defense applications.

1.2. Alternatives to the p - n junction

In 1991 M. Gratzel and co-workers introduced a radically different type of solar cell based on a wide band gap semiconductor, an electrolyte solution, and a metal-organic dye (11). In this “dye-sensitized solar cell”, illustrated in Figure 1.4, a mesoporous matrix of sintered TiO_2 nanoparticles (not displaying quantum size effects) deposited on a transparent conducting electrode (anode) is covered in a metal-organic ruthenium dye and immersed in an electrolyte solution containing a redox couple (e.g., I^-/I_3^-). The electrolyte solution, which is also in contact with the opposite electrode (cathode), forms a high surface area junction between the cathode and the dye-coated nanoparticles. When sunlight is absorbed by the dye, an electron is promoted from an occupied Ru valence orbital to an unoccupied antibonding orbital of the ligand which is higher in energy than the TiO_2 conduction band edge. This excited electron quickly and efficiently transfers to TiO_2 , then travels through the network of interconnected TiO_2 nanoparticles to the anode and on through the load. The positively charged dye oxidizes I^- to form I_3^- , and the I_3^- is in turn reduced by electrons at the cathode to regenerate I^- . The dye cell is capable of ~10% efficiency and various components are synthesized in solution at low temperatures, negating the need for expensive high temperature vacuum manufacturing.

Since the advent of the dye cell, numerous similarly configured “excitonic” solar cells have been imagined (12). Many of these new devices are based on a light absorber in high-surface-area contact with separate electron-transporting and hole-transporting phases. The light absorber need not be distinct from either of the transporting phases, but all of these cells rely on high surface area interfaces for charge separation. Examples of such devices include: i) nanowire dye-sensitized solar cells, where the mesoporous matrix is replaced by an array of ZnO (13-16) or TiO_2 nanowires (17), ii) quantum dot-sensitized solar cells (18, 19), where the dye is replaced by semiconductor nanocrystals, or “quantum dots”, iii) all-quantum dot heterojunction solar cells, based on a high surface area interface between two quantum dot layers (20, 21), iv) Schottky-quantum dot solar cells (not, strictly speaking, an excitonic solar cell as described below), based on formation of a Schottky barrier between an inorganic quantum dot film and a metal electrode (22-24), v) organic bulk heterojunction solar cells (25-27) consisting of two or more blended semiconducting polymer/organic phases, and vi) hybrid organic-inorganic

heterojunction solar cells (28, 29) combining a polymer/organic phase and a nanostructured inorganic phase.

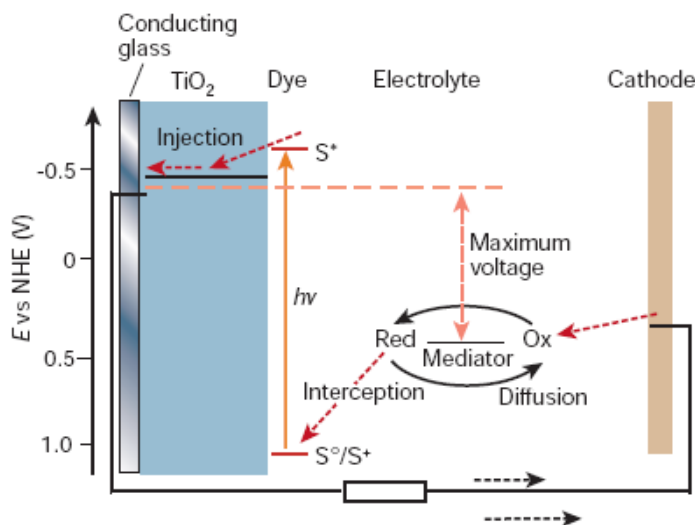


Figure 1.4 Grätzel's dye-sensitized solar cell (11). The red and black dashed arrows indicate the direction of electron flow. The energy scale used is the normal hydrogen electrode (NHE), referenced to hydrogen's standard electrode potential. The zero level corresponds to $\sim -4.5\text{eV}$ on a vacuum-reference scale.

Gregg (12) notes that the physical mechanism responsible for solar-to-energy conversion in these excitonic solar cells is fundamentally different from that of the inorganic photovoltaic cell based on the p - n junction. In p - n junction solar cells, absorption of sunlight results directly in free electrons and holes which are readily separated by the built-in field of the p - n junction. In excitonic solar cells, there is no built-in field. Further, the electron and hole generated by photon absorption are localized to the same molecule or quantum dot. The source of the photocurrent is separation of these electron-hole pairs at an interface where there is favorable alignment of energetic levels. Consequently, knowledge of the fundamental mechanisms underlying interfacial charge separation – a central topic of this Dissertation – is paramount to designing efficient excitonic solar cells.

1.3. Quantum dot solar cells

Semiconductor nanocrystals, or quantum dots (30), are particularly attractive candidates for active materials in next-generation photovoltaic devices. As the size of a piece of semiconductor material is reduced to the nanometer length scale, its optical absorption spectrum changes from a step-function-like continuum characteristic of bulk semiconductors to a series of peaks similar to molecular absorption spectra. This change is due to discretization of electronic energy levels within the nanocrystal and results from quantum confinement of charge carriers within the nanoscale crystallite (see Figure 1.5). The energetic position of these absorption features is tunable via control over nanocrystal size. The size-tunability of the optical absorption spectrum could be a powerful tool for designing efficient photovoltaic devices because the band gap and the semiconductor material are now decoupled to some extent. Additionally, semiconductor nanocrystals may offer considerable cost-saving benefits because they are synthesized as solution-processable colloidal dispersions. Quantum dot solar cells can be fabricated by large-area low-temperature manufacturing techniques such as roll-to-roll transfer, dip coating, spin casting, or inkjet printing, which can offer significant cost savings compared to high-temperature vacuum techniques and enable integration with flexible substrates.

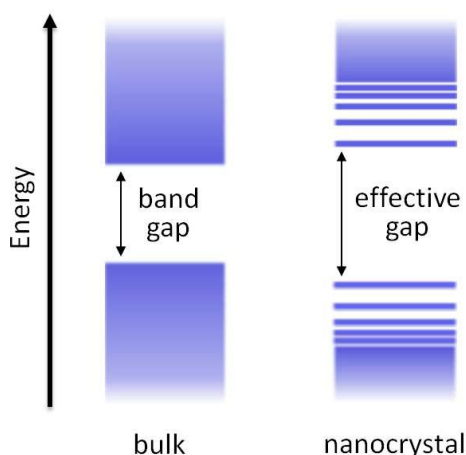


Figure 1.5 Bulk semiconductors are characterized by bands of continuous energy levels (blue) separated by a band gap. Semiconductor nanocrystals, or quantum dots, have a discrete spectrum of energy states.

In addition to the size-tunability of the optical absorption spectrum, semiconductor nanocrystals are predicted to have other novel electronic properties which are very exciting for photovoltaic applications (31). One of these properties is the efficient conversion of a single high-energy electron-hole pair to multiple lower-energy charge carriers (32, 33). For instance, absorption of a single photon with three times the energy of the band gap ($h\nu = 3E_g$) would quickly and efficiently produce three band-edge electron-hole pairs. In this way, some or all of the energy losses from carrier thermalization would be avoided. This process, termed *carrier multiplication* (32) or *multiple exciton generation* (33), has become quite controversial in recent years due to variability in multiplication yields with changing sample conditions. The growing consensus is that original claims were overstated and carrier multiplication will have little impact on improving solar cell device efficiency (34, 35). Nevertheless, other unique properties of nanocrystals (described below) still hold great potential for enabling cheap, efficient solar-to-electric energy conversion.

1.3.1. Hot carrier cells

One of the most exciting properties of nanocrystals for photovoltaic applications is the slowed thermalization of photoexcited charge carriers (36). When a bulk semiconductor absorbs a photon with more energy than the semiconductor band gap, electrons are promoted from energy states within the valence band to high energy states in the conduction band. As shown in Figure 1.6, these photoexcited electrons and holes scatter with other charge carriers to quickly (within ~ 0.1 -1.0 ps) form a Boltzmann distribution of electrons (holes) within the conduction band (valence band). This distribution is characterized by an electron (hole) temperature T_e (T_h) that is much higher than the lattice temperature*. Over the course of picoseconds, this “hot” electron or “hot” hole distribution gradually channels its energy to the nuclear coordinates (and on to the thermal bath) via phonon emission as the electron (hole) temperature approaches the lattice temperature. It is this undesirable conversion of excess electron or hole energy to

* T_e is dependent on the intensity and spectral distribution of the photons absorbed and can be many thousands of degrees Kelvin.

heat that results in the solar-to-electric efficiency losses represented by the yellow region in Figure 1.3.

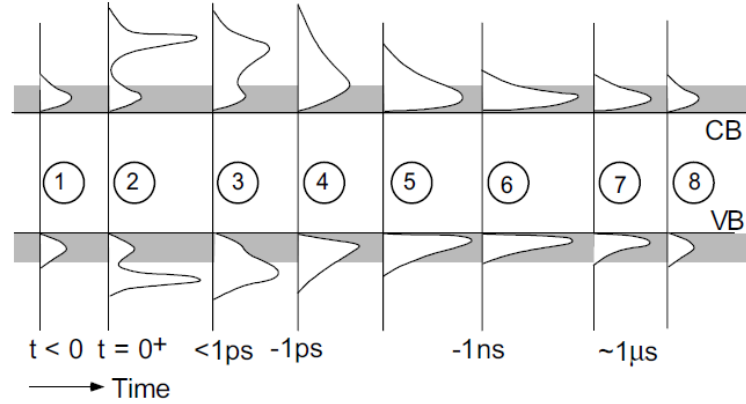


Figure 1.6 Temporal evolution of electron and hole distributions following absorption of a monochromatic pulse of light with $h\nu > E_g$. (1) Thermal equilibrium before the light pulse is absorbed; (2) initial distribution immediately following absorption before any carrier-carrier or carrier-phonon scattering has taken place; (3-4) sub-picosecond carrier-carrier scattering leading to electron and hole distributions (“hot carriers”) characterized by a temperature much higher than the lattice temperature; (5-6) thermalization of the hot carriers by phonon scattering and equilibration with the lattice temperature; (7-8) return to equilibrium over the course of nanoseconds by electron-hole recombination. From (8).

The loss of the excess energy stored in the hot carrier distribution is due the relative timescales involved in the processes of photon absorption, carrier cooling, and electron/hole transport within the device. In these cells, the transport of charges to collecting electrodes is faster than interband recombination (panels 6-8 in Figure 1.6), but slower than hot carrier cooling (panels 4-6). If transport could be accelerated or if the cooling of carriers could be slowed, then device efficiencies would improve dramatically. Ross & Nozik (37) showed that a hot carrier cell can, in theory, perform very near (within $\sim 1\%$ efficiency) the black-body or infinite tandem cell limit. For an infinitesimal band gap and “direct” illumination, the limiting efficiency is 85.4%, which is very close to the black-body value of 86.8% (6). The reason the hot carrier cell is slightly less efficient is because it must operate at one optimum chemical potential (the difference in energy between the conduction band and valence band nonequilibrium Fermi levels), whereas the infinite tandem stack is composed of many cells each operating at the optimum chemical potential corresponding to the wavelength of light it absorbs. However, this

minor limitation is of little practical significance. Also promising is the observation that infinitesimal band gaps are not required for very efficient operation. Under diffuse illumination conditions relevant for terrestrial use, the hot carrier cell is capable of better than 60% overall power conversion efficiency for band gaps as large as 1.1eV (6). While these numbers are certainly promising, it should be emphasized that an actual functioning hot carrier solar cell has never been reported. The preceding analysis serves to motivate the potential utility of such a device – particularly if one could be constructed in such a way as to minimize cost and complexity.

Semiconductor nanocrystals have great potential for use in hot carrier solar cells because the discretization of their electronic energy levels (Figure 1.5) leads to slower cooling of hot electrons and hot holes (36).^{*} Intraband cooling rates have been measured to be >1000 times slower than in the corresponding bulk material (38). This might allow the extraction of photogenerated charge carriers before they can relax to their respective band minima and avoid the energy losses associated with hot carrier relaxation. Another important consideration in hot carrier solar cell design is the way the semiconductor is contacted. Because the charge carriers in the contacts are in thermal equilibrium with the lattice, carrier-carrier interactions across the interface must be minimized and all charges must be extracted at the same voltage to avoid thermalization losses within the electrodes (see Figure 1.7). The molecules, or ligands, coating the surface of colloidal quantum dots offer a convenient means for controlling electronic coupling and charge transfer across the interface.[†] Finally, because quantum dots are solution processable, the quantum-dot hot-carrier cell could be both extremely efficient *and* cost-effective.

^{*} This topic is addressed in considerable detail in Section 2.2.

[†] See Section 2.3.

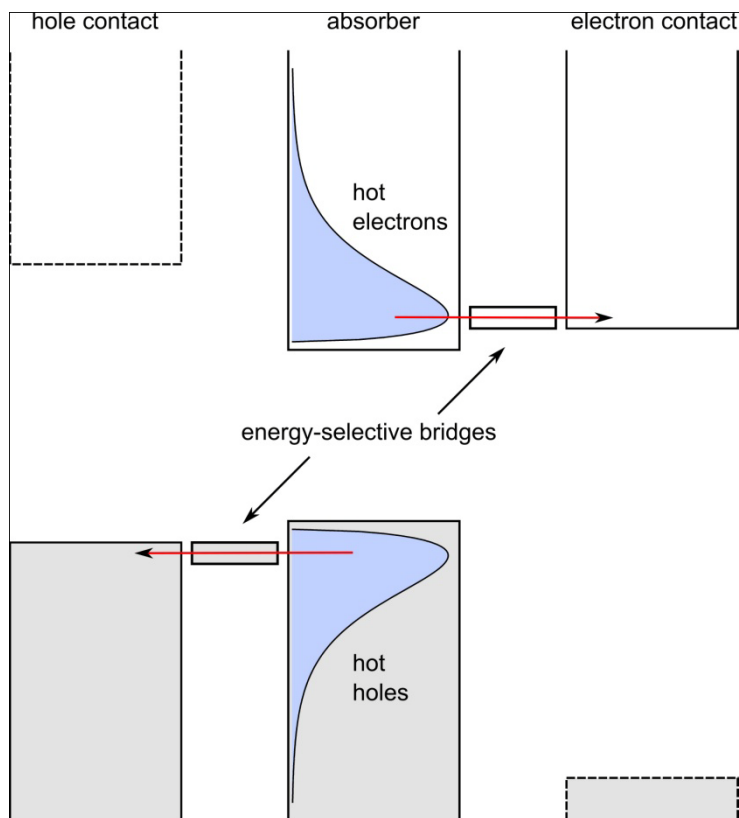


Figure 1.7 Energy-selective contacts for a hot carrier solar cell based on semiconductor quantum dots. The “absorber” layer is a film of electronically-coupled nanocrystals. The electron- and hole-contacts are bulk semiconductor materials (organic or inorganic) capable of efficiently transporting electrons or holes to metal electrodes. The energy-selectivity of the bridges might arise from HOMO or LUMO resonances in the molecular layer coating the surface of the quantum dot film.

1.4. Organization of this Dissertation

Though there is great potential for semiconductor quantum dots in hot carrier solar cells, many outstanding questions remain unanswered. What is the best choice of semiconductor material? How will charge carriers on neighboring nanocrystals interact with one another? Is it even possible to extract a charge carrier from a nanocrystal before it cools to its band minimum? What effect does the surface ligand have on interfacial charge transfer? What role, if any, does temperature play? What is the role of electronic coupling between neighboring quantum dots? What is the role of electronic coupling

between the quantum dot and the electron or hole contacts? How does the presence or disorder of a nearby surface affect the rate of hot electron cooling?

The motivation of this Dissertation is to experimentally investigate, at a fundamental level, the answer to some of these questions. Chapter 2 presents the theoretical framework for addressing these issues as well as a review of others' research contributing to our knowledge in these areas. In particular, considerable attention is paid to the development of a theoretical framework for understanding electron (or hole) transfer from quantum dots to bulk semiconductor acceptors. Many of the processes in question involve electron dynamics on sub-picosecond timescales. Consequently, experimental investigations require advanced time-resolved laser spectroscopy techniques. Two of these techniques, time-resolved two-photon photoelectron spectroscopy (2PPE) and time-resolved surface second harmonic generation (TR-SHG), are described in detail in Chapter 3 and Chapter 4. In Chapter 5, a comprehensive study of electron relaxation dynamics near the $(10\bar{1}0)$ surface of ZnO is presented. ZnO is a wide band gap semiconductor that is a promising candidate for electron-transporting layers in quantum dot solar cells and other third-generation photovoltaic devices, and provides a technologically-relevant model system for investigating the effects of a nearby surface on hot electron dynamics in bulk semiconductors. The remaining chapters (Chapter 6 and Chapter 7) summarize a series of experimental studies on electronically coupled thin films of colloidal PbSe nanocrystals supported on solid surfaces. In Chapter 6, changes to the structure, composition, and optical properties of the PbSe nanocrystal film following various chemical treatments and modifications to the surface ligands are presented. The topics addressed include the ultrafast nonlinear optical response of the PbSe nanocrystal film, which offers some insight into intra-nanocrystal electron dynamics and vibrational modes of the nanocrystals. Finally, in Chapter 7, strong evidence is presented for the *first experimental observation* of ultrafast hot electron transfer from the higher excited states of a semiconductor nanocrystal (PbSe) to delocalized conduction band states of a technologically relevant electron transporting material (TiO_2).

Chapter 2

Theoretical Framework and Historical Perspective

Portions of this chapter have been submitted for publication as:

W.A. Tisdale & X.-Y. Zhu, “Artificial atoms and molecules on semiconductor surfaces: electron transfer between 0D and 3D”, *Proc. Natl. Acad. Sci. USA*, submitted (2010).

This chapter serves as the conceptual foundation on which my experimental strategies are built and describes the theoretical framework within which experimental results are interpreted. This chapter also serves to orient the reader with respect to the current state of knowledge within the field of quantum dot interfacial dynamics with short reviews of the published literature. However, not all of the material presented in this chapter is textbook knowledge. In particular, Section 2.3 offers a unique, original perspective on electron transfer from quantum dots. Throughout this Dissertation, the terms “nanocrystal” and “quantum dot” are used interchangeably. We use these terms to refer to quantum dots prepared in colloidal solutions – not epitaxial quantum dots grown by molecular beams in ultrahigh vacuum. The reader should note that there are two separate presentations of nanocrystal electronic structure within this chapter. Section 2.1.2 presents a more traditional development of quantum dot electronic structure that is useful for understanding energy levels, optical transitions, and scaling laws for quantum-confined charge carriers. In Section 2.3.4, electronic structure in quantum dots is revisited with an emphasis on the charge carrier’s wave function and its implications for interfacial

electronic coupling and charge transfer. All equations are expressed in the S.I. system of units.

2.1. Semiconductor nanocrystal quantum dots

Bulk semiconductors are characterized by a continuum of occupied (valence band) and unoccupied (conduction band) states separated in energy by a band gap, E_g . A photon with energy $h\nu > E_g$ may be absorbed by the semiconductor, producing an electron in the conduction band and a hole in the valence band. If the size of the semiconductor sample is reduced to the natural length scale of these charge carriers, then the normal periodic boundary conditions invoked in solving the Schrödinger Equation for the electronic states in a solid no longer apply exclusively. The confinement of the electron and hole to within the boundaries of the sample must also be considered in addition to the Coulomb attraction between the electron and the hole, which are now confined to a smaller region of space than they would otherwise mutually occupy in the bulk material. These considerations lead to (measurable) quantization of the eigenstates of the system, producing a ladder-like structure of conduction and valence band electronic energy levels (Figure 2.1). Transitions among these discretized states are readily observable in UV/visible light absorption spectra, which exhibit sharp peaks above the first excited state energy instead of the typical step-function continuum observed in bulk semiconductor samples.

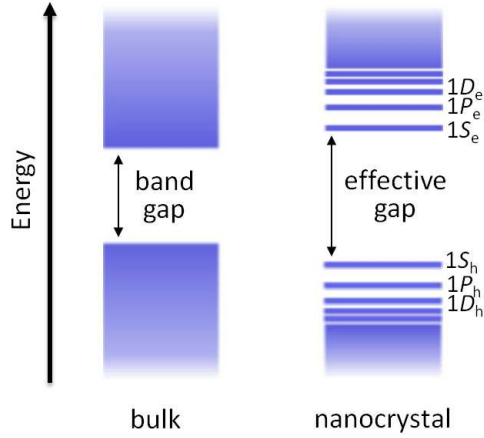


Figure 2.1 Quantum confinement of charge carriers results in quantization of electronic energy levels within a quantum dot. The atomic-like electron and hole energy levels are labeled by the principle quantum number, n , the orbital angular momentum, S , P , D , etc., and a suffix to denote an electron (“e”) or hole (“h”) state.

In defining the “natural length scale” of the charge carriers, it is convenient to use the Bohr radius (39),

$$a_B = \varepsilon \frac{m_0}{m_{eff}} a_0, \quad (2.1)$$

where ε is the dielectric constant of the semiconductor, m_0 is the electron rest mass, m_{eff} is the effective mass of the elementary particle (electron, hole, or exciton)*, and a_0 is the Bohr radius of the hydrogen atom. Semiconductor crystallites exhibiting such size-dependent behavior are referred to as *nanocrystals* because samples often must be less than $\sim 10\text{nm}$ in size before such effects appear, or *quantum dots* (QD), because the electronic structure is a result of quantum confinement of the charge carriers. The effect of quantum confinement is illustrated in Figure 2.1. The resulting discretized electronic structure is similar to that of an atom or a molecule, and each eigenstate has well-defined angular momentum.

* In this section, I reserve use of the word “particle” for an electron, hole, or exciton. The nanocrystal or quantum dot will always be referred to as such, and never as a “nanoparticle.”

2.1.1. Nanocrystal synthesis

Modern synthetic routes to colloidal compound semiconductor (i.e. II-VI, III-V, etc.) nanocrystals are based on the pioneering work of Murray, Norris, and Bawendi (40). These authors prepared extremely high quality (i.e. monodisperse) solutions of CdS, CdSe, and CdTe quantum dots by injection of precursors into a hot surfactant solution (tri-*n*-octylphosphine [TOP] and tri-*n*-octylphosphine oxide [TOPO]). The homogeneous nucleation event is rapid and short-lived, followed by nanocrystal growth by “monomer” addition from solution and, once excess dissolved precursor has been exhausted, growth by Ostwald ripening (41). Nanocrystal size is controlled by varying the growth temperature and time. The nominally spherical nanocrystals, which are coated by a coordinating layer of TOP and TOPO, are isolated by precipitation (via addition of a nonsolvent to the product mixture) and subsequent centrifugation. The TOP/TOPO-capped nanocrystals can then be re-dispersed in a variety of nonpolar solvents and the TOP/TOPO ligands can be exchanged for other capping agents to provide desired functionality. A conceptualized illustration of a nanocrystal, consisting of an inorganic semiconductor core and an organic ligand shell, is shown in Figure 2.2.

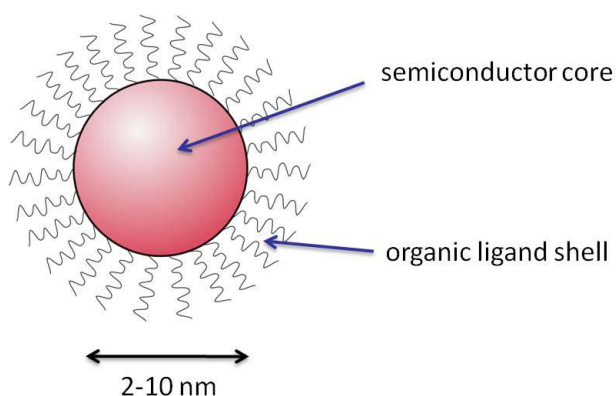


Figure 2.2 Schematic of a semiconductor nanocrystal, or quantum dot, consisting of a (nominally) spherical core of crystalline inorganic semiconductor material coated with a layer of molecules that acts to stabilize the colloidal suspension and passivate surface electronic states.

Absorption spectra for CdS, CdSe, and CdTe nanocrystals prepared by this procedure are presented in Figure 2.3(a) (40). The sharp absorption peaks are characteristic of the quantized energy levels depicted in Figure 2.1 and monodispersity in

the nanocrystal size distribution. The ability to control nanocrystal size by this synthesis method is demonstrated in Figure 2.3(b). The blue-shift of the first absorption peak indicates increasing quantum confinement as nanocrystal size decreases. Since CdSe was the first nanocrystal to be prepared with extremely high quality (40), it has served as the prototypical quantum dot system for both fundamental and applied studies. However, other compound semiconductors are readily prepared by this method as well. Since the original publication of Murray *et al.* in 1993, procedures for more II-VI semiconductor nanocrystals (e.g. ZnSe), IV-VI nanocrystals (e.g. PbSe, PbS, etc.) and III-V nanocrystals (e.g. InP, GaAs, InAs) have also been developed and are reviewed elsewhere: (41).

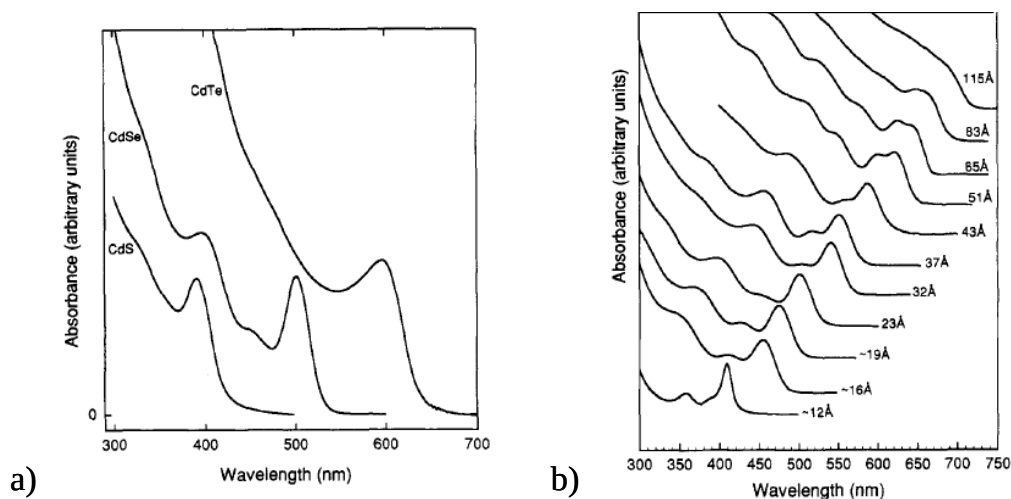


Figure 2.3 (a) Absorption spectra of ~2-3nm CdS, CdSe, and CdTe nanocrystals. The sharp absorption features indicate quantization of energy levels and monodispersity in the nanocrystal size distribution. (b) Room temperature optical absorption spectra of various sizes of TOP/TOPO-capped CdSe nanocrystals dispersed in hexane. As nanocrystal size decreases, the transition energy from the ground state to the lowest excited state increases due to confinement of the electron-hole pair. From (40).

2.1.2. Electronic structure

If the nanocrystal diameter is much larger than the lattice constant of the material, then we can treat the crystallite as a sample of bulk material and single-particle (sp) wave functions (i.e. wave functions of the electron or hole) can be expressed as linear combinations of Bloch functions (39),

$$\Psi_{\text{sp}}(\vec{r}) = \sum_k C_{nk} u_{nk}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}), \quad (2.2)$$

where the functions u_{nk} have the periodicity of the crystal lattice. Since u_{nk} generally have a weak k -dependence, then we can re-cast Eq. (2.2) into the form,

$$\Psi_{\text{sp}}(\vec{r}) = u_{n0}(\vec{r}) f_{\text{sp}}(\vec{r}), \quad (2.3)$$

where the functions $f_{\text{sp}}(\vec{r})$ are the single-particle envelope functions,

$$f_{\text{sp}}(\vec{r}) = \sum_k C_{nk} \exp(i\vec{k} \cdot \vec{r}). \quad (2.4)$$

The envelope functions are given by the solution to the quantum mechanical particle-in-a-spherical well model (c.f. Zettili, p.329 (42)). In it, we consider a particle of mass m confined to a spherical infinite square well of radius a ,

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}. \quad (2.5)$$

Solution of the Schrödinger Equation yields wave functions,

$$f_{\text{sp}}(\vec{r}) = \Phi_{n,\ell,m}(r, \theta, \phi) = C \cdot j_{\ell}(k_{n,\ell} r) Y_{\ell}^m(\theta, \phi), \quad (2.6)$$

and eigenvalues,

$$E_{n,\ell} = \frac{\hbar^2 k_{n,\ell}^2}{2m} = \frac{\hbar^2 \alpha_{n,\ell}^2}{2ma^2}, \quad (2.7)$$

where C is a normalization constant, $\alpha_{n,\ell}$ is the n th zero of the ℓ th-order spherical Bessel function $j_{\ell}(k_{n,\ell} r)$, and $Y_{\ell}^m(\theta, \phi)$ is a spherical harmonic. Thus, single-particle states in nanocrystals can be described by atomic-like orbitals with the usual quantum numbers $n(1,2,3\dots)$, $\ell(s,p,d\dots)$, and m . If we invoke the effective mass approximation, then particle masses in Eq. (2.7) are replaced by the effective mass of the electron or hole.

In treating the Coulomb attraction between the electron and hole, we invoke the *strong confinement approximation*. Because the confinement of carriers scales as $1/a^2$ (see (2.7)) and the Coulomb interaction scales as $1/a$, then for small nanocrystals the confinement term dominates and electron and hole states can be treated independently

with the Coulomb term added as a first-order perturbation correction, E_c . The electron-hole pair (ehp) states in nanocrystals are then written (39),

$$\begin{aligned}\Psi_{\text{ehp}}(\vec{r}_e, \vec{r}_h) &= \Psi_e(\vec{r}_e) \Psi_h(\vec{r}_h) \\ &= u_c f_e(\vec{r}_e) u_v f_h(\vec{r}_h) \\ &= C \left(u_c j_{L_e}(k_{n_e, L_e} r_e) Y_{L_e}^{m_e} \right) \left(u_v j_{L_h}(k_{n_h, L_h} r_h) Y_{L_h}^{m_h} \right)\end{aligned}\quad (2.8)$$

The energy of the electron-hole pair state is,

$$E_{\text{ehp}}(n_h L_h n_e L_e) = E_g + \frac{\hbar^2}{2a^2} \left[\frac{\alpha_{n_h, L_h}^2}{m_{\text{eff}}^v} + \frac{\alpha_{n_e, L_e}^2}{m_{\text{eff}}^c} \right] - E_c. \quad (2.9)$$

This treatment is sometimes referred to as the *effective mass model*, or the *particle-in-a-sphere model*. The electron-hole pair states are labeled by the quantum numbers $n_h L_h n_e L_e$. Selection rules for optical transitions from the ground state to excited electron-hole pair states are obtained by considering the dipole matrix element for such a transition (39),

$$M_{|0\rangle \rightarrow |n_h L_h n_e L_e\rangle} = \left| \langle u_c | \vec{e} \cdot \hat{p} | u_v \rangle \right|^2 \left| \langle f_e | f_h \rangle \right|^2. \quad (2.10)$$

Since the envelope functions are orthogonal in the spherical well approximation (through the spherical harmonics - see Eq. (2.6)), (2.10) reduces to,

$$M_{|0\rangle \rightarrow |n_h L_h n_e L_e\rangle} = \left| \langle u_c | \vec{e} \cdot \hat{p} | u_v \rangle \right|^2 \delta_{n_e, n_h} \delta_{L_e, L_h}, \quad (2.11)$$

and the selection rules $\Delta n = 0$ and $\Delta L = 0$ are obtained.

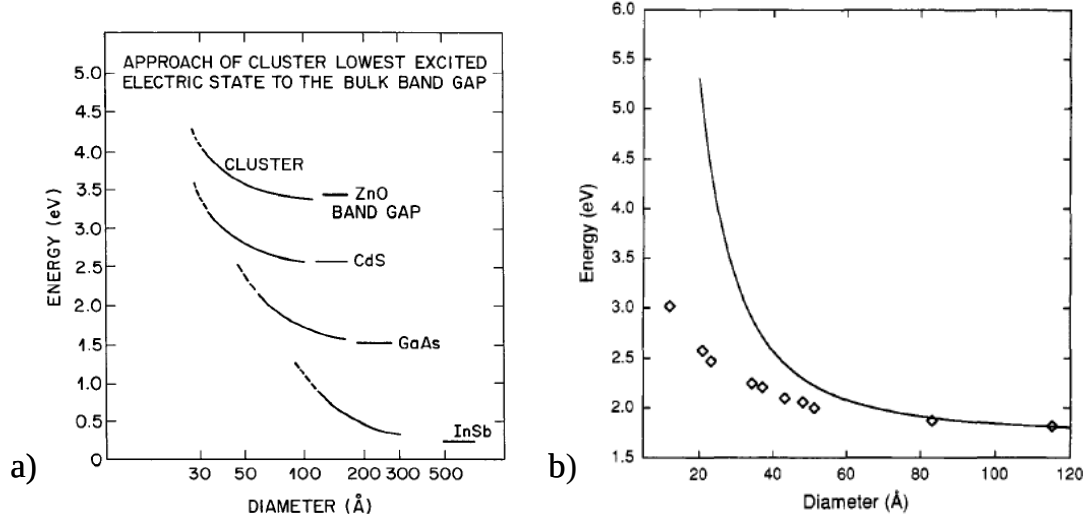


Figure 2.4 (a) Energy of the lowest excited electron-hole pair state in several semiconductor nanocrystals calculated by the effective mass model; from (43). (b) Deviation from the effective mass model in a real system (CdSe); the solid line is the model prediction and the diamonds are experimental data obtained by absorption spectroscopy and high-resolution electron microscopy; from (40).

As an example, consider a transition from the ground state to the first excited electron-hole pair state $1S_h1S_e$. Solutions to the particle-in-a-sphere problem for $\ell=0$ are given by $k_{n,0} = n\pi/a$, so $\alpha_{1,0} = \pi$. For pair states with the electron in the $1S_e$ level, the first-order Coulomb correction term is $E_c = 1.8q^2/4\pi\epsilon\epsilon_0a$ (44).^{*} Plugging into (2.9), we find that the energy needed to excite the lowest excited electronic state of the nanocrystal is given (in SI units) by:

$$E_{1S_h1S_e} = E_g + \frac{\hbar^2\pi^2}{2a^2} \left[\frac{1}{m_{eff}^v} + \frac{1}{m_{eff}^c} \right] - \frac{1.8q^2}{4\pi\epsilon_0\epsilon a} \quad (2.12)$$

where the high-frequency dielectric constant ϵ_∞ is typically used in the Coulomb correction term. The behavior of this expression is depicted in Figure 2.4(a). As nanocrystal size increases, the excitation energy asymptotically approaches the bulk band gap. Figure 2.4(b) compares Eq. (2.12) to experimental data obtained for CdSe. The deviation is attributed to the finite potential barrier at the surface of the particle ($V \neq \infty$, so

^{*} The numerical constant ≈ 1.8 arises from integration of the $1S$ wave functions, $\psi(r) \propto \frac{\sin(\pi r/a)}{r}$.

the wave functions increasingly penetrate the nanocrystal surface as size decreases – see Section 2.3.4 for a more thorough discussion of these effects) and deviations from the band-edge effective mass as the energy of the confined state increases.

2.1.3. The effect of dielectric environment

In addition to the confinement energy for each charge carrier and the direct Coulomb attraction, additional terms in Eq. (2.9) accounting for the discontinuity of the dielectric function across the nanocrystal boundary are needed to completely describe the excited state of the nanocrystal. A charged particle inside a finite-size crystallite will polarize the surrounding medium. If the dielectric constant outside the nanocrystal is less than the dielectric constant inside (this is almost always the case), then the self-polarization energy will be positive, representing a loss of electrostatic solvation energy compared to the infinite bulk semiconductor crystal. However, if the dielectric constant outside the nanocrystal is greater than inside, then the self-polarization term will be negative and electrostatic stabilization will act to lower the overall energy of the excited state. If more than one charge carrier is confined to the nanocrystal (such as an electron and hole), the interaction of each particle with the image charge of the others must also be included. These purely classical contributions to the electron-hole-pair state energy can lead to measurable solvatochromic shifts in the optical transition frequency (45).

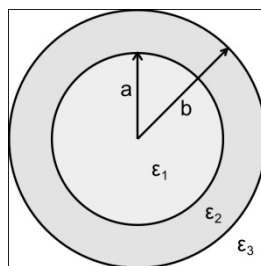


Figure 2.5 Nanocrystal model used for calculation of the dielectric solvation energy. The spherical nanocrystal consists of an inorganic core (ϵ_1) of radius a , a ligand shell (ϵ_2) with thickness $b-a$, and surrounding solvent environment (ϵ_3).

Iwamatsu *et al.* (46) and Leatherdale & Bawendi (45) considered these electrostatic interactions between charge carriers within the core of a nanocrystal and the

surrounding medium, including dielectric screening by the ligand shell. The optical gap of a quantum dot, $E_{\text{gap}}^{\text{opt}}$ (the lowest-energy interband transition, or the difference in energy between the $1S_h1S_e$ electron-hole-pair state and the ground state), can be expressed as (45),

$$E_{\text{gap}}^{\text{opt}} = E_{\text{gap}}^{\text{bulk}} + E_e^{\text{kin}} + E_h^{\text{kin}} + E_{\text{Coul}} + \Sigma_e^{\text{pol}} + \Sigma_h^{\text{pol}} + J_{e,h}^{\text{pol}}. \quad (2.13)$$

The first four terms are those included in Eq. (2.12) and depend only on the dielectric constant within the nanocrystal, ε_1 . The last three terms are the electrostatic interaction terms just described and depend strongly on the difference between the inner and outer dielectric constants (Figure 2.5). For $1S$ electron and hole wave functions, $\psi(r) \propto \sin(\pi r/a)/r$, the self-polarization energies are given by (46),

$$\begin{aligned} \Sigma_{e(h)}^{\text{pol}} &= \frac{1}{2} \langle \Psi_0(r) | V_{\text{in}}(r, r') | \Psi_0(r') \rangle \\ &= \frac{1}{2} \frac{q^2}{4\pi\varepsilon_1\varepsilon_0 a} \cdot \left(2\pi^2 \sum_{l=0}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x) x^{2l+2} dx \right), \end{aligned} \quad (2.14)$$

where the term A_l is,

$$A_l = \frac{l+1}{a^{2l+1}} \frac{a^{2l+1}(\varepsilon_2 - \varepsilon_3)[\varepsilon_1 + l(\varepsilon_1 + \varepsilon_2)] + b^{2l+1}(\varepsilon_1 - \varepsilon_2)[\varepsilon_3 + l(\varepsilon_2 + \varepsilon_3)]}{a^{2l+1}(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)l(l+1) + b^{2l+1}[\varepsilon_2 + l(\varepsilon_1 + \varepsilon_2)][\varepsilon_3 + l(\varepsilon_2 + \varepsilon_3)]}. \quad (2.15)$$

Here, a is the radius of the nanocrystal core, $b-a$ is the thickness of the ligand shell, and ε_1 , ε_2 , and ε_3 are the dielectric constants of the nanocrystal core, the ligand shell, and the surrounding solvent, respectively (Figure 2.5). In Eq. (2.14), ε_0 is the permittivity of free space and $j_0(\pi x)$ is a spherical Bessel function. In the absence of a ligand shell ($b=a$), A_l reduces to,

$$A_l = \frac{l+1}{a^{2l+1}} \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_3 + l(\varepsilon_1 + \varepsilon_3)}. \quad (2.16)$$

Leatherdale & Bawendi pointed out that the term $J_{e,h}^{\text{pol}}$ exactly cancels the $l=0$ terms in Σ_e^{pol} and Σ_h^{pol} . The net contribution, δ , of electrostatic solvation to the electron-hole-pair state energy is then (45),

$$\begin{aligned}
\delta &\equiv \Sigma_e^{pol} + \Sigma_h^{pol} + J_{e,h}^{pol} \\
&= \frac{\pi q^2}{2\epsilon_1\epsilon_0 a} \sum_{l=1}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x) x^{2l+2} dx .
\end{aligned} \tag{2.17}$$

2.2. Hot carrier cooling in nanocrystals

An exciting property of semiconductor nanocrystals that may lead to highly efficient quantum dot solar cells is greatly reduced rates of hot carrier cooling. In bulk semiconductors (Figure 2.6), electrons excited to states in the conduction band will relax down to the band minimum within ~ 1 ps by a series of phonon emission events (see ref. (36) or Chapter 5 of this Dissertation). The discretization of energy levels in quantum dots, as depicted in Figure 2.7, can greatly slow this rate of hot electron cooling. For a nanocrystal of a semiconductor such as PbSe, where bulk electron and hole effective masses are relatively small, the intraband level spacing can be as much as 10 or more times the LO phonon energy (47). Thus, carrier cooling by phonon emission requires simultaneous emission of multiple phonons – a substantially less likely event than step-by-step single-phonon emission in bulk semiconductors. This phenomenon, known as the *phonon bottleneck*, is expected to result in hot carrier lifetimes nanoseconds or longer. However, the slowing of electron cooling by electron-phonon interaction opens the door for other cooling mechanisms with characteristically slower time scales. Chief among these is an Auger process, shown schematically in Figure 2.8, wherein the hot electron transfers its excess energy to a hole (48). The hole will relax within the valence band levels much faster because of its larger effective mass, which leads to smaller energy level spacing and correspondingly more efficient carrier-phonon coupling. Auger processes such as this one are greatly accelerated in quantum dots, as compared to bulk semiconductors, because of stronger electron-hole Coulomb coupling ($E_C \sim 1/a$) and relaxed momentum conservation requirements.

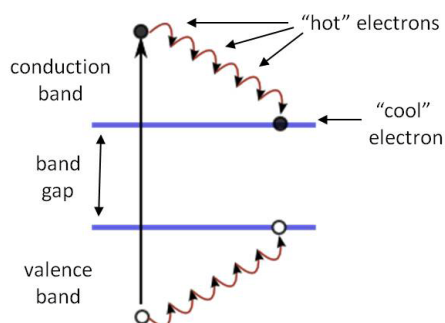


Figure 2.6 Hot carrier cooling in bulk semiconductors occurs by sequential emission of phonons while electrons and holes relax to their respective band minima in less than ~ 1 ps.

Experimental studies support the dominance of the Auger mechanism on hot electron cooling rates in CdSe nanocrystals (49). Guyot-Sionnest *et al.* conducted the most comprehensive and carefully-controlled of these studies in colloidal CdSe quantum dots (50). In their experiment, they used a visible pump laser pulse to first excite electrons to the $1S_e$ state. Then, an IR pump pulse resonant with the $1S_e$ - $1P_e$ transition followed 10ps later. A third laser pulse, the IR probe, followed closely behind. By monitoring the absorption of the third pulse, they were able to monitor exclusively the decay of electrons from the $1P_e$ state to the $1S_e$ state. The decay dynamics were bi-exponential, exhibiting a fast 1-2ps component and a slow ~ 200 ps component. By studying a series of nanocrystals with carefully selected ligands, the authors were able to control the trapping of the photoexcited hole. They determined that the 1-2ps component is due to the Auger process and the ~ 200 ps component is due to the phonon bottleneck, which only manifests itself when the hole is trapped at the surface of the nanocrystal and unavailable for participation in the Auger mechanism. These conclusions were corroborated later by Klimov *et al.* (51).

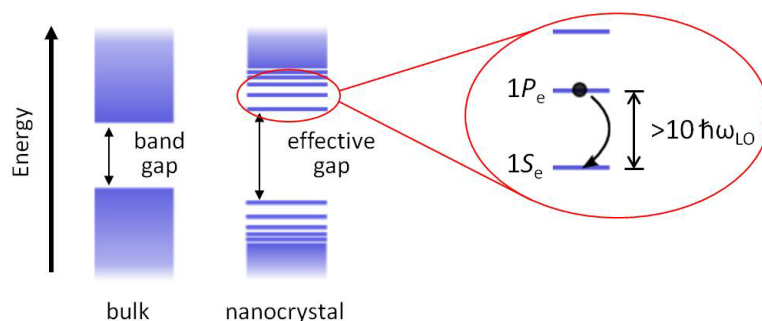


Figure 2.7 The “phonon bottleneck” in semiconductor nanocrystals. Intraband cooling of charge carriers in quantum dots is expected to be much slower than in bulk semiconductors because the energy difference between eigenstates is many times larger than the optical phonon energy, rendering phonon emission an inefficient pathway for electron or hole relaxation.

Hot electron relaxation in PbSe nanocrystals shows markedly different behavior from CdSe. Like CdSe, hot electron relaxation is *faster* for *smaller* nanocrystals – the opposite trend we would expect for a phonon bottleneck since energy levels are spaced farther apart in smaller nanocrystals. Klimov and co-workers observed $1P_e$ lifetimes increasing from 0.25ps to 2.58ps as nanocrystal diameter is increased from 2.8nm to 7.0nm (47). Unlike in CdSe, $1P_e$ -to- $1S_e$ relaxation in PbSe shows significant temperature dependence (Figure 2.9). Temperature-activated relaxation strongly suggests the involvement of phonons, and these authors suggest a mechanism based on efficient multi-phonon emission (47).

Guyot-Sionnest and co-workers continued their investigations of intraband relaxation in CdSe quantum dots by examining the effect of the surface ligands. By electrochemically doping (adding an extra electron), instead of photoexciting, a CdSe nanocrystal they were able to investigate hot electron cooling in the absence of a hole (52). They found that dipole-dipole coupling to high-frequency vibrations of the ligand molecules* – particularly hydrogen bonding modes of phosphonic acids and carboxylic acids – can offer yet another pathway for circumventing the phonon bottleneck. Alkylamines and alkanethiols facilitated slower cooling rates (52). It was only by growing a thick ZnSe shell around the CdSe nanocrystal core to separate the electron

* Molecular vibration frequencies (up to several hundred meV) can be an order of magnitude larger than optical phonon frequencies in semiconductor crystals (tens of meV).

(confined to CdSe) from the ligands by a large distance that Pandey & Guyot-Sionnest were ultimately able to demonstrate nanosecond intraband relaxation times (38).

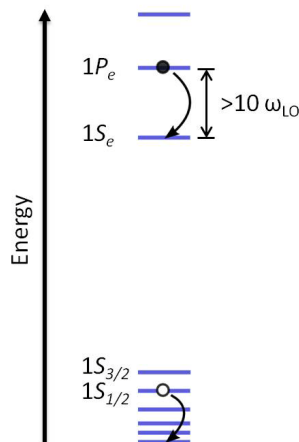


Figure 2.8 The Auger mechanism for hot electron relaxation in CdSe nanocrystals. Because of the enhanced Coulomb interaction between charge carriers within a nanocrystal ($E_c \sim 1/a$), the electron is able to relax to the conduction band minimum by quickly and efficiently transferring its energy to the hole, which then cools to the valence band maximum by a series of phonon emission events involving the more closely-spaced hole energy levels.

While the phonon bottleneck may never have as dramatic an effect as anticipated, the slowed cooling of hot carriers nonetheless suggests the possibility of *hot carrier extraction* from photoexcited quantum dots, enabling the design of ultra-efficient solar cells (see Section 1.3.1). Pandey & Guyot-Sionnest published the first evidence for hot electron extraction from a quantum dot (to an unknown surface trap or solvated electron state) earlier this year (53), but noted that the hot electron extraction pathway was only observable in the absence of a hot hole. These and previous studies suggest that a key component to designing a hot carrier solar cell may be the fast extraction of the hole. However, if the interface is designed so that electron transfer from the nanocrystal is sub-picosecond or faster, then the Auger relaxation pathway may be of little consequence.

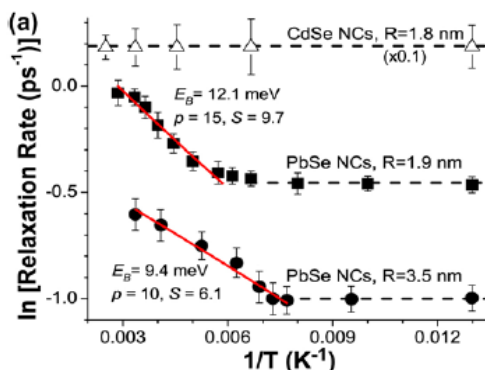


Figure 2.9 Temperature dependence of the $1P_e$ -to- $1S_e$ relaxation rate in CdSe and PbSe nanocrystals. Unlike in CdSe (empty triangles), where hot electron relaxation occurs via a temperature-independent Auger process, hot electron relaxation in PbSe (filled circles, squares) shows marked temperature dependence, which strongly suggests the involvement of phonons. From (47).

2.3. Electron transfer from quantum dots

In general, electron transfer from a photoexcited quantum dot to a bulk semiconductor acceptor* can be thought of as bridge-mediated electron transfer from a donor state (the nanocrystal) to a continuum of acceptor states (the semiconductor), as depicted in Figure 2.10. The meaning of this generalization and the conditions under which it is valid will be developed over the course of this section. We will see that the molecular bridge – the stabilizing ligands covering the nanocrystal surface – plays a crucial role in determining the rate of interfacial electron transfer and offers a powerful handle for controlling interfacial electronic coupling. We begin by reviewing some basics of quantum mechanical tunneling and consider how the chemical identity of the bridge molecule can influence the tunneling transmission probability. Next, we develop in detail the Marcus theory for non-adiabatic electron transfer, wherein we consider the effects of nuclear coordinates and the thermal bath on electron transfer in condensed phases and at surfaces. We then consider the role of interfacial electronic coupling and discuss how this important parameter can strongly influence the way we think of electron transfer. In light

* TiO_2 and ZnO nanoparticles and nanowires used in dye- and quantum dot-sensitized solar cells are considered “bulk” semiconductors here because they do not exhibit quantum size effects.

of this newfound understanding, we revisit the electronic structure in nanocrystals and estimate values for the reorganization energy and interfacial electronic coupling strength. Finally, we reconsider the role of the ligands and review some previous published studies of electron transfer from nanocrystals to bulk semiconductor electron acceptors.

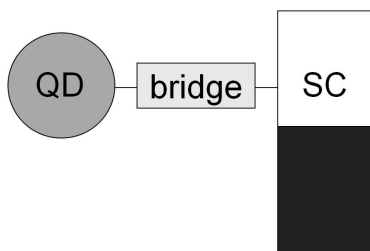


Figure 2.10 The quantum dot (QD) – bridge – semiconductor (SC) model for interfacial electron transfer. The molecules coating the surface of the QD serve as electron “bridges” for interfacial electron transfer and offer a powerful mechanism for controlling interfacial electronic coupling.

Before proceeding, I should first address a possible point of confusion in the language. The terms *adiabatic* and *non-adiabatic* used in the proceeding discussion of electron transfer are unrelated to the same terms used in classical thermodynamics. This is particularly misleading in view of Marcus theory, where we describe the treatment as *non-adiabatic* while taking into account the interaction of our system with the thermal bath. The term *non-adiabatic* here refers to the description of the nuclear potential energy surfaces, and not to the interchange of energy with the surroundings.

A quantum mechanical *adiabatic* process is one in which the Hamiltonian of a system evolves sufficiently slowly in time that each instantaneous state of the system can be described by a solution of the time-independent Schrödinger Equation. As such, the charge carrier under consideration never undergoes a real transition to another state. Instead, its wave function evolves slowly with the changing Hamiltonian. *Non-adiabatic* or *diabatic* processes are ones in which perturbations are sudden enough that the wave function does not evolve as fast as the Hamiltonian. As a result, the wave function after the perturbation is expressed as a linear combination of eigenstates of the new Hamiltonian, and transitions to new states may occur. In connecting these ideas to electron transfer, we consider the (parabolic) nuclear potential energy surfaces of two states: donor (*D*) and acceptor (*A*). In the *diabatic limit*, we consider the two states to be

weakly coupled, so that each potential energy surface is derived from interaction with only one nucleus/molecule. In the *adiabatic limit*, we describe the transition as taking place on one continuous potential energy surface (see Section 2.3.3). In this picture, the donor and acceptor centers represent two local minima on the same potential energy surface.

2.3.1. Tunneling

The simplest picture of tunneling is described by a particle with energy E incident on a barrier of height $V(x) > E$ as depicted in Figure 2.11. A classical particle will not be able to penetrate the barrier, whereas a quantum mechanical particle has some chance of doing so. The transmission probability (or “coefficient”) is equal to the ratio of the amplitudes squared of the transmitted and incident wave functions. A useful method for estimating the transmission coefficient is the WKB approximation (c.f. Zettili, p.508 (42)). We assign wave vectors of the form,

$$k(x) = \begin{cases} \hbar^{-1} \sqrt{2m[E - V(x)]} & E \geq V(x) \\ -i\hbar^{-1} \sqrt{2m[V(x) - E]} & E \leq V(x) \end{cases}, \quad (2.18)$$

where m is the mass of the particle. The transmission coefficient is given by,

$$T \sim \exp \left[-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m[V(x) - E]} dx \right]. \quad (2.19)$$

It is important to note that the WKB approximation is quantitatively valid only for smoothly varying potentials, i.e. $dk(x)/dx \ll k^2(x)$, but retains its qualitative dependence on distance and barrier height regardless. Equation (2.19) tells us everything we need to know about how a potential barrier affects tunneling efficiency. We see that the probability decreases exponentially with barrier width and the square root of height. It also confirms our instinct that particles incident with more kinetic energy have a greater chance of tunneling through the barrier.

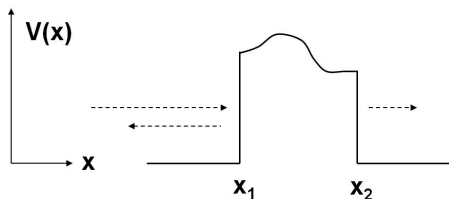


Figure 2.11 When a quantum mechanical particle encounters a potential barrier of arbitrary shape (from the left in this figure), a small fraction of the incident wave function amplitude is transmitted to the other side of the barrier. The rest of the amplitude is reflected backward.

If we turn our attention once again to Figure 2.10, we will note the similarity to Figure 2.11. The molecular bridge acts as a potential barrier for tunneling from the nanocrystal to the semiconductor. However, the position of the lowest unoccupied molecular orbital (LUMO) level of the molecular bridge effectively acts to raise or lower the potential height of the barrier. This mechanism of bridge energy level-mediated electron transfer is known as *superexchange*. Though the electron never resides in the molecular orbital in this mechanism, its presence alone helps facilitate charge transfer. Superexchange rate constants for electron transfer are often expressed in terms of a “ β ” value for the molecular bridge (54):

$$k_{ET} = k_{tunn} = k_0 \exp(-\beta d_{DA}) \quad (2.20)$$

where d_{DA} is the distance between the donor and acceptor (i.e. the length of the molecular bridge). This expression shares the same dependence on barrier width as was derived from the WKB approximation in (2.19). The energy-dependence on the LUMO position is contained in the β value. These values can be deduced from the dependence of experimentally determined tunneling rates on the number of “repeat units” in a molecular bridge. Typical β values are $0.2\text{-}0.6\text{\AA}^{-1}$ for highly conjugated chains, $0.9\text{-}1.2\text{\AA}^{-1}$ for saturated hydrocarbons, and $\sim 2\text{\AA}^{-1}$ for vacuum (54).

2.3.2. Non-adiabatic electron transfer

Modern theory of non-adiabatic electron transfer is due in large part to the contributions of Rudolph Marcus, who won the Nobel Prize in Chemistry in 1992 for his

pioneering work in this field. As such, the theory developed in this section is sometimes referred to as “Marcus theory” or a “Marcus picture” of electron transfer.

We begin our analysis with consideration of two states, a donor (D) and an acceptor (A), in a polar solvent. The solvent has organized itself in such a way as to stabilize the excess electron in the donor state. If the electron were to make a transition to the acceptor on a time scale much faster than the motion of the solvent molecules, then the solvent would no longer be in its most stable configuration. The free energy released in the subsequent relaxation of the solvent to its new most stable configuration is called the solvent *reorganization energy*. The reorganization energy is typically assigned the symbol λ , and takes on values ~ 0.1 - 1 eV in aqueous solutions (55). Marcus observed that if the electron transfer step were to proceed as just described, it would generate a system with λ excess energy – considerably more than the available $k_B T$ at room temperature. Since electron transfer in aqueous solution is observed to occur at reasonable rates, the mechanism must be different. Marcus reasoned that, because of the disparate time scales for electronic and nuclear motion, electron transfer will only take place when the donor and acceptor are *both* in such a configuration that the charge-transfer step is energy-conserving. This means that the instantaneous nuclear configuration during the charge transfer step is one in which the free energy of the system does not change whether the electron is found on the donor or the acceptor. The activation energy for such a charge transfer reaction is only that energy required to deform the nuclear coordinates to the charge transfer configuration – considerably less energy than required for the vertical transition from the stable donor configuration initially suggested.

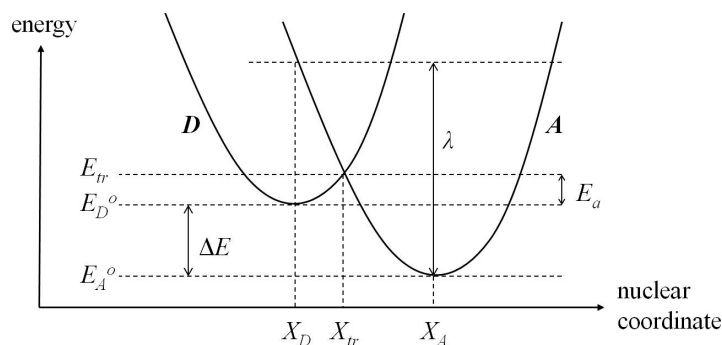


Figure 2.12 Diabatic free energy surfaces for two system states D and A corresponding to localization of an electron on a donor or acceptor species, respectively. The X -coordinate represents nuclear configuration of the system. When $X=X_D$, the nuclear environment has arranged itself in such a way as to stabilize the electron on the donor species. Similarly, when $X=X_A$, the electron is stabilized on the acceptor species.

This mechanism is best illustrated with a pair of diabatic free energy surfaces for the donor-acceptor system as shown in Figure 2.12. The two parabolas^{*} represent two electronic states of the entire donor-acceptor-solvent system that are coupled to each other by the full system Hamiltonian ($V_{DA} \neq 0$). The parabola on the left (denoted “ D ”) corresponds to the electronic state in which the electron is stabilized on the donor molecule; the parabola on the right (denoted “ A ”) corresponds to the electronic state in which the electron is stabilized on the acceptor. We assume that the curvatures are the same. The X -coordinate represents the nuclear configuration of the system. When $X=X_D$, the solvent is configured in such a way as to stabilize the charge on the donor molecule; when $X=X_A$, the electron is stabilized on the acceptor molecule. $X=X_{tr}$ corresponds to the nuclear configuration of the transition state. It is clearly seen from Figure 2.12 that the activation energy in the Marcus picture is substantially less than for a vertical transition from D to A . It is straightforward to show (see Section 2.4) that the activation energy, E_a , can be expressed in terms of the free energy difference between the two electronic states, ΔE , and the reorganization energy, λ ,

$$E_a = \frac{(\Delta E + \lambda)^2}{4\lambda}. \quad (2.21)$$

^{*} Marcus showed that these surfaces *should* be parabolic – this is not just a harmonic approximation.

The likelihood of the system reaching the charge transfer configuration is proportional to the Boltzmann factor, $\exp\left(\frac{-(\Delta E + \lambda)^2}{4\lambda k_B T}\right)$. The probability (per unit time) of the reaction occurring once this nuclear configuration has been reached is given by Fermi's golden rule for the thermally averaged transition rate between vibronic levels associated with the donor (D) and acceptor (A) electronic states,

$$k_{ET}(\Delta E) = \frac{2\pi}{\hbar} |V_{DA}|^2 F(\Delta E), \quad (2.22)$$

where V_{DA} is the electronic coupling matrix element and the function,

$$F(\Delta E) = \frac{1}{Q_D} \sum_i e^{-E_{D,i}/k_B T} \sum_f |\langle \chi_{D,i} | \chi_{A,f} \rangle|^2 \delta(\Delta E + E_{D,i} - E_{A,f}), \quad (2.23)$$

is the thermally averaged Franck-Condon factor. Here, $Q_D = \sum_i \exp(-E_{D,i}/k_B T)$ is the nuclear partition function in the donor electronic state, $\langle \chi_{D,i} | \chi_{A,f} \rangle$ is the overlap of initial and final state nuclear wave functions, and the summations are over vibronic levels associated with the initial (i) and final (f) electronic states. In the high-temperature (i.e. classical) limit, $F(\Delta E)$ is given by (56),

$$F(\Delta E) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta E + \lambda)^2}{4\lambda k_B T}\right). \quad (2.24)$$

This expression assumes that $k_B T \gg \hbar\omega_Q$, where ω_Q is any vibrational mode involved in the transition, and that vibrational frequencies are not changed by charge transfer. The complete Marcus rate expression, in the high-temperature and weak-coupling limit, is,

$$k_{ET}(\Delta E) = \frac{2\pi}{\hbar} |V_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta E + \lambda)^2}{4\lambda k_B T}\right). \quad (2.25)$$

Equation (2.25) is generally valid at room temperature for most polar solvents – particularly in aqueous environments and for biological systems (56).

When electron (hole) transfer occurs between a localized donor species and a bulk semiconductor electrode, one must consider a continuum of energy levels that may participate in the transition (57). The Marcus rate expression in Eq. (2.25) is now integrated over all possible electron (hole) accepting (donating) levels within the solid. For the case of molecule-to-semiconductor electron transfer, such as electron injection in dye-sensitized solar cells, the electron transfer rate is given by,

$$k_{ET} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_B T}} \int |V_{DA}(E)|^2 (1 - f(E)) \rho(E) \exp\left(\frac{-(E - E_D + \lambda)^2}{4\lambda k_B T}\right) dE, \quad (2.26)$$

where $\rho(E)$ is the density of states, $f(E)$ is the fractional occupation of states at energy E , and $V_{DA}(E)$ is the k -space integrated and energy-dependent electronic coupling strength.

2.3.3. Adiabaticity and the effect of strong electronic coupling

While Marcus theory has found broad applicability in a variety of systems, the preceding discussion of non-adiabatic electron transfer may have limited validity when it comes to charge transfer between nanocrystals and bulk semiconductor electrodes. The central assumption underlying Eqs. (2.25) and (2.26) is that thermally activated nuclear rearrangement is the rate-limiting step in the charge transfer reaction. Further, it is assumed that electronic coupling is weak enough to be treated perturbatively via the golden rule. This is not always the case. When electronic coupling between the donor and acceptor is strong relative to the reorganization energy, electron transfer occurs adiabatically. Instead of thinking of electron transfer as a discrete event occurring between two localized states, the adiabatic charge transfer reaction is best described as a time-dependent redistribution of charge on one continuous equilibrated potential energy surface (Figure 2.13). In extreme cases, the donor and the acceptor are no longer distinguishable and electron “transfer” reduces to a quantum mechanical dephasing process.

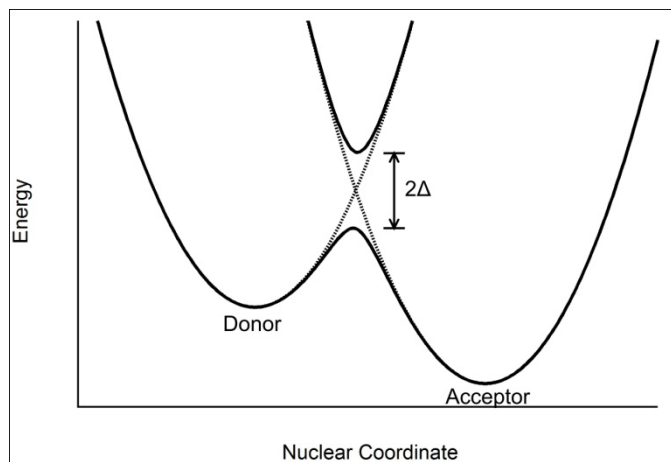


Figure 2.13 Nuclear potential energy surfaces for an electron donor-acceptor system. The x-axis represents various states of molecular organization, and the reorganization energy λ is the amount

of energy that would be released if electron transfer were to proceed vertically (i.e. with nuclear coordinates frozen). The dotted (crossing) curves are parabolic diabatic free energy surfaces for separate donor and acceptor species in the weak-coupling limit, wherein the thermal activation energy for electron transfer is completely determined by nuclear rearrangement. The solid (anti-crossing) curves are adiabatic free energy surfaces of the coupled donor-acceptor system. In the intermediate coupling regime where electron transfer occurs adiabatically, the activation energy is lowered by the electronic coupling strength, Δ .

At surfaces, the treatment of adsorbate-substrate electronic interaction is best handled within the framework of chemisorption theories, which deal with the coupling of atomic or molecular orbitals to electronic bands in solids. Newns, recognizing the similarity to Anderson's work on impurity centers in metals, considered the interaction of a single valence state $|m\rangle$ with a substrate band $|k\rangle$ (58). When the adsorbate level is located within a large substrate band, the projection of the density of eigenstates of the total Hamiltonian onto the adsorbate state is,

$$N_m(E) = \frac{1}{\pi} \frac{\Delta(E)}{(E - E_m)^2 + \Delta(E)^2}, \quad (2.27)$$

where E_m is the original energy of the valence orbital and $\Delta(E)$ is given by,

$$\Delta(E) = \pi \sum_k |V_{mk}|^2 \delta(E - E_k), \quad (2.28)$$

Equations (2.27) and (2.28) show how the interaction of the valence orbital with the substrate electronic band results in the formation of an *adsorbate resonance* with a broadened Lorentzian line shape and width 2Δ . The adsorbate valence orbital “borrows” delocalization and spectral density from the substrate band and the resulting resonance has both molecular orbital and delocalized Bloch wave character, as illustrated in Figure 2.14. The term “adsorbate resonance” is used to distinguish it from an “adsorbate state”: an *adsorbate resonance* is a mixture of atomic and substrate wave functions and has probability density both within the solid and at the surface; an *adsorbate state* is localized at the surface and has a spatial probability density distribution which decays exponentially into the solid (59). Adsorbate energy levels located within the projected band gap of the semiconductor substrate will always form adsorbate states since there are no $|k\rangle$ states close in energy available for coupling. Note that Eq. (2.27) neglects any shifting of E_m relative to the vacuum level due to changes in the surface potential resulting from inevitable charge redistribution following adsorption. Such changes to the

surface potential affect only the position of the resonance relative to the vacuum level and do not have consequences for electronic coupling as described here.

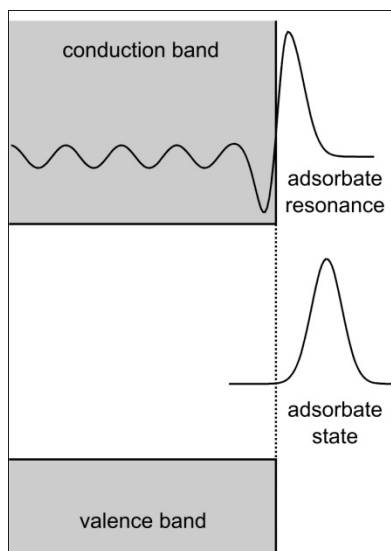


Figure 2.14 Representative wave functions of *adsorbate resonances* and *adsorbate states* at semiconductor surfaces. If an atom, molecule, or nanocrystal is brought into close contact with a bulk semiconductor surface, electronic coupling between valence orbitals of the adsorbate and Bloch waves of the substrate may occur. The *adsorbate state* is localized in the surface normal direction and represents, for instance, an occupied molecular orbital situated energetically within the band gap of the substrate. If an unoccupied molecular orbital is energetically positioned within the conduction band and electronic coupling to the substrate is strong, then an *adsorbate resonance* will form. The wave function of the resonance extends throughout the solid.

The term Δ as defined in Eq. (2.28) is a measure of the electronic coupling strength between an adsorbate orbital, such as an atomic, molecular, or nanocrystal energy level, and a substrate electronic band, such as the conduction band of a bulk semiconductor. Surface electron transfer processes are usually discussed within three coupling regimes, depending on the relative magnitude of Δ and λ (59). In the first regime $\Delta \ll 2\lambda/\pi$ and Δ has little effect on the activation energy for charge transfer, which is determined almost entirely by λ . This is the Marcus limit, and was treated at length in the previous section. In the second regime, or the intermediate coupling regime, $k_B T < \Delta \leq 2\lambda/\pi$. In this case, electron transfer occurs adiabatically and the activation energy is lowered by Δ (Figure 2.13). Electron transfer is still a thermally activated process and depends on nuclear rearrangement, but the constraints on the charge transfer

configuration are lifted to some extent. Finally, when $\Delta > 2\lambda/\pi$, we have reached the strong-coupling regime and nuclear rearrangement plays little or no role in the charge transfer process. In the strong-coupling limit the donor and acceptor states are no longer distinguishable. The donor energy level is itself an eigenstate of the entire coupled system and has probability density throughout the solid (Figure 2.14). Charge transfer in this limit amounts to electronic dephasing between the adsorbate resonance and continuum states within the solid. This ultrafast process occurs on femtosecond or sub-femtosecond timescales.

2.3.4. *Electronic structure in nanocrystals – revisited*

In this section we develop the electronic structure of quantum-confined semiconductor nanocrystals in order to illustrate the similarities between nanocrystal electronic states and atomic or molecular orbitals and extend the concepts developed in the preceding sections for electronic coupling at surfaces. Most treatments of nanocrystal electronic structure are motivated by a desire to reproduce or predict optical transition energies (60, 61). When considering electronic coupling between a bulk semiconductor substrate and a nanocrystal electronic state, it is the *wave function* – and not the energy of the state – that we care most about, since it is the spatial overlap of electronic wave functions that determines the magnitude of electronic coupling. Consequently, the ensuing discussion of nanocrystal electronic structure is motivated primarily by a desire to model those aspects of the wave function that are important for understanding interfacial electronic coupling and charge transfer. Specifically, we focus our attention on tunneling and the effect of semiconductor material and surface-bound molecules on the extent or “spillage” of the wave function outside the nanocrystal core.

The electronic structure of a semiconductor nanocrystal is determined by both the constituent atoms that make up the nanocrystal and by the size and shape of the crystallite. If the crystallite is much larger than the lattice constant of the semiconductor ($\gtrsim 2$ nm, so that the band structure is fully developed), then single-electron wave functions can be expressed as,

$$\Psi(\vec{r}) = u(\vec{r})f(\vec{r}), \quad (2.29)$$

where $u(\vec{r})$ is a function with the periodicity of the crystal lattice and $f(\vec{r})$ is the *envelope function* that contains the dependence of the eigenstate on nanocrystal size and shape (39). Conveniently, $u(\vec{r})$ is the same periodic function used to describe Bloch waves $\Psi(\vec{r}) = u(\vec{r})\exp(i\vec{k} \cdot \vec{r})$ in the bulk material. All of the information relevant for interfacial electron transfer, such as the energy of the eigenstate, its angular momentum, and the probability density near the nanocrystal surface, is contained within the envelope function $f(\vec{r})$, which is determined by the boundary conditions on the crystallite. For spherical nanocrystals the envelope functions are the solutions to the quantum mechanical particle-in-a-sphere problem. For a spherically symmetric potential well of depth V_0 and radius a ,

$$V(r) = \begin{cases} 0 & r < a \\ V_0 & r > a \end{cases}, \quad (2.30)$$

the eigenfunctions satisfying the Schrodinger Equation are of the form,

$$f_{k\ell m}(r, \theta, \phi) = \psi(kr)Y_{\ell m}(\theta, \phi), \quad (2.31)$$

where $Y_{\ell m}(\theta, \phi)$ are spherical harmonics and k is the wave vector. The radial part of the wave function $\psi(kr)$ takes the form of a spherical Bessel function $j_\ell(k_{in}r)$ inside the potential well and a spherical Hankel function $h_\ell(k_{out}r)$ outside the well. These atomic-like single-electron (or single-hole) eigenstates are labeled by the usual quantum numbers $n = 1, 2, 3, \dots$ and $\ell = s, p, d, \dots$ with a subscript “e” (“h”) denoting an electron (hole) wave function. For instance, the lowest-energy electron and hole states are labeled $1S_e$ and $1S_h$, respectively.

As an example, we consider an electron in the conduction band of a nanocrystal (the additional presence of a hole will be considered later). In order for our model to accurately describe variations among crystallites of different materials, we must take into account the effects of dielectric constant and charge carrier effective mass. Following Brus (62), we assign wave vectors,

$$\begin{aligned} k_{in}^2 &= \frac{2m^*}{\hbar^2} [E - P_0] \\ k_{out}^2 &= \frac{2m_0}{\hbar^2} [V_0 - (E - P_0)] \end{aligned}, \quad (2.32)$$

where m^* is the effective mass of the charge carrier within the semiconductor and the energy E is referenced to the bulk band minimum. The energy correction term P_0 ,

$$P_0 = \frac{1}{2} \frac{q^2}{4\pi\epsilon_{in}\epsilon_0 a} \sum_{n=0}^{\infty} \frac{(\epsilon-1)(n+1)}{\epsilon n + n + 1}, \quad (2.33)$$

where $\epsilon = \epsilon_{in}/\epsilon_{out}$ is the ratio of dielectric constants and q is the elementary charge, accounts for some of the electrostatic polarization energy lost by discontinuity of the dielectric function across the nanocrystal boundary. For S states ($\ell = 0$), the wave functions are,

$$\psi_{in} = A \frac{\sin(k_{in}r)}{r}, \quad r < a \quad (2.34)$$

and

$$\psi_{out} = B \frac{\exp(-k_{out}r)}{r}, \quad r > a, \quad (2.35)$$

where A and B are normalization constants. The boundary conditions are the continuity of the wave function at the nanocrystal boundary $\psi_{in}(a) = \psi_{out}(a)$ and the conservation of probability density flux across the interface,

$$\frac{1}{m^*} \frac{\partial \psi_{in}}{\partial r} = \frac{1}{m_0} \frac{\partial \psi_{out}}{\partial r} \quad \text{at } r = a. \quad (2.36)$$

In principle, the effective mass $m^* = \hbar^2(d^2E/dk^2)^{-1}$ is a function of energy and crystal direction, but for simplicity we take it to be a scalar constant. Wave vectors satisfying Eq. (2.34)–(2.36) are found numerically, yielding S states with energies,

$$E_n = \frac{\hbar^2 k_{in,n}^2}{2m^*} + P_0, \quad (2.37)$$

where the energy E_n is referenced to the bulk band minimum. For an infinite potential barrier at the nanocrystal surface ($V_0 = \infty$ so that $\psi \rightarrow 0$ @ $r \geq a$ – see Section 2.1.2), the confinement energy scales with the inverse square of crystallite radius, $E_n \propto 1/a^2$.

For the purposes considered here, a good estimate of the effective surface potential barrier V_0 can be obtained through electron tunneling measurements. Within the WKB approximation, the tunneling probability through a potential barrier of height V_0 is proportional to $\exp(-\beta d)$, where $\beta = 2\sqrt{2mV_0/\hbar^2}$ and d is the width of the barrier. As synthesized, colloidal nanocrystals are covered with a layer of organic molecules that acts

to stabilize the colloidal suspension and passivate surface electronic states. Typically, these molecules are thiol- or acid-functionalized alkane chains. A typical β value for an aliphatic hydrocarbon chain is $\sim 1 \text{ \AA}^{-1}$ (54), yielding an effective barrier height of $V_0 \approx 1\text{eV}$.

The radial probability density distributions $\rho(r) = 4\pi r^2 |\psi|^2$ for the two lowest-energy S states of a 3nm radius CdSe nanocrystal (surrounded by an organic shell, $\varepsilon = 2$) are shown in Figure 2.15(A). The confinement potential is $V_0 = 1.0\text{eV}$ and the effective mass is $m^* = 0.11m_0$. As seen in Figure 2.15(A) there is substantially greater probability density outside of the nanocrystal core for the higher energy $2S$ state ($\int_a^\infty \rho(r)dr = 14.0\%$) than for the more strongly bound $1S$ state (5.1%). Electronic coupling between an electron-accepting substrate and a nanocrystal electronic state is determined by the overlap of electronic wave functions. Since higher-energy wave functions extend farther beyond the nanocrystal surface, electronic coupling of the substrate to higher-energy nanocrystal electronic states should be stronger than coupling to lower-energy excited states. This has the important consequence that (all other things being equal) electron transfer from “hot” electronic states of the nanocrystal will be faster than from electronically relaxed excited states, prompting the possibility of next-generation photovoltaics based on hot carrier extraction from semiconductor nanocrystals (see Section 1.3).

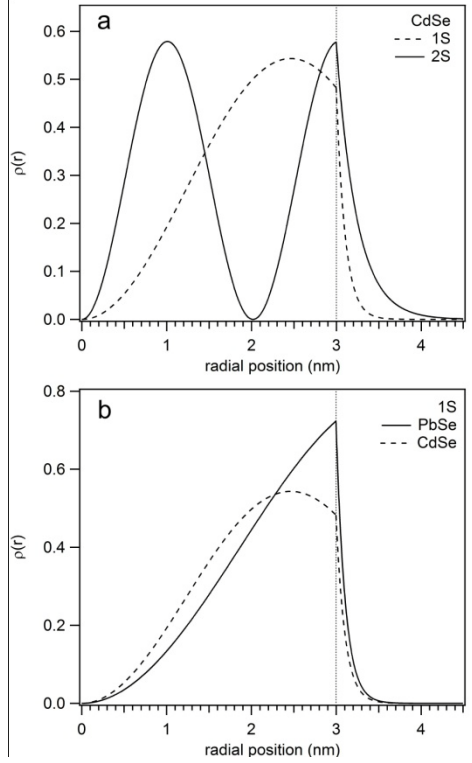


Figure 2.15 Radial probability density distributions $\rho(r) = 4\pi r^2 |\psi|^2$ for (a) the two lowest-energy S ($\ell = 0$) eigenstates in a 6nm diameter CdSe nanocrystal and (b) the lowest-energy eigenstates in 6nm diameter CdSe and PbSe nanocrystals, calculated according to the method described in the text. The discontinuity in the first derivative of the probability density at the nanocrystal surface arises from different effective masses of the electron inside and outside the nanocrystal core. The wave functions of higher-energy eigenstates extend farther beyond the nanocrystal surface, facilitating strong electronic coupling to neighboring nanocrystals or bulk semiconductor substrates.

The choice of semiconductor material can also have a dramatic effect on the envelope function. A particularly striking comparison can be made between CdSe and PbSe. CdSe has an electron effective mass of $m^* = 0.11m_0$ and dielectric constant $\epsilon = 6.2$ at optical frequencies; in contrast, the corresponding properties in PbSe are $m^* = 0.04m_0$ and $\epsilon = 23.9$. Intuitively, we would expect that quantum confinement will have a more dramatic effect on the less massive charge carrier in PbSe, resulting in a shift of probability density away from the nanocrystal core and greater tunneling beyond the surface. Indeed, this is what the model reveals. The radial probability density distributions of the $1S_e$ states in CdSe and PbSe with $V_0 = 1.0\text{eV}$ are shown in Figure 2.15(B). The effect of dielectric constant on *single-electron* states is weak: P_0 is on the order of $\sim 0.1\text{eV}$ and the difference between 3nm radius CdSe and PbSe is less than 30

meV. Effective mass plays a much larger role in determining the single-electron (or single-hole) wave function and its behavior at the nanocrystal surface.

While the dielectric constant is only a minor factor in determining single-electron (or single-hole) eigenstates in nanocrystals, its effect on electron-hole pair binding energies can greatly influence interfacial charge separation. When a photon with energy near the band gap is absorbed by a bulk semiconductor, an electron-hole pair is formed that is bound by the mutual Coulomb attraction between the charge carriers. This bound pair, called an exciton, has an effective size approximately equal to the exciton Bohr radius,

$$a_B = \varepsilon \frac{m_0}{m^*} a_0, \quad (2.38)$$

where ε is the dielectric constant of the medium, m_0 is the rest mass of the electron, m^* is the reduced mass of the electron-hole pair, and a_0 is the Bohr radius of the hydrogen atom. This length scale offers a convenient estimate of the size a crystallite must reach before exhibiting quantum size effects. For instance, the exciton Bohr radii in CdSe and PbSe are 6nm and 46nm, respectively. When the size of a crystallite is smaller than the exciton Bohr radius, the kinetic energy imparted to the charge carriers by quantum confinement is larger than the binding energy of the exciton. Strictly speaking, the electron-hole pair is no longer considered an exciton since the motion of the charge carriers is not correlated (63), but the terminology is widely used nonetheless. Because of the large confinement energy, the Schrodinger Equation can be solved separately for each charge carrier and the Coulomb attraction between the electron and hole within the nanocrystal is added as a perturbative correction to the final electron-hole pair state energy. For charge carriers in the 1S eigenstates, the Coulomb binding energy is,

$$E_C = \frac{1.8q^2}{4\pi\varepsilon\varepsilon_0a}, \quad (2.39)$$

where q is the fundamental charge, ε is the (high-frequency) dielectric constant inside the nanocrystal, a is the nanocrystal radius, and the numerical constant 1.8 arises from integration of the 1S eigenfunctions. Continuing our comparison of the representative materials CdSe and PbSe, we note that the Coulomb binding energies in PbSe nanocrystals (~25-100meV for 2-8nm diameter) are a quarter of those in CdSe

nanocrystals ($\sim 100\text{-}400\text{meV}$ for similar sizes). This energy represents the electrostatic attraction between the electron and hole that must be overcome in order to extract a charge carrier from a photoexcited nanocrystal. Consequently, it is not surprising that resonant energy transfer is a common fate for excitons in cadmium salt nanocrystals whereas exciton dissociation dominates in strongly coupled lead salt nanocrystals (64, 65).

2.3.5. *Estimates for the electronic coupling strength and reorganization energy at interfaces between nanocrystals and bulk semiconductors*

We have just demonstrated that the electronic eigenstates of semiconductor nanocrystals are atomic-like orbitals with discrete energy spectra and well-defined angular momentum. Consequently, the concepts developed in Sections 2.3.2 and 2.3.3 for electronic coupling and charge transfer between adsorbate valence orbitals and bulk semiconductor electronic bands are directly applicable to nanocrystal electronic states near semiconductor surfaces. In this sense, nanocrystals are indeed “artificial atoms” and surface electron transfer theories offer an intriguing framework for considering the coupling between 0D and 3D. As discussed earlier, charge transfer is considered within three coupling regimes depending on the relative magnitude of Δ , the interfacial coupling energy defined in Eq. (2.28), and λ , the reorganization energy. While these parameters are difficult to predict *a priori* for molecular systems due to the strong dependence of Δ on binding geometry and the sensitivity of λ to molecular symmetry and composition, they are perhaps easier to estimate for isotropic nanocrystals.

Estimates of the interfacial coupling energy Δ can be obtained from measurements of nearest-neighbor coupling between nanocrystals. Earlier work from our lab (see Chapter 6) addressed the magnitude of nearest-neighbor exchange coupling in 2D assemblies of PbSe nanocrystals (66). By observing the magnitude of the red-shift in the first optical transition frequency and assuming a hexagonal close-packed 2D arrangement (verified by atomic force microscopy), we were able to estimate nearest-neighbor coupling energies (between neighboring quantum dots a and b) of $V_{ab} = \langle a | \hat{H} | b \rangle = 7\text{-}13\text{meV}$. Stronger coupling was observed for smaller nanocrystals, consistent with greater overlap of neighboring electronic wave functions due to increased tunneling

beyond the nanocrystal core. Liljeroth *et al.* used scanning tunneling spectroscopy to study electronic coupling in similar 2D arrays of PbSe nanocrystals (67). These authors observed formation of mini-bands with bandwidths of 50-150meV. Tight-binding theory predicts that the bandwidth, BW , in a lattice is proportional to twice the number of nearest neighbors, N , and the nearest-neighbor coupling energy, V_{ab} , according to the formula: $BW = 2N * V_{ab}$ (68). Assuming a 2D hexagonal close-packed array with six nearest neighbors, the nearest-neighboring coupling is $V_{ab} \approx 4\text{-}13\text{meV}$. For coupling between a nanocrystal and a bulk semiconductor surface, one might expect that V_{ab} should be roughly half of the nanocrystal-nanocrystal value. Employing Eq. (2.28) and taking V_{ab} to be in the range 2-7meV, we obtain the strongly size-dependent interfacial coupling energy $\Delta = \pi|V_{ab}|^2 \approx 10\text{-}150\text{meV}$, with Δ increasing in magnitude as nanocrystal size decreases.

The reorganization energy is the amount of energy that would be released during nuclear relaxation following an instantaneous vertical transition from the donor potential energy surface to the acceptor surface (Figure 2.13). The bulk semiconductor substrate is expected to contribute little to the reorganization energy since any excess charge is dissipated quickly within the solid. To generate an estimate of the donor contribution to λ , we consider the donor state to be a photoexcited nanocrystal with an electron and a hole residing in the $1S_e$ and $1S_h$ levels, respectively, and take the product state to be the singly-ionized quantum dot (either negative or positive, resulting from electron or hole transfer). Contributions to the reorganization energy can be separated into inner-sphere components (nuclear relaxation within the nanocrystal) and outer-sphere components (relaxation of the surrounding solvent environment). Inner-sphere contributions to the reorganization energy are expected to be small. Sagar *et al.* report reorganization energies $<1\text{meV}$ for interband optical transitions in CdSe nanocrystals (69). Similarly, outer-sphere contributions from the ligand shell are expected to be small since these molecules are covalently bound to the nanocrystal surface and pack closely together, preventing reorientation. Consequently, λ is determined almost entirely by nuclear relaxation of the outer solvent environment. This contribution can be estimated by comparing the electrostatic solvation energy of the photoexcited and ionized quantum dot at dc

(electronic + nuclear contributions) and optical (electronic contributions only) frequencies.

The size-dependent electrostatic solvation energy of photoexcited and ionized quantum dots, including dielectric screening by the ligand shell, was considered by Iwamatsu *et al.* (46) and later by Leatherdale & Bawendi (45). The addition of a charge q to a 1S orbital ($\psi \propto \sin(\pi r/a)/r$) within a nanocrystal results in a self-polarization energy (46),

$$\sigma = \frac{1}{2} \frac{\pi q^2}{2\epsilon_0\epsilon_1 a} \sum_{l=0}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x) x^{2l+1} dx, \quad (2.40)$$

where A_l is given by,

$$A_l = \frac{l+1}{a^{2l+1}} \frac{a^{2l+1}(\epsilon_2 - \epsilon_3)[\epsilon_1 + l(\epsilon_1 + \epsilon_2)] + b^{2l+1}(\epsilon_1 - \epsilon_2)[\epsilon_3 + l(\epsilon_2 + \epsilon_3)]}{a^{2l+1}(\epsilon_1 - \epsilon_2)(\epsilon_2 - \epsilon_3)l(l+1) + b^{2l+1}[\epsilon_2 + l(\epsilon_1 + \epsilon_2)][\epsilon_3 + l(\epsilon_2 + \epsilon_3)]}. \quad (2.41)$$

Here, a is the radius of the nanocrystal core, $b-a$ is the thickness of the ligand shell, and ϵ_1 , ϵ_2 , and ϵ_3 are the dielectric constants of the nanocrystal core, the ligand shell, and the surrounding solvent, respectively (Figure 2.16). In Eq. (2.40), ϵ_0 is the permittivity of free space and $j_0(\pi x)$ is a spherical Bessel function. The electrostatic solvation energy of the photoexcited quantum dot contains contributions from the self-polarization energy of the electron and the hole as well as the interaction of each charge carrier with the image charge of the other. The net electrostatic solvation energy for the photoexcited quantum dot is (45),

$$\delta = \frac{\pi q^2}{2\epsilon_0\epsilon_1 a} \sum_{l=1}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x) x^{2l+1} dx, \quad (2.42)$$

where A_l has the same expression as Eq. (2.41) and the summation is from $l = 1$ instead of $l = 0$. The reorganization energy is therefore,

$$\lambda = \Phi_{dc} - \Phi_{\infty}, \quad (2.43)$$

where,

$$\Phi \equiv |\sigma - \delta|, \quad (2.44)$$

is the difference in electrostatic solvation energy between the photoexcited and ionized states of the quantum dot. The subscripts “dc” and “ ∞ ” denote calculation of the

solvation energies using the static (dc) or optical (dielectric constant for the outer solvent environment).

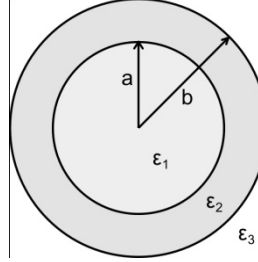


Figure 2.16 Nanocrystal model used for estimation of the reorganization energy, λ . The spherical nanocrystal consists of an inorganic core (ϵ_1) of radius a , a ligand shell (ϵ_2) with thickness $b-a$, and surrounding solvent environment (ϵ_3).

The reorganization energy, λ , calculated using Eq. (2.43) and summarized in Table 2.1 varies weakly with shell thickness and core material, but is strongly dependent on nanocrystal size. For CdSe nanocrystals with a 1.0nm thick alkanethiol shell ($\epsilon_2 = 2.4$) embedded in an organic matrix such as poly(3-hexylthiophene) (P3HT; $\epsilon_3^{(dc)} = 6.5$, $\epsilon_3^{(\infty)} = n^2 = 4.0$), λ increases from 12meV to 33meV as the core size is decreased from 8nm to 2nm in diameter. For a PbSe core, λ varies between 14meV and 35meV over the same size range. The difference between core materials becomes more significant for larger quantum dots embedded in a strongly polar solvent such as water ($\epsilon_3^{(dc)} = 80$, $\epsilon_3^{(\infty)} = 1.7$). For CdSe with a 1.0nm thick shell in water, λ increases from 46meV to 200 meV as the core size is decreased from 8nm to 2nm in diameter; with a PbSe core, λ varies between 81meV and 206meV over the same size range. If the surrounding medium is vacuum, the outer-sphere contribution to the reorganization energy vanishes entirely.

The estimation of Δ and λ sheds some light on the nature of interfacial charge transfer processes involving nanocrystals. We estimated the interfacial coupling energy to be in the range $\Delta \approx 10\text{-}150\text{meV}$, with larger values of Δ for smaller nanocrystals. In an aqueous environment, the reorganization energy varies between $\lambda \approx 50\text{-}200\text{meV}$, with larger values of λ again for smaller nanocrystals. This is the intermediate coupling regime ($k_B T < \Delta \leq 2\lambda/\pi$), where electron transfer occurs adiabatically and the thermal activation energy for charge transfer depends strongly on Δ . In a weakly polar organic

medium ($\lambda \approx 10\text{-}40\text{meV}$) or in vacuum ($\lambda < 10\text{meV}$), $\Delta > 2\lambda/\pi$ and we have reached the strong-coupling regime depicted for the adsorbate resonance in Figure 2.14. In this limit, the electron transfer time constant – or, more accurately speaking, the charge redistribution time – can be approximated as (59),

$$\tau \approx \hbar/\Delta. \quad (2.45)$$

For an interfacial coupling strength $\Delta > 15\text{meV}$, charge transfer occurs on a timescale $\tau < 50\text{fs}$. This theoretical treatment is in nice agreement with recent results from our lab demonstrating sub-50fs electron transfer times from photoexcited PbSe nanocrystals to TiO_2 electrodes in vacuum (see Chapter 7).

Table 2.1 Estimates of the reorganization energy, λ , following electron transfer from a photoexcited quantum dot to a bulk semiconductor electrode. Estimates are calculated from Eqs. (2.40)-(2.44) and include electrostatic screening by a 1.0nm thick alkanethiol ligand shell. λ is found to be strongly size-dependent with larger values corresponding to smaller quantum dots. Values reported in the table are for core sizes ranging in diameter from 8nm to 2nm.

Surrounding Environment	Reorganization Energy, λ		Coupling Regime
	CdSe	PbSe	
strongly polar/aqueous	40-200 meV	80-210 meV	<i>intermediate</i>
organic/polymer	10-35 meV	15-35 meV	<i>strong</i>
vacuum	<10 meV	<10 meV	<i>strong</i>

2.3.6. The role of surface-bound ligands

As synthesized, colloidal nanocrystals are covered with a layer of organic molecules that acts to stabilize the colloidal suspension and prevent aggregation. These surface-bound molecules, or ligands, also serve the important role of passivating surface electronic states and mitigating nonradiative recombination. In the context of interfacial charge transfer, the ligands act as bridges mediating the electronic interaction of the nanocrystal with the semiconducting substrate (Figure 2.10). They provide a powerful lever for controlling interfacial coupling. By varying the length and saturation of the molecular bridge, one may tune across the strong-coupling, adiabatic, and Marcus regimes of charge transfer.

The radial dependence of the nanocrystal wave functions shown in Figure 2.15 illustrates the importance of a short ligand for obtaining strong interfacial electronic coupling. However, the energetic position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) relative to the Fermi level can also have a profound effect on coupling strength and molecular conductance. Electron transfer across a short molecular bridge occurs via coherent tunneling characterized by an exponential dependence on bridge length, d ,

$$k_{ET} \propto \exp(-\beta d). \quad (2.46)$$

Typical β values are $0.2-0.6\text{\AA}^{-1}$ for highly conjugated chains, $0.9-1.2\text{\AA}^{-1}$ for saturated hydrocarbons, and $\sim 2\text{\AA}^{-1}$ for vacuum (54). Additionally, the chemical nature of the functional group binding the molecular bridge to the nanocrystal and substrate surfaces can be as important as the molecular backbone itself. The conductance of a short molecular wire can be expressed as (59),

$$g = g_c \Gamma_D \Gamma_A G^2, \quad (2.47)$$

where $g_c = 2e^2/h$ is the quantum of conductance, G is the Green's function matrix element for the molecular bridge, and Γ_D and Γ_A represent the electronic coupling strength between the molecular bridge and the donor and acceptor contacts. Equation (2.47) demonstrates that the conductance of the contacts is equally important for efficient charge transfer as the conjugation or saturation of the molecular bridge.

For sufficiently long bridges, electron transfer may occur by a “hopping” mechanism (54). In this picture, the electron undergoes a series of thermally activated (Marcus-type) “hops” from site-to-site along the molecular bridge. This type of mechanism can be shown to have relatively weak $k_{ET} \propto 1/d$ distance dependence, contrasted to the strong $k_{ET} \propto \exp(-\beta d)$ dependence of coherent tunneling. In general, hopping and tunneling transfer pathways operate in parallel,

$$k_{ET} = k_{tunn} + k_{hop}. \quad (2.48)$$

The tunneling mechanism will dominate for short bridges, while the hopping mechanism will be more efficient for longer bridges. Additionally, the hopping mechanism is thermally activated while the tunneling mechanism is largely independent of temperature.

Elegant experiments have been performed showing the transition from a hopping mechanism at room temperature to coherent tunneling low temperatures (55). Temperature and bridge length can also raise the likelihood for inelastic or incoherent tunneling channels, wherein the electron scatters off of molecular deformations as it traverses the molecular bridge.

2.3.7. Previous experimental investigations

In order to experimentally resolve the dynamics of electron transfer events, spectroscopic techniques employing sub-picosecond pulsed lasers are often necessary. Time-resolved spectroscopies utilizing sub-picosecond pulsed lasers are sometimes referred to as *pump-probe* spectroscopies because a first laser pulse (the *pump* pulse) is used to excite the system, then a second laser pulse (the *probe* pulse) is used to probe how the system has changed some time later as a result of the excitation. In such experiments, femtosecond time resolution is achieved by varying the relative distance the pump and probe pulses must travel before reaching the sample. Experimental observables probed by the second laser pulse may include fluorescence, absorption, photoemission, or changes in the linear (e.g. reflectivity, transmittivity) and non-linear (e.g. sum- and difference-frequency generation) optical response of the system.

The most widely-used laser for such applications is the Ti:sapphire laser, which features a lasing medium of Ti^{4+} ions imbedded in a single-crystal Al_2O_3 matrix. The Ti:sapphire laser is broadly tunable over the range ≈ 700 -1000nm and is capable, in certain embodiments, of producing pulses just a few femtoseconds in duration, though 50-250fs pulses are more common. Wavelengths in the visible and near UV are easily obtained by frequency-doubling or frequency-tripling of the Ti:sapphire fundamental in nonlinear crystals. Other frequencies intermediate to these integer multiples of the fundamental are attainable through the use of slightly more complex peripherals, including, for instance, a regenerative amplifier and an optical parametric amplifier (OPA).

A particularly versatile type of femtosecond spectroscopy is transient absorption (TA) spectroscopy. In TA experiments, one looks for pump-induced changes in the absorption spectrum as a function of pump-probe delay. The pump pulse is usually a

higher harmonic of the Ti:sapphire fundamental (typically the second harmonic, which is a visible blue or violet color), and the probe pulse is either a white-light continuum generated by focusing the amplified Ti:sapphire fundamental onto a sapphire plate or, more commonly, a specific wavelength in the mid-IR obtained via an OPA. Transient absorption has been the technique of choice in studying interfacial charge transfer in nanostructured solar cells for many years (70, 71). In studies of interfacial charge transfer from dyes to semiconductors, one typically uses the Ti:sapphire second harmonic to excite the dye, then uses a tunable mid-IR probe to detect intra-band excitation of electrons that have transferred to the semiconductor as well as changes in the vibrational spectrum of the dye associated with oxidation. A main limitation when using transient absorption spectroscopy to study interfacial charge transfer is that high surface area samples are required to generate a reasonable signal-to-noise ratio in the data. Consequently, TA cannot be used to study controlled interfaces consisting of sub-monolayer coverages on single-crystal surfaces. Two ultrafast laser techniques capable of single crystal surface sensitivity are developed in detail in the next Chapter.

Evidence for charge separation at a quantum dot/wide band gap semiconductor interface has been demonstrated for a number of donor/acceptor systems. These include electron transfer from CdS, PbS, Bi₂S₃, CdSe, InP, and InAs to TiO₂ or SnO₂ (see (72) or (73) and references therein), and from CdS, CdSe, and PbSe to ZnO (18, 74-76). These studies employed steady state optical techniques (such as fluorescence quenching) or fabrication of model devices (such as solar cells) to demonstrate interfacial charge separation. There are a growing number of papers addressing the *kinetics* of interfacial electron transfer from photoexcited quantum dots to wide band gap semiconductor acceptors (19, 77-80), but the results are varied.

The difficulty with using TA to probe quantum-dot-to-semiconductor charge transfer lies in de-convolution of dynamic contributions from electron transfer, electron trapping, hole quenching, and hot electron relaxation. The mid-IR absorption relied upon in dye-to-semiconductor electron transfer studies is not reliable in quantum-dot-to-semiconductor systems because the mid-IR probe wavelength is often resonant with intraband transitions in the nanocrystal (like $1S_e \rightarrow 1P_e$) and would therefore probe simultaneously both the transferred and un-transferred electrons. Instead, TA study of

electron transfer from nanocrystals typically focuses on the bleaching recovery of the ground-state $\rightarrow 1S_h 1S_e$ transition within the nanocrystal, which is characteristic of electron population of the $1S_e$ level. When the pump pulse initially excites electron-hole pairs in the quantum dot, “state filling” occurs wherein occupation of the quantized excited states reduces the oscillator strength associated with transitions to these states. As a result, bleaching of transitions to these states will occur. Reduction of the ground-state $\rightarrow 1S_h 1S_e$ bleach with increasing pump-probe delay is indicative of removal of electrons from the $1S_e$ level. However, the removal of the $1S_e$ electron could be due to many processes, including electron transfer, recombination, or electron trapping at the surface of the QD. In order to differentiate electron transfer from these other processes, it is necessary to compare the visible bleach recovery in the coupled donor/acceptor system to the visible bleach recovery in systems of isolated quantum dots. The electron transfer rate is then determined by,

$$k_{ET} = k_{QD+SC} - k_{QD} \quad (2.49)$$

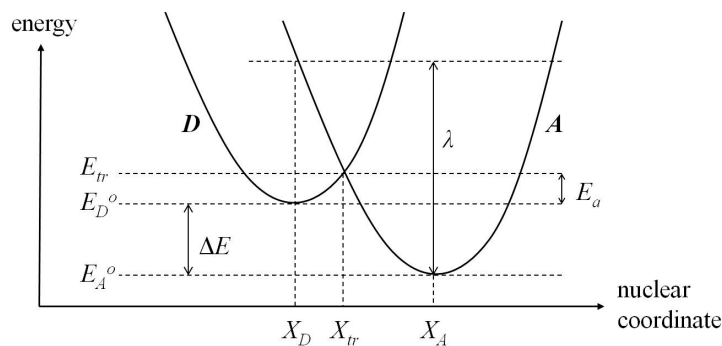
Even still, El-Sayed and co-workers showed that the hole can contribute significantly to the visible bleach, preventing the separation of electron and hole dynamics (81). Further, separation of the electron and hole, whether due to electron transfer or trapping of one of these carriers at the surface of the nanocrystal, will generate a static electric field causing changes in the visible bleach via the Stark effect (78). These contributions make isolation of electron transfer dynamics exceedingly complicated. Nonetheless, attempts have been made.

Nozik and co-workers used TA to study electron transfer from CdS quantum dots grown directly on TiO_2 via chemical bath deposition (82). They determined that electron injection from CdS to TiO_2 occurs within $\sim 10\text{-}50\text{ps}$. Later, Nozik and co-workers studied charge transfer from pyridine-capped InP quantum dots attached to nanocrystalline TiO_2 in the presence of a hole conductor, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) (78). They observed a fast 4ps component to the visible bleach recovery, but did not feel confident assigning the source of this transient. They did, however, feel confident in claiming that electron transfer from pyridine-capped InP to TiO_2 only takes place from electrons at the surface of the nanocrystal and that electrons confined to the core do not

participate directly in electron transfer. Kamat and co-workers studied electron transfer from CdSe quantum dots capped with mercaptopropionic acid (MPA = HS-CH₂-CH₂-COOH) to nanocrystalline TiO₂ films (19). They claimed to observe electron transfer over a wide range of timescales, from 5 to 140 ps. These authors also believed they observed hot electron transfer from the $1P_e$ state, but were unable to resolve these dynamics with their 130fs laser pulses or provide convincing evidence for their claim. More recently, Hyun *et al.* (79) used TA to study electron transfer from photoexcited MPA-capped PbS quantum dots to nanocrystalline TiO₂. These authors observed no dynamics whatsoever, which led them to conclude that electron transfer occurs exceedingly slowly in this system (i.e. hundreds of nanoseconds or microseconds).

In each of these studies, the wide range of reported timescales (picoseconds to microseconds) reflects uncertainty in the measurement. The TA data is difficult to model with standard rate equations due to multi- and non-exponential behavior of the visible bleach recovery, which originates from interface heterogeneity in these porous TiO₂ scaffolds and a variety of dynamical processes contributing to absorption transients. As such, alternative techniques are needed to fully elucidate the dynamics of these complex systems. In the following chapter, two such techniques are presented.

2.4. Derivation of the diabatic activation energy



The figure on the preceding page is a re-production of Figure 2.12. It is included again for reference. We seek here to derive the activation energy in the diabatic limit in terms of the free energy difference between the donor (D) and acceptor (A) and the nuclear reorganization energy, λ :

$$E_a = \frac{(\Delta E + \lambda)^2}{4\lambda} \quad (2.50)$$

We start by writing equations for each of the free energy surfaces:

$$E_D = E_D^o + \frac{1}{2}\omega^2(X - X_D)^2 \quad (2.51)$$

$$E_A = E_A^o + \frac{1}{2}\omega^2(X - X_A)^2 \quad (2.52)$$

Equating these two expressions at $X=X_{tr}$:

$$\begin{aligned} -\Delta E &= E_D^o - E_A^o \\ &= \frac{1}{2}\omega^2 \left[(X_{tr} - X_A)^2 - (X_{tr} - X_D)^2 \right] \\ &= \frac{1}{2}\omega^2 \left[(X_A - X_D)(X_A + X_D) - 2X_{tr}(X_A - X_D) \right] \end{aligned} \quad (2.53)$$

Solving for X_{tr} :

$$X_{tr} = \frac{1}{2}(X_A + X_D) + \frac{\Delta E}{\omega^2(X_A - X_D)} \quad (2.54)$$

The reorganization energy is:

$$\begin{aligned} \lambda &= E_A(X_D) - E_A^o \\ &= \frac{1}{2}\omega^2(X_D - X_A)^2 \end{aligned} \quad (2.55)$$

$$\lambda = \frac{1}{2}\omega^2(X_A - X_D)^2 \quad (2.56)$$

Using Eq. (2.54) for X_{tr} , we find the activation energy:

$$\begin{aligned}
E_a &= E_D(X_{tr}) - E_D^o \\
&= \frac{1}{2} \omega^2 [X_{tr} - X_D]^2 \\
&= \frac{1}{2} \omega^2 \left[\frac{1}{2} (X_A + X_D) + \frac{\Delta E}{\omega^2 (X_A - X_D)} - X_D \right]^2 \\
&= \frac{1}{2} \omega^2 \left[\frac{1}{2} (X_A - X_D) + \frac{\Delta E}{\omega^2 (X_A - X_D)} \right]^2
\end{aligned} \tag{2.57}$$

$$E_a = \frac{1}{2} \omega^2 \left[\frac{1}{4} (X_A - X_D)^2 + \frac{\Delta E}{\omega^2} + \frac{\Delta E^2}{\omega^4 (X_A - X_D)^2} \right] \tag{2.58}$$

Plugging (2.56) into (2.58), we now have:

$$\begin{aligned}
E_a &= \frac{\lambda}{4} + \frac{\Delta E}{2} + \frac{\Delta E^2}{4\lambda} \\
&= \frac{1}{4\lambda} (\lambda^2 + 2\lambda\Delta E + \Delta E^2) \\
&= \frac{1}{4\lambda} (\lambda + \Delta E)^2
\end{aligned} \tag{2.59}$$

q.e.d.

Chapter 3

Two-Photon Photoelectron Spectroscopy (2PPE)

In this Chapter and in Chapter 4, two experimental techniques central to the research in this Dissertation are discussed in some detail: time-resolved two-photon photoelectron spectroscopy (TR-2PPE) and time-resolved surface second harmonic generation (TR-SHG). Since the development of SHG as an experimental tool for probing interfacial electron dynamics was one of the central achievements of this Dissertation, this technique is addressed in greater detail. Both 2PPE and SHG employ femtosecond lasers in a pump-probe arrangement to achieve femtosecond resolution of surface dynamics. Both techniques are surface-sensitive. However, SHG is an all-optical technique: light is the input and the output; 2PPE is a photoelectron spectroscopy: light is the input, but photoelectrons are the output. 2PPE probes the surface in both the time and energy domains, while SHG primarily elicits information in the time domain^{*}. 2PPE experiments must be performed in ultrahigh vacuum (UHV), but an SHG experiment can be performed on bench top in ambient; 2PPE always probes the top-most surface, but SHG can probe buried interfaces, including solid-solid (83-85), solid-liquid (86, 87), and liquid-liquid interfaces (88). 2PPE probes only the electron, but SHG can follow hole

^{*} A limited amount of energetic information may be obtained through wavelength-dependence of the second harmonic response.

dynamics as well (89). Each technique has its limitations, but each technique also reveals information unattainable by other means.

3.1. 2PPE principle

The principle of two-photon photoemission (2PPE) is illustrated in Figure 3.1. A material (metal shown for simplicity) is irradiated with short pulses (ps or sub-ps) of laser light separated in time by an amount τ ($10^{-15} - 10^{-10}$ seconds). Absorption of one photon promotes an electron from a normally occupied initial state below the Fermi level to an unoccupied intermediate state above the Fermi level. Absorption of a second photon promotes this electron to a free electron-like final state above the vacuum level. This electron, which now has sufficient energy to overcome the surface potential barrier, is ejected into the vacuum and subsequently probed in the energy, momentum, and time domains to extract information about the transiently populated intermediate state from which it was photoemitted.

Such three-level transitions can take a number of forms (59). The first class of transitions is that for which the initial state is a pure bulk state. In order for the transition dipole moment to be non-zero, there must be spatial overlap of the initial and intermediate state wave functions. Thus, pure bulk states can serve as initial states for transitions to other pure bulk states, surface states or resonances, or molecular adsorbate states with reasonably strong electronic coupling to the substrate. An occupied surface state may also serve as the initial state. Since a surface state has substantial probability density at the surface, transitions to other states localized at the surface are the most likely. These include transitions to other surface states, or to molecular states of adsorbed species. A final type of three-level transition is that of direct, or coherent, two-photon absorption. Here, the high intensity laser field directly couples the initial and free electron-like final states. The transition occurs via a virtual state, and the probability of such transitions will be enhanced if the virtual state is resonant with a real eigenstate of the system.

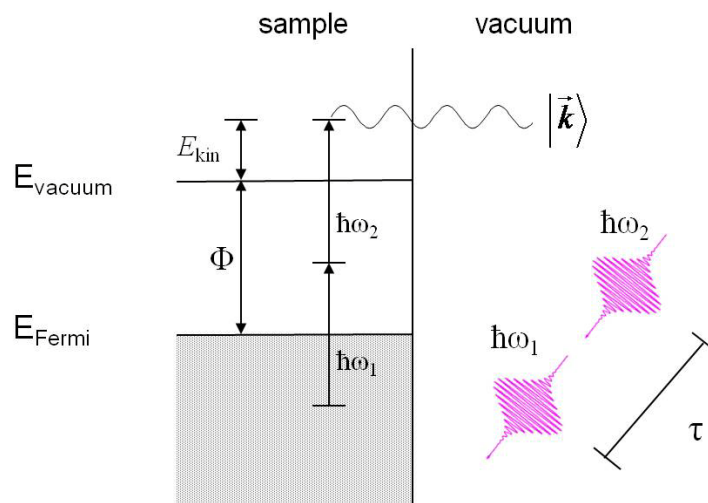


Figure 3.1 The principle of two-photon photoelectron spectroscopy (2PPE); metal sample shown for simplicity. Two laser pulses eject an electron from an occupied state near the Fermi level to an unoccupied vacuum state, where the electron's kinetic energy is then measured. Each laser pulse has photon energy less than the work function, Φ , so that two-photon absorption is required to reach an unbound energy state above the vacuum level.

In addition to three-level transitions, transitions involving four or more levels are also possible. The difference between a four-level and a three-level transition is illustrated in Figure 3.2. The first photon absorption step ($|0\rangle$ to $|1\rangle$) proceeds in the same manner described above, but after population of state $|1\rangle$, the electron undergoes some scattering, relaxation, or tunneling transition to state $|2\rangle$ before photoemission. These types of transitions are often the most interesting to observe because they involve the appearance of spectral features only after a time delay between the pump and probe pulses. Examples include the scattering of bulk electrons into surface states (90, 91), electron solvation and small polaron formation in molecular thin films (92, 93), and photoinduced electron transfer (94, 95).

2PPE is a form of photoelectron spectroscopy, and like all photoelectron spectroscopies, it must be performed under ultra-high vacuum (UHV) conditions so that photoelectrons are not scattered by gas molecules before they are collected and analyzed. Additionally, 2PPE, like all photoelectron spectroscopies, is inherently surface sensitive. This is due to the ease with which free electrons scatter in solids. For a typical electron kinetic energy of 2 eV, the inelastic mean free path is approximately 50 angstroms (96).

As a result, most of the 2PPE intensity is derived from electrons originating from within the first $\sim 15\text{nm}$ near the surface.

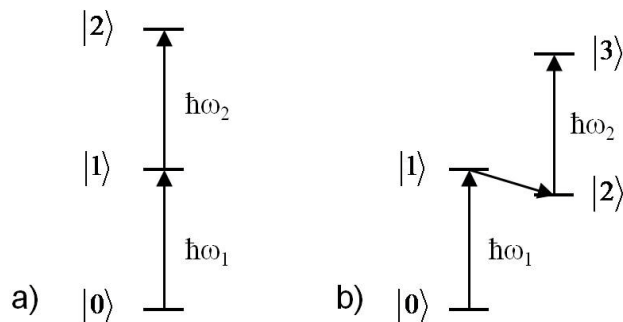


Figure 3.2 Photoelectron transitions involving three (a) or four (b) levels. In the four-level transition, an incoherent scattering process is involved.

3.2. Modes of operation

There are three basic operating modes within 2PPE experimentation. These operating modes probe the photoelectron in the energy, momentum, and time domains, respectively. The first form of data collection involves measuring photoelectron signal intensity (electron counts per second) as a function of the photoelectron kinetic energy. This type of measurement is usually carried out with both pump and probe pulses overlapped in time. Peaks in the kinetic energy spectrum can be due to features in the initial, intermediate, or final state density of states. It is possible to determine which state is responsible for a spectral feature by seeing how the energetic position of the peak shifts with small variations in the photon energy. For a one-color experiment^{*}, as illustrated in Figure 3.3, initial state features (i.e. photoemission from an occupied surface state via a virtual state) will scale with twice the photon energy, while spectral features dominated by the intermediate state (i.e. an exciton, conduction band state, or unoccupied surface state) will scale with one times the photon energy. Final state features (i.e. density-of-states anomalies in bulk bands above the vacuum level) will not shift with changing

^{*} An experiment is referred to as “one-color” or “monochromatic” if both pump and probe pulses are the same wavelength of light; a “two-color” or “bichromatic” experiment is one in which pump and probe pulses are different wavelengths of light.

photon energy, though these features are rarely observed. Sometimes it is also necessary to determine whether a low-energy feature in the kinetic energy spectrum is due to one- or two-photon photoemission. While in principle 2PPE employs photon energies less than the work function of the sample, the precise surface work function is not always known *a priori*, and because photon energies close to the work function are commonly used, one-photon emission is sometimes observed. In order to determine if a spectral feature is one- or two-photon in origin, one may monitor the variation of photoemission intensity with changing photon flux. Photoemission intensity due to one-photon absorption processes scale linearly with photon flux, while two-photon processes scale with photon flux squared.

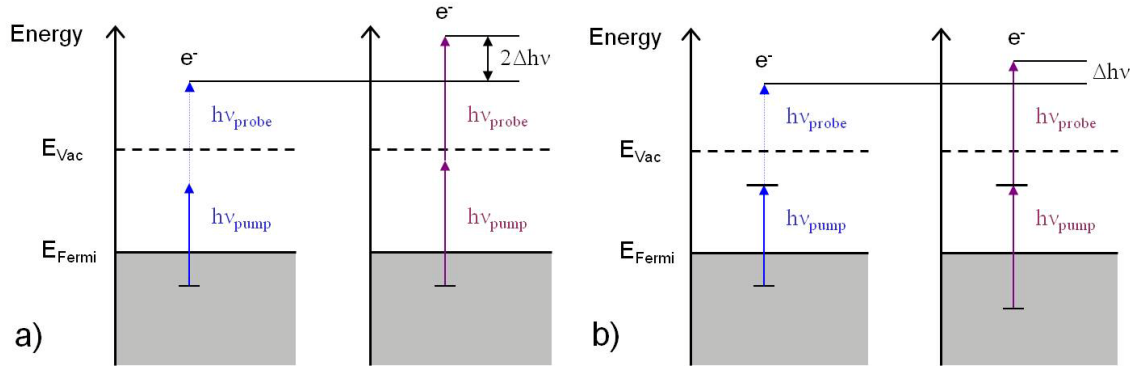


Figure 3.3 Illustration of the scaling of spectral features with photon energy in a one-color 2PPE experiment. (a) Peaks due to initial states scale with 2x the photon energy; (b) peaks in the 2PPE spectrum dominated by the intermediate state scale with 1x the photon energy.

In addition to energetic location of unoccupied states, the two-photon photoemission technique can also provide information about unoccupied state band structure. This information is obtained through angle-resolved photoemission, where peak shifts are monitored as the photoemission detection angle is varied. To understand this process, first consider the free-electron dispersion relation,

$$E_{kin} = \frac{\hbar^2 k^2}{2m_e}. \quad (3.1)$$

The free electron momentum vector can be decomposed into components parallel and normal to the surface plane (Figure 3.4),

$$\vec{k} = \vec{k}_\perp + \vec{k}_\parallel. \quad (3.2)$$

The total kinetic energy is expressed as,

$$E_{kin} = \frac{\hbar^2 k_\perp^2}{2m_e} + \frac{\hbar^2 k_\parallel^2}{2m_e}. \quad (3.3)$$

When an electron crosses the surface plane, it feels a force due to the potential step at the surface. Because the potential gradient of a uniform surface exists only in the surface normal direction, only the momentum component of the electron perpendicular to the surface, $k_\perp$, is changed. As a result, $k_\parallel$ is conserved during the photoemission process. Its value is then,

$$k_\parallel = \sqrt{\frac{2m_e E_{kin}}{\hbar^2}} \sin(\theta). \quad (3.4)$$

For states confined in the surface normal direction (i.e. surface states, image states, and adsorbate molecular orbitals), $k_\perp = 0$. For such states, a plot of E_{kin} vs. $k_\parallel$ yields a quantitative measure of the extent of electron delocalization in the surface plane. Delocalized states will produce parabolic dispersion relations near the center of the surface Brillouin zone, while localized states will produce flat-band dispersions. A parabolic equation can often be fit to the dispersion curve near the $\bar{\Gamma}$ point of the surface Brillouin zone,

$$E_k = E_0 + \frac{\hbar^2 k_\parallel^2}{2m_{eff}}. \quad (3.5)$$

E_0 is the energy at normal emission, and m_{eff} is the electron effective mass, obtained from the fit. For bulk states, exact band structure determination is complicated by dispersion in the surface normal direction ($k_\perp \neq 0$), but methods for accounting for $k_\perp$ do exist (97).

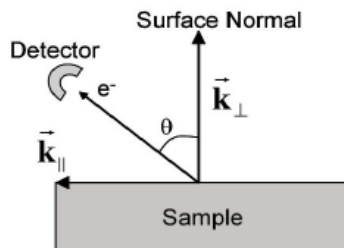


Figure 3.4 Decomposition of the free electron momentum vector into components normal and parallel to the surface plane. From (98).

The final and often most powerful mode of 2PPE operation is one in which photoemission intensity, peak position, or parallel dispersion is measured as a function of the time delay between the pump and probe pulses. Plots of photoemission intensity at a fixed energy vs. pump-probe delay are called two-pulse correlations. By fitting an appropriate model to the correlation the lifetime (τ), or decay constant (τ^{-1}), of an electron in this energetic state can be extracted. If parallel dispersion plots are generated at a series of pump-probe delays, one may observe the flattening of the band (increasing effective mass) with increasing pump-probe delay. Such an observation is indicative of localization of the electron wave function in time arising from, for instance, electron solvation or small polaron formation (92, 92). The same event will coincide with a downward shift (in energy) of this peak in the kinetic energy spectrum with increasing pump-probe delay as the electron relaxes to lower energy by coupling to nuclear deformations.

3.3. Experimental implementation

3.3.1. Optical configuration

The laser setup used for the experiments discussed in this Dissertation is outlined in Figure 3.5. Short pulses (<100 fs, <20 nJ) of laser light in the near-infrared (tunable ~ 700 -900 nm) are generated by a mode-locked Ti:sapphire oscillator (Coherent MIRA), which is pumped by an 8 watt continuous-wave (CW) diode-pumped Nd:vanadate laser (Coherent Verdi) at 532nm. The Ti:sapphire produces pulses at a repetition rate of 76

MHz (one pulse every 13 ns) and average power <1000 mW. The energy resolution of these femtosecond laser pulses is fundamentally limited by the uncertainty principle,

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}. \quad (3.6)$$

As time resolution of the experimental probe is improved, energy resolution is lost. For a typical 80fs pulse at 850nm central wavelength, the laser pulse spectrum FWHM is ~15nm. This results in an energy uncertainty of ± 15 meV.

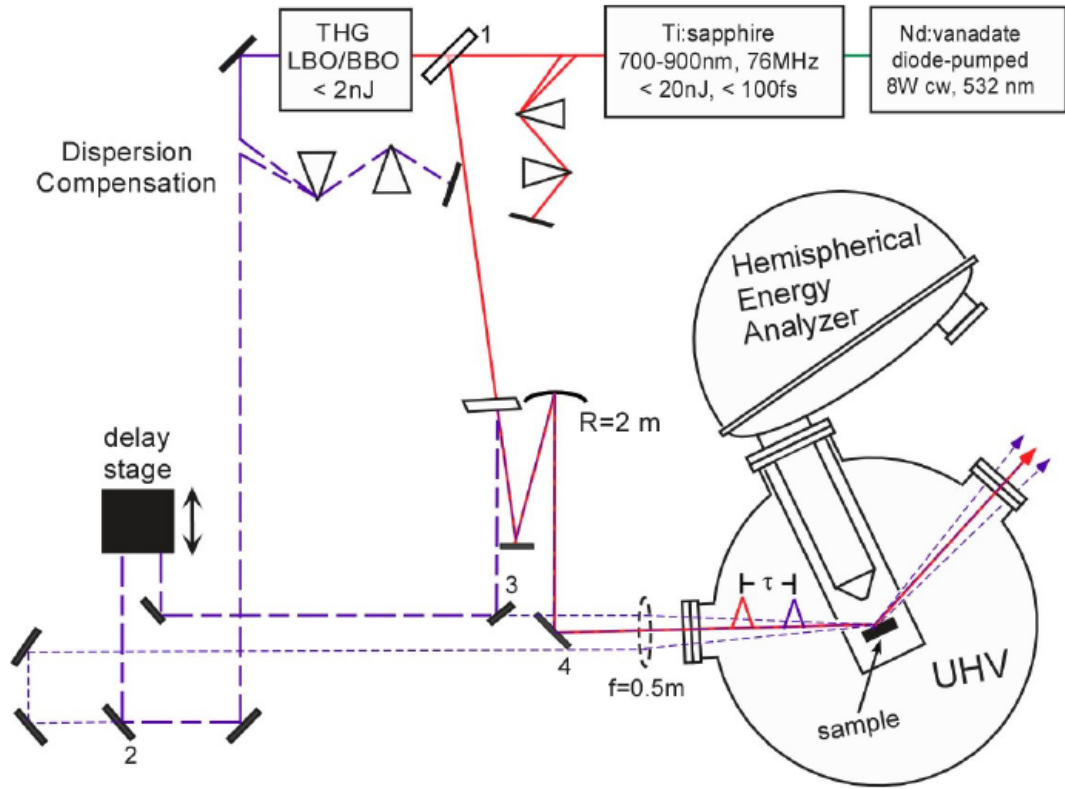


Figure 3.5 Schematic of the 2PPE setup used for the experiments discussed in this Dissertation. “1” and “2” are beamsplitters; “3” and “4” are removable mirrors. THG = third harmonic generation; LBO, BBO = common borate crystals used for nonlinear optical conversion. From (98).

The temporal intensity profile of femtosecond laser pulses is roughly gaussian, but femtosecond pulses are more commonly described by a hyperbolic secant squared (sech^2) pulse shape:

$$I(t) = I_0 \cdot \text{sech}^2 \left(\frac{t_0 - t}{\text{width}} \right) \quad (3.7)$$

The sech^2 profile is similar to a gaussian profile, but slightly broader near the base of the bell. A laser pulse will be temporally broadened every time it passes through a lens, beam splitter, waveplate, nonlinear crystal, or is reflected off of a dielectric mirror. This broadening is called *chirping* and it is due to the frequency dependence of the refractive index of normally dispersive materials. As a laser pulse passes through a normally dispersive material (quartz, glass, sapphire, or other transparent optical material), the high-frequency portion of the wave packet propagates more slowly than the low-frequency portion. The result is an “up-chirped” pulse, so-called because the frequency of light appears to increase as the wave packet passes a point in space. To compensate for this group velocity dispersion (GVD), pulse compression trains are employed. These consist of pairs of Brewster-cut prisms made from normally dispersive materials, but arranged in a configuration such that longer wavelength light must pass through more of one of the prisms than shorter wavelength light. The net result is negative dispersion, which compensates for the positive dispersion encountered in the other optical components. The prisms are manually adjusted for optimum GVD compensation, and are often set to pre-compensate (down-chirp) the laser pulse for up-chirping encountered later in the optical path. The ultimate goal is to have the shortest pulse possible at the sample surface. These prism pairs are indicated in Figure 3.5 before and after the harmonic generator.

For a two-color experiment, a beam splitter (labeled “1” in Figure 3.5) picks off 30% of the Ti:sapphire output and directs this toward focusing optics near the UHV chamber window. The remaining Ti:sapphire fundamental beam enters a harmonic generator (Inrad) where it is incompletely frequency-doubled in a β -barium borate (BBO) nonlinear crystal. The second harmonic (visible) is re-combined with the residual fundamental (near-IR) in a lithium triborate (LBO) nonlinear crystal to generate the third harmonic (near-UV) via sum frequency generation. The residual fundamental and second harmonic are filtered out before the third harmonic beam enters the second prism pair for GVD compensation. The UV beam next passes through a computer-controlled delay stage before being focused co-linearly with the IR onto the sample. Note that in the two-

color configuration, components “2”, “3”, and “4” in Fig. 3.5 represent fully reflective mirrors and the $f=0.5\text{m}$ lens is removed. At normal emission, the laser beam is incident on the sample 30° above the surface plane (60° off-normal). The projection of the circular beam on the sample at 30° incidence is an ellipse with large radius exactly twice the small radius. Typical irradiated areas are $300\mu\text{m}$ by $600\mu\text{m}$, or $\sim 0.15\text{ mm}^2$.

In a typical configuration, both pump and probe pulses are *p*-polarized. Information about the symmetry of certain types of states can be obtained by independently varying the polarization of the pump and probe pulses. For instance, there is a node at $\phi=90^\circ$ ($\angle$ between polarization vector and photoelectron wave vector) in the photoemission cross section of an electron residing in an image state on a metal. If the probe pulse is *s*-polarized then the polarization is completely in the surface plane and a drastic decrease in photoelectron yield will be observed. These types of symmetry arguments can help identify the source of a feature in the 2PPE kinetic energy spectrum.

In a one-color experiment, the beam splitter “1” is removed so that all of the Ti:sapphire fundamental enters the harmonic generator. Mirror “2” is replaced by a 50% beam splitter, and mirrors “3” and “4” are completely removed. Half of the UV pulse passes through the delay stage, while the other half travels directly on to the chamber. Both beams are focused symmetrically through an $f=0.5\text{m}$ lens onto the sample at a mutual angle of $\sim 2^\circ$.

The two-color configuration offers some advantages over the one-color configuration. In a two-color experiment, the UV intensity can be kept low while maintaining high IR intensity. This is advantageous because coherent two-photon absorption of two UV photons is suppressed while probability of two-color two-photon absorption remains high (absorption of two IR photons does not promote an electron above the vacuum level). As a result, photoemission intensity due to direct ionization of occupied states below the Fermi level (which are generally not of interest in a 2PPE experiment) is minimized. Another advantage of the two-color configuration is ease of alignment. Because the IR and UV beams are collinear, spatial overlap of the pulses is always ensured. The UV-UV configuration is non-collinear, so care must be taken each day to ensure that the beams are overlapped on the sample. For semiconductor samples with direct band gaps, fluorescence enables alignment with the help of a CCD camera.

For metal samples, non-collinear alignment of UV beams is exceedingly more difficult. Despite the advantages of the two-color configuration, the energetics of the system under investigation may necessitate the use of the UV-UV configuration. This is the case for large-work function metals and wide band gap semiconductors such as ZnO or TiO₂.

3.3.2. *Vacuum system, electron detection, and sample preparation*

As mentioned previously, all 2PPE experiments are carried out in an ultra-high vacuum chamber (UHV). Typical background pressures is $< 3 \cdot 10^{-10}$ Torr. The sample is suspended from a manipulator with independent control of three-axis translation and one-axis rotation. The sample can be resistively heated either directly (passing current through the sample) or indirectly (passing current through Ta wires attached to the back of the sample), and cooled to ~ 100 K with liquid nitrogen. The path photoelectrons take from the sample surface to the electron energy analyzer is enclosed in μ -metal shielding ($\sim 75\%$ Ni, $\sim 15\%$ Fe, plus Cu and Mo) to prevent any external magnetic fields from deflecting the electrons as they travel to the detector. Photoelectron detection is accomplished with a commercial VG-100AX hemispherical analyzer. Briefly, electron optics at the opening of the hemispherical analyzer allow only the entrance of electrons within a narrow trajectory range; a voltage applied across the inner and outer hemispheres of the analyzer selects for electron kinetic energy; a channeltron multiplier at the exit of the analyzer amplifies the electron signal. The analyzer electronics convert the time-averaged current pulses to a voltage signal which is sent to a personal computer, where data collection and movement of the delay stage are coordinated with LABVIEW.

Sample preparation abilities include Ar⁺ ion sputtering, thermal oven evaporation of nonvolatile precursors (home-built Knudsen cells heated by a tungsten filament), and a leak valve for dosing volatile precursors. *In situ* sample characterization abilities include Auger electron spectroscopy (AES) for surface composition analysis, low energy electron diffraction (LEED) for analysis of surface structure and symmetry, and a quadrupole mass spectrometer (QMS) for residual gas analysis and temperature-programmed desorption (TPD).

Chapter 4

Time-Resolved Surface Second Harmonic Generation (TR-SHG)

In this Chapter, the principle, motivation, theory, and implementation of time-resolved surface second harmonic generation (TR-SHG) is presented. Since the development of SHG as an experimental tool for probing interfacial electron dynamics is a central achievement of this Dissertation, it is discussed in considerable detail. TR-SHG differs from TR-2PPE in several important ways. Both techniques employ femtosecond lasers in a pump-probe arrangement to achieve femtosecond resolution of surface dynamics. Both techniques are surface-sensitive. However, SHG is an all-optical technique: light is the input and the output; 2PPE is a photoelectron spectroscopy: light is the input, but photoelectrons are the output. 2PPE probes the surface in both the time and energy domains, while SHG primarily elicits information in the time domain^{*}. However, 2PPE experiments must be performed in ultrahigh vacuum (UHV), but an SHG experiment can be performed on bench top in ambient. 2PPE always probes the top-most surface, but SHG can probe buried interfaces, including solid-solid (83-85), solid-liquid (86, 87), and liquid-liquid interfaces (88). 2PPE probes only the electron, but SHG can

^{*} A limited amount of energetic information may be obtained through wavelength-dependence of the second harmonic response.

follow hole dynamics as well (89). Each technique has its limitations, but each technique also reveals information unattainable by other means.

4.1. TR-SHG principle

Second harmonic generation (SHG) is a specific case of a general type of nonlinear optical response known as sum frequency generation (SFG) (99). During SFG, a material absorbs two photons of arbitrary frequency ω_1 & ω_2 and emits a single photon at frequency $\omega_3 = \omega_1 + \omega_2$. SHG refers to the particular case where $\omega_1 = \omega_2$, so that $\omega_3 = 2\omega$. The SHG concept is illustrated in Figure 4.1. When an electromagnetic wave with frequency ω passes through a nonlinear medium, some of the incident photons at frequency ω are converted to photons at frequency 2ω . The incident light need not pass directly through the nonlinear medium in order for SHG to occur. Harmonic generation may also occur when light is reflected off of a surface or interface. If the materials on either side of the interface each possess a center of inversion (they are “centrosymmetric”), then the harmonic generation process only occurs within the first few atomic layers near the interface. In this type of configuration, the efficiency of the second harmonic response will be highly sensitive to changes in the structure and local electronic environment at the surface. It is this extreme sensitivity to *surface* electronic interactions that makes SHG a powerful tool for probing interfacial electron dynamics.

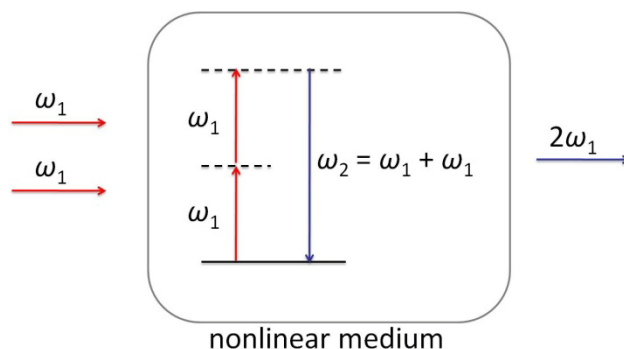


Figure 4.1 Basic concept of optical second harmonic generation (SHG), wherein a nonlinear medium converts two photons at the same frequency to a single photon with twice the frequency (or energy). The energy levels involved in the transitions within the nonlinear medium may be real or virtual states.

The nonlinear optical response is “nonlinear” in the sense that it depends nonlinearly on the strength of the applied optical field. For instance, the intensity of the second harmonic response tends to vary quadratically with the intensity of the incident electromagnetic wave. Though the surface nonlinear optical response can be quite sensitive to changes in the surface environment, the nonlinear response is, in general, much weaker than the linear response. As we will see in sections 4.2.4 and 4.2.2, the efficiency of the nonlinear conversion process depends strongly on the geometry of the experiment. For second harmonic generation at semiconductor surfaces, typically one signal photon is generated per 10^{13} - 10^{17} incident photons (100). As a result, nonlinear optical behavior is typically not observed without the use of focused laser light with high peak power.

The geometry of the time-resolved surface second harmonic generation (TR-SHG) experiment discussed in this Dissertation is shown in Figure 4.2. The sample consists of monolayers or sub-monolayers of nanocrystals (or molecular chromophores) adsorbed on the surface of a semiconductor electron acceptor, such as TiO_2 . The *pump* pulse has sufficient photon energy to excite the quantum dots but not enough to excite the TiO_2 band gap. The *probe* pulse, which is spatially overlapped with the pump pulse on the sample surface, probes the second harmonic susceptibility of the interface. By monitoring the intensity of the reflected second harmonic (SH) light as a function of time-delay between the pump and probe pulses, one may obtain information about the evolving electronic environment at the nanocrystal/semiconductor interface over time. The nature of this interaction and the type of information obtained with this technique is detailed throughout the course of this section.

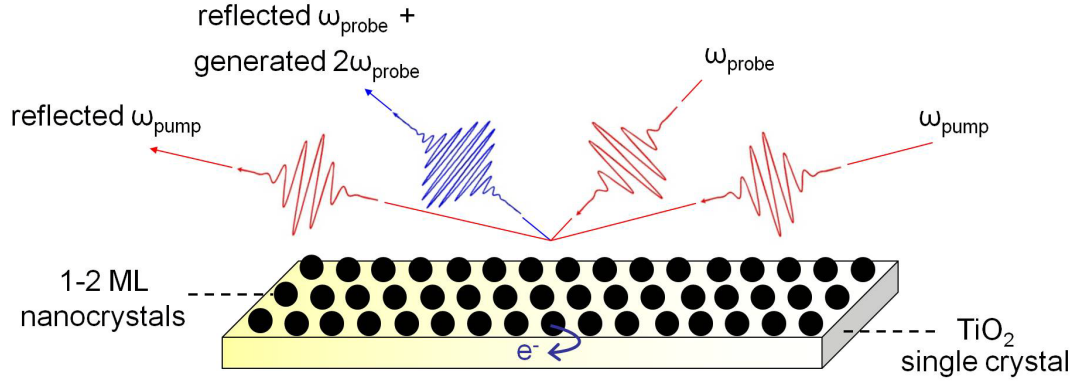


Figure 4.2 The TR-SHG experiment. The sample consists of 1-2 monolayers of nanocrystals (such as PbSe) adsorbed on the surface of single-crystal TiO₂. A femtosecond laser pulse with photon energy less than the TiO₂ band gap (the “pump”) photoexcites the nanocrystal film. A second laser pulse (the “probe”) arrives later to determine the second harmonic generation efficiency. The intensity of the SHG signal is measured as function of time delay between the pump and probe pulses. ML=monolayer.

4.2. Theoretical foundations

4.2.1. Phenomenological description of the nonlinear optical response

In the classical picture, when an electromagnetic wave encounters a material, electrons within the material are accelerated by the driving electric field component of the incident radiation. The optical response of a dielectric medium to an electromagnetic wave $\mathbf{E}(\mathbf{r}, t)$ is described by the electric polarization $\mathbf{P}(\mathbf{r}, t)$, which is defined as the dipole moment per unit volume [C·m/m³]. These induced oscillating dipoles, in turn, act as a source of re-emitted radiation. This interaction is described by the wave-equation (99),

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E}(\mathbf{r}, t) = -\frac{1}{\epsilon_0 c^2} \mathbf{P}(\mathbf{r}, t). \quad (4.1)$$

The wave equation is solved independently for each Fourier component, ω_m , admitting solutions for the emitted radiation in the form of travelling plane waves,

$$E_m(z, t) = A_m e^{i(k_m z - \omega_m t)} + \text{c.c.}, \quad (4.2)$$

where A_m is the amplitude, k_m is the wave vector, ω_m is the frequency, z is the direction of propagation, and c.c. represents the complex conjugate.

In the linear optics of isotropic source-free media, the polarization at a given frequency, $\mathbf{P}(\omega)$, is dependent on the incident field through the dielectric susceptibility,

$$\mathbf{P}(\omega) = \varepsilon_0 \chi^{(1)}(\omega) \mathbf{E}(\omega), \quad (4.3)$$

where ε_0 is the permittivity of free space and the unitless proportionality constant $\chi^{(1)}$ is the linear susceptibility, which is frequency-dependent in a dispersive medium. The linear susceptibility is more easily recognized by its relationship to the dielectric constant,

$$\varepsilon = 1 + \chi^{(1)}. \quad (4.4)$$

In general, $\mathbf{P}(\omega)$ need not respond linearly to the applied field; higher-order *nonlinear* interactions may be possible, though these interactions are usually not observed unless high-intensity laser light is involved.* The nonlinear optical response of a material to a monochromatic plane wave can be described by expanding (4.3) as a power series in the electric field,

$$\mathbf{P} = \varepsilon_0 \left[\chi^{(1)}(\omega) \cdot \mathbf{E}(\omega) + \chi^{(2)}(2\omega) : \mathbf{E}^2(\omega) + \chi^{(3)}(3\omega) : \mathbf{E}^3(\omega) + \dots \right], \quad (4.5)$$

or, equivalently,

$$\mathbf{P} = \mathbf{P}^{(1)}(\omega) + \mathbf{P}^{(2)}(2\omega) + \mathbf{P}^{(3)}(3\omega) + \dots \quad (4.6)$$

Thus, the total polarization of the medium can be expressed as a sum of its frequency components. The terms $\mathbf{P}^{(2)}$ and $\mathbf{P}^{(3)}$ in (4.6) are the second- and third-order nonlinear polarizations. Correspondingly, the terms $\chi^{(2)}$ and $\chi^{(3)}$ in Eq. (4.5) are the second- and third-order nonlinear susceptibilities. The second-order parameter $\chi^{(2)}$ governs processes such as SHG, sum- and difference-frequency generation, and optical rectification. For instance, if we extend our analysis to the case of incident radiation consisting of two distinct frequency components ω_1 & ω_2 , the second-order polarization takes on terms,

$$\mathbf{P}^{(2)} = \mathbf{P}(2\omega_1) + \mathbf{P}(2\omega_2) + \mathbf{P}(\omega_1 + \omega_2) + \mathbf{P}(\omega_2 - \omega_1) + \mathbf{P}(0 = \omega_1 - \omega_1 + \omega_2 - \omega_2). \quad (4.7)$$

* Indeed, one of the first observations of nonlinear optical phenomena (209) did not occur until shortly after the invention of the laser by Maiman in 1960.

These terms represent, in order, SHG, SHG, sum frequency generation (SFG), difference frequency generation (DFG), and optical rectification. Similarly, the third-order parameter $\chi^{(3)}$ governs processes such as third harmonic generation, four-wave mixing, and the optical Kerr effect. Due to the vector nature of the fields, $\chi^{(1)}$ is a dyad (or second-rank tensor), $\chi^{(2)}$ is a triad (or third-rank tensor), $\chi^{(3)}$ is a tetrad (or fourth-rank tensor), etc.

For the case of monochromatic light consisting of components with arbitrary polarization described in a Cartesian basis, the nonlinear polarization governing SHG is given by,

$$P_i^{(2)} = \epsilon_0 \chi_{ijk}^{(2)} (2\omega, \omega) E_j(\omega) E_k(\omega). \quad (4.8)$$

The subscripts i, j , and k run over the Cartesian coordinates x, y , and z . The subscript i denotes the direction of the medium polarization induced by the electromagnetic waves polarized in the j and k directions. In principle, $\chi^{(2)}$ is a triad composed of $3^3=27$ distinct components and $\chi_{ijk}^{(2)}$ is the specific tensor component involved in the particular nonlinear interaction. However, due to symmetry of the lattice and the degeneracy of E_j and E_k , the number of distinct nonzero components of $\chi^{(2)}$ is greatly reduced.

The simplest understanding of how nonlinear polarizations are induced within a material is obtained by considering the driven motion of electrons in an anharmonic potential well. Far from resonance, this classical picture of anharmonic bond polarizability offers a simple and (reasonably) accurate description of the nonlinear optical interaction in semiconductors and insulators (99-101). Consider a one-dimensional potential energy function,

$$U = - \int F_{restoring} dx = \frac{1}{2} m_0 \omega_0^2 x^2 + \frac{1}{3} m_0 a x^3 + \dots, \quad (4.9)$$

where x is the electron coordinate, m_0 is the electron mass, and a is a parameter describing the anharmonicity of the potential. If the motion of our electron is driven by an electric field $E(t)$ then the equation of motion is,

$$m_0 \frac{d^2 x}{dt^2} + 2\gamma m_0 \frac{dx}{dt} + m_0 \omega_0^2 x + m_0 a x^2 = -eE(t), \quad (4.10)$$

where γ is the dipole damping rate and e is the fundamental charge. For SHG, we need only consider a monochromatic plane wave,

$$E(t) = E_0 e^{-i\omega t}. \quad (4.11)$$

The solution to Eq. (4.10), given an applied field of the form (4.11), can be found by perturbative methods. We replace $E(t)$ in (4.10) by $\lambda E(t)$ and seek a solution of the form,

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \dots \quad (4.12)$$

Since the instantaneous polarization, $P(t)$, is simply the dipole moment per unit volume, the second-order nonlinear polarization can be written,

$$\begin{aligned} P^{(2)}(2\omega) &= -Nex^{(2)}(2\omega) \\ &= \chi^{(2)}(2\omega, \omega) E^2(\omega), \end{aligned} \quad (4.13)$$

where N is the number density of valence electrons. Finding $x^{(2)}$ and plugging in, we arrive at (99),

$$\chi^{(2)}(2\omega, \omega) = \frac{N(e^3/m_0^2)a}{(\omega_0^2 - 4\omega^2 - 4i\gamma\omega)(\omega_0^2 - \omega^2 - 2i\gamma\omega)^2}. \quad (4.14)$$

By similar means, the linear susceptibility can be determined,

$$\chi^{(1)}(\omega) = \frac{N(e^2/m_0)}{(\omega_0^2 - \omega^2 - 2i\gamma\omega)}. \quad (4.15)$$

By combining Eqs. (4.14) and (4.15), we can see that the second-order susceptibility $\chi^{(2)}$ depends on the linear susceptibility $\chi^{(1)}$ at the fundamental and second harmonic frequency,

$$\chi^{(2)}(2\omega, \omega, \omega) = \frac{m_0 a}{N^2 e^3} [\chi^{(1)}(2\omega)] [\chi^{(1)}(\omega)]^2. \quad (4.16)$$

Indeed, it is generally observed that materials with a large linear dielectric constant tend to also exhibit a strong nonlinear optical response (102).

The intensity (field magnitude squared) of far-field radiation observed at the second harmonic frequency varies quadratically with the incident light intensity through the relationship in Eq. (4.5),

$$\begin{aligned} I^{(2\omega)} &\propto |P^{(2)}|^2 \\ &\propto |\chi^{(2)} E^{(\omega)} E^{(\omega)}|^2. \\ &\propto |\chi^{(2)}|^2 (I^{(\omega)})^2 \end{aligned} \quad (4.17)$$

However, when SHG is observed in reflection off of an interface between two dielectrics, the Fresnel reflectivity at the fundamental and second-harmonic frequencies must also be considered. Bloembergen & Pershan (103) showed that the reflected SHG field intensity varies with the angle of laser incidence θ_i through linear (L) and nonlinear (NL) Fresnel factors,

$$I^{(2\omega)} \propto |\chi^{(2)}|^2 (I^{(\omega)})^2 |F_{\text{NL}}(\theta_i, n_{1,2}(\omega), n_{1,2}(2\omega))|^2 |F_{\text{L}}(\theta_i, n_{1,2}(\omega))|^4, \quad (4.18)$$

where $n_{1,2}(\omega)$ and $n_{1,2}(2\omega)$ represent the refractive indices on each side of the interface at the fundamental and second harmonic frequencies. Expressions for F_{L} and F_{NL} can be obtained from (104). The importance of Eq. (4.18) lies in the ability to separate contributions to the experimental observable, $I^{(2\omega)}$. Thus, real changes in $\chi^{(2)}$ can be distinguished from variations in the refractive index due to, for example, changes in temperature or the number of free charge carriers.

4.2.2. Phase-matching

In Section 4.2.1, we saw that there are many ways in which three photons can add or subtract from each other in an energy-conserving way (see Eq. (4.7)). However, usually only one of these processes is observed for any given geometry (i.e. incident polarizations, wave vectors, and crystal orientation). The reason for this has to do with conservation of momentum for the photons involved. In nonlinear optics the conservation-of-momentum condition is referred to as *phase-matching* because the electromagnetic waves involved must have a fixed phase relationship in order for the

nonlinear conversion process to proceed to any appreciable extent. The generalized perfect phase-matching condition is,

$$\Delta k = 0. \quad (4.19)$$

For SFG ($\omega_3 = \omega_1 + \omega_2$), we write,

$$\Delta k = k_1 + k_2 - k_3 = 0. \quad (4.20)$$

With collinear beams, this expression reduces to,

$$n_1 \omega_1 + n_2 \omega_2 = n_3 \omega_3. \quad (4.21)$$

For SHG with collinear beams, the condition can be simplified even more,

$$n(\omega) = n(2\omega). \quad (4.22)$$

Clearly, perfect phase-matching cannot occur in optically isotropic materials because of normal dispersion: $n(2\omega)$ will always be larger than $n(\omega)$! However, the condition (4.22) can be achieved when the fundamental and second-harmonic beams are orthogonally polarized in a birefringent crystal.

When the perfect phase-matching condition is not met, nonlinear conversion is still possible but proceeds with reduced efficiency. As two collinear beams ω_1 & ω_2 pass through a nonlinear medium with propagation length L , the generation of the sum-frequency $\omega_3 = \omega_1 + \omega_2$ occurs (in the limit of undepleted beams) as,

$$I^{(\omega_3)} \propto L^2 \text{sinc}^2(L/L_c), \quad (4.23)$$

where L_c is the *coherence length* of the interaction, defined as,

$$L_c \equiv \frac{2}{\Delta k}. \quad (4.24)$$

As the phase-mismatch Δk increases, the coherence length L_c decreases and the nonlinear conversion process becomes less efficient. As shown mathematically in Eq. (4.23) and graphically in Figure X, the coherence length should be much larger than the interaction length, $L/L_c \ll \pi$, for nonlinear conversion to proceed efficiently. Additionally, the expression in Eq. (4.23) confirms our intuitively expected result that the nonlinear

conversion efficiency scales with the square of interaction length, since χ^2 is proportional to the atomic number density, N , and $I^{(2\omega)} \propto |\chi^{(2)}|^2$.

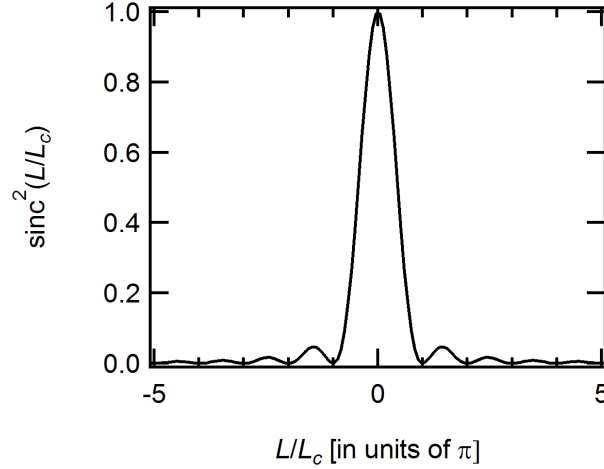


Figure 4.3 The effect of phase mismatch, Δk , on the efficiency of SHG. The coherence length, $L_c = 2/\Delta k$, should be much larger than the interaction length, L , for nonlinear conversion to proceed efficiently.

4.2.3. Quantum mechanical description and the effect of resonances

In Section 4.2.1, we described the nonlinear optical response of a material far from resonance in terms of the classical motion of electrons in an anharmonic potential. In this section, we consider the behavior of the nonlinear optical interaction when the frequency of the incident radiation field is near a characteristic electronic or vibrational frequency of the nonlinear medium. This is equivalent to the case when one or both of the dashed lines in Figure 4.1 represent real electronic or vibrational energy levels of the system.

Following Boyd (99), our objective in this section is to find an expression for the electric polarization $\mathbf{P}(\omega)$, or equivalently, the expectation value of the induced dipole moment per unit volume,

$$\mathbf{P}(\omega) = N \langle \boldsymbol{\mu}(\omega) \rangle, \quad (4.25)$$

where N is the atomic number density and $\boldsymbol{\mu} = -e\mathbf{r}$ is the electric dipole moment operator. This is most easily accomplished within the density matrix formalism of

quantum mechanics. The density matrix, $\rho(t)$, is an n by m square matrix with as many rows and columns as there are energy levels in the system. The diagonal elements ρ_{nn} give the probability of finding the system in energy eigenstate n . The off-diagonal elements ρ_{nm} represent the coherence between eigenstates n and m . In equilibrium, only the diagonal elements of the density matrix are non-zero. However, when a perturbation is applied to the system, off-diagonal elements may become non-zero and transitions among energy levels can occur. The density matrix is useful for calculating the (ensemble average) expectation value of an observable quantity $\mathbf{M}$,

$$\langle \mathbf{M} \rangle = \sum_{n,m} \rho_{nm} \mathbf{M}_{nm} = \sum_n \left(\hat{\rho} \hat{\mathbf{M}} \right)_{nn} \equiv \text{tr} \left(\hat{\rho} \hat{\mathbf{M}} \right), \quad (4.26)$$

where the operation on the right is the trace of the operator product. The off-diagonal elements of $\rho(t)$, which are required for evaluating Eq. (4.26), are found by solving the density matrix equation of motion,

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm} (\rho_{nm} - \rho_{nm}^{\text{eq}}), \quad (4.27)$$

where $[\hat{H}, \hat{\rho}] \equiv \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$ is the commutator, γ_{nm} is the dephasing rate between states n and m , and (as stated above) $\rho_{nm}^{\text{eq}} = 0$ for $n \neq m$. Equation (4.27) must be solved by perturbative expansion, yielding a solution of the form,

$$\rho_{nm} = \rho_{nm}^{(0)} + \lambda \rho_{nm}^{(1)} + \lambda^2 \rho_{nm}^{(2)} + \dots \quad (4.28)$$

The Hamiltonian is split into two parts,

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (4.29)$$

where H_0 represents the Hamiltonian of the free system and $\hat{V}$ represents the energy of interaction of the system with the perturbation. Within the electric dipole approximation, we express $\hat{V}$ as,

$$\hat{V}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t), \quad (4.30)$$

where $\boldsymbol{\mu} = -e\mathbf{r}$ is the electric dipole moment operator. The q^{th} -order solution to Eq. (4.27) is then,

$$\rho_{nm}^{(q)}(t) = \int_{-\infty}^t \frac{-i}{\hbar} \left[\hat{V}(t'), \rho_{nm}^{(q-1)} \right] e^{(i\omega_{nm} + \gamma_{nm})(t'-t)} dt', \quad (4.31)$$

where,

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar}. \quad (4.32)$$

The zeroth-order solution is the equilibrium density matrix in the absence of any perturbation,

$$\rho_{nm}^{(0)} = \rho_{nm}^{(\text{eq})}. \quad (4.33)$$

We can now express the linear response of the system in terms of the equilibrium occupation probability for each energy level in the system and the transition dipole moment coupling each pair of n, m energy levels,

$$\begin{aligned} P_i^{(1)}(\omega) &= N \langle \mu_i(\omega) \rangle \\ &= \sum_j \chi_{ij}^{(1)}(\omega) E_j(\omega), \end{aligned} \quad (4.34)$$

where,

$$\chi_{ij}^{(1)}(\omega) = \frac{N}{\hbar} \sum_{n,m} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega) - i\gamma_{nm}}. \quad (4.35)$$

We can see that the linear susceptibility is proportional to the population difference between states m and n . $\chi^{(1)}$ takes on negative values when there is a population inversion, and it vanishes entirely when the populations of states m and n are equal. Another way of stating this result is to say that the induced linear polarization in the excited state (n) is 180° out-of-phase with the ground state (m), resulting in destructive interference between these two contributions to the total linear susceptibility.

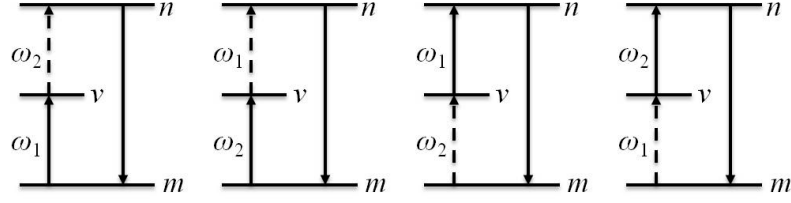


Figure 4.4 The four resonance conditions described by Eq. (4.37). All four terms contain a dependence on two-photon resonance between energy levels n and m . Each term differs in the one-photon resonance condition, indicated by the solid arrow.

Similarly, we can use the density matrix to determine the second-order nonlinear polarization. We proceed as before, plugging the solution for $\rho_{nm}^{(1)}$ (which we used to obtain (4.35)) into Eq. (4.31) to obtain a final expression in terms of only the equilibrium occupation probabilities $\rho_{nn}^{(0)}$. However, there is now a third intermediate energy level, v , which also participates in the transition. The second-order nonlinear polarization is then (99),

$$P_i^{(2)}(\omega_1 + \omega_2) = N \langle \mu_i(\omega_1 + \omega_2) \rangle = \sum_{j,k} \sum_{1,2} \chi_{ijk}^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2), \quad (4.36)$$

where,

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = & \frac{N}{2\hbar^2} \\ & \times \sum_{m,v,n} \left\{ (\rho_{mm}^{(0)} - \rho_{vv}^{(0)}) \left[\frac{\mu_{mn}^i \mu_{nv}^j \mu_{vm}^k}{[(\omega_{nm} - \omega_1 - \omega_2) - i\gamma_{nm}][(\omega_{vm} - \omega_1) - i\gamma_{vm}]} \right. \right. \\ & + \left. \frac{\mu_{mn}^i \mu_{nv}^k \mu_{vm}^j}{[(\omega_{nm} - \omega_1 - \omega_2) - i\gamma_{nm}][(\omega_{vm} - \omega_2) - i\gamma_{vm}]} \right] \\ & - (\rho_{vv}^{(0)} - \rho_{nn}^{(0)}) \left[\frac{\mu_{mn}^i \mu_{vm}^j \mu_{nv}^k}{[(\omega_{nm} - \omega_1 - \omega_2) - i\gamma_{nm}][(\omega_{nv} - \omega_1) - i\gamma_{nv}]} \right. \\ & + \left. \left. \frac{\mu_{mn}^i \mu_{vm}^k \mu_{nv}^j}{[(\omega_{nm} - \omega_1 - \omega_2) - i\gamma_{nm}][(\omega_{nv} - \omega_2) - i\gamma_{nv}]} \right] \right\} \end{aligned} \quad (4.37)$$

The meaning of these four terms is illustrated in Figure 4.4. All four terms contain a dependence on the two-photon resonance condition $\omega_{nm} = \omega_1 + \omega_2$ as well as a one-photon resonance condition. Interestingly, the population differences appearing in Eq. (4.37) are always between two levels separated by a one-photon resonance. For the case of SHG, the frequencies ω_1 and ω_2 are the same ($\omega_1 = \omega_2$) and the indices j and k are interchangeable. In this case, the first two terms are identical to each other and the last two terms are identical to each other. Eq. (4.37) also tells us that in order for an optical resonance to contribute to $\chi^{(2)}$, it must be *dipole-allowed*. Thus, intraband transitions and interband transitions in indirect semiconductors will not contribute a resonance enhancement to SHG.

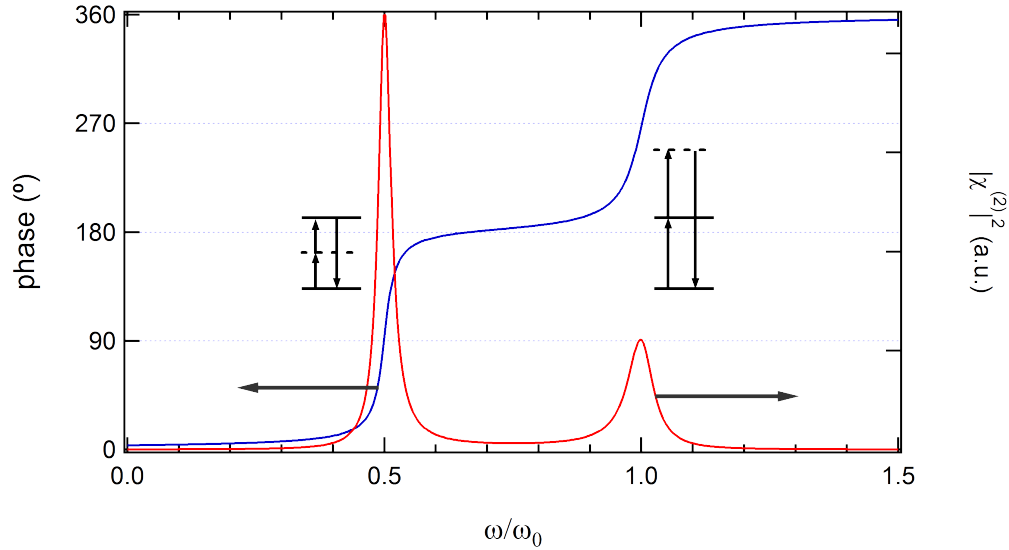


Figure 4.5 Behavior of the second-order nonlinear susceptibility as the frequency of the incident radiation field is tuned across a single resonance ω_0 with dephasing rate $\gamma_0/\omega_0 = 0.03$. When $\omega/\omega_0 = 0.5$, the incident field is two-photon resonant; when $\omega/\omega_0 = 1.0$, the incident field is one-photon resonant. The resonances have Lorentzian line-shapes and follow dipole selection rules. The two-photon resonance is narrower because the detuning of ω is faster for the condition $2\omega = \omega_0$. On-resonance, the induced polarization is phase-shifted by $\pm \pi/2$ radians relative to the non-resonant field.

An important consequence of resonance is the phase-shift of the induced polarization $P(2\omega)$ relative to the incident field $E(\omega)$. Far from resonance, $P(2\omega)$ is in-phase with $E(\omega)$; near a resonance, $P(2\omega)$ lags behind $E(\omega)$ by an amount,

$$\theta = \tan^{-1} \left[\text{Im}(\chi^{(2)}) / \text{Re}(\chi^{(2)}) \right]. \quad (4.38)$$

In Figure 4.5, the frequency-dependence of the phase-lag θ is plotted alongside $|\chi^{(2)}|^2$ for SHG in a two-level system with a single resonant frequency ω_0 . On-resonance, $P(2\omega)$ is phase-shifted by an amount $\pm \pi/2$. The consideration of phase is practically important when there are two separate and simultaneous contributions to the observed SHG intensity. If one of these contributions is resonant (such as the nonlinear polarizability of a molecular adsorbate) and one is non-resonant (such as the contribution from a semiconducting or insulating substrate), then the resonant field will be phase-shifted by an amount $\pm \pi/2$ relative to the non-resonant field.* As shown in Figure 4.6, the two fields interfere constructively but they do not add linearly. It is possible to decompose the experimentally-measured total field amplitude into its resonant and non-resonant components by measuring the phase of the SHG signal (from the system of interest) relative to a non-resonant reference wave (from, for example, a BBO crystal). A detailed methodology for this procedure is outlined in (105).

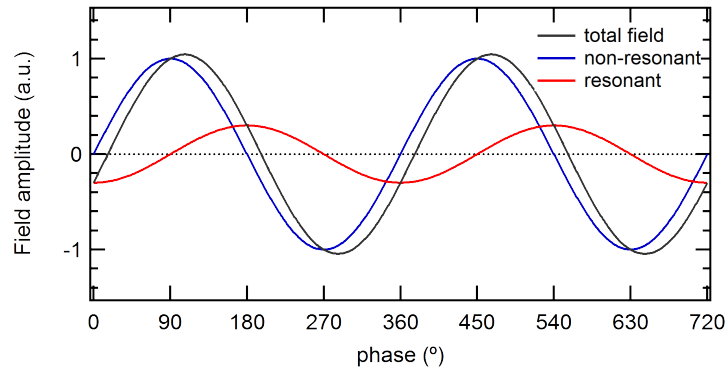


Figure 4.6 Simulated time-varying fields of the non-resonant SHG field and the 90°-phase-shifted resonant SHG field for the hypothetical case $E_{\text{NR}}(2\omega) = 2.5 * E_{\text{R}}(2\omega)$. The total field at frequency 2ω is the sum of both contributions and has a phase intermediate to the two that depends on the relative amplitudes of the resonant and non-resonant components. The resonant and non-resonant contributions interfere constructively, but they do not add linearly. The total SHG field amplitude is maximized when $E_{\text{NR}} = E_{\text{R}} = E$; in that case, $E_{\text{tot}} = \sqrt{2} * E$.

* An exception to this is the rare case of a three-level system when one- and two-photon resonances occur simultaneously. In this case, the phase shift is $\pm \pi$ and the resonant and non-resonant contributions to the total SHG field interfere destructively.

4.2.4. Symmetry considerations

If a semiconductor or insulating crystal possesses inversion symmetry – that is to say it is *centrosymmetric* – then the potential felt by an electron moving in the crystal must be isotropic. This requirement is expressed mathematically as $U(x) = U(-x)$, and consequently, only even-order terms in x are allowed in the potential energy function of Eq. (4.9). Therefore, the anharmonicity parameter a vanishes ($a = 0$), and the second-order nonlinear susceptibility $\chi^{(2)}$ disappears for centrosymmetric media. This point is more generally explained via the polarization,

$$\mathbf{P} = \varepsilon_0 \left[\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \chi^{(4)} \mathbf{E}^4 + \dots \right]. \quad (4.39)$$

If the medium possesses inversion symmetry, then the sign of the polarization must change with the sign of the electric field. If we take $\mathbf{E}$ into $-\mathbf{E}$, then Eq. (4.39) becomes,

$$-\mathbf{P} = \varepsilon_0 \left[-\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 - \chi^{(3)} \mathbf{E}^3 + \chi^{(4)} \mathbf{E}^4 - \dots \right]. \quad (4.40)$$

We see that only odd-order terms in Eq. (4.40) have changed their sign. Thus, in order for Eq. (4.40) to make physical sense, even-order terms must vanish completely,

$$\chi^{(2)} = \chi^{(4)} = \chi^{(2n)} = 0. \quad (4.41)$$

This means that, *within the electric-dipole approximation*, SHG will not occur in the bulk of centrosymmetric media such as gases, liquids, and amorphous or glassy materials, or within certain centrosymmetric crystalline materials, including Si, Ge, and TiO₂. Electric-quadrupole and magnetic-dipole contributions to $\mathbf{P}^{(2)}$ do not vanish, but these elements are often negligible.

When describing the second-order nonlinear optical response far from resonance, the medium is usually taken to be lossless and dispersionless (99). Under these circumstances, it is customary to use the notation d_{ijk} instead of $\chi_{ijk}^{(2)}$, where d_{ijk} is *frequency-independent* and is defined through the relation,

$$P_i = 2d_{ijk} E_j E_k. \quad (4.42)$$

Here, d_{ijk} represents the element in the 27-term triad (third-rank tensor) relating the i -directed polarization of the medium to the j - and k -polarized incident fields. Since there is

no physical significance to exchanging E_j and E_k in (4.42), the subscripts kj are usually replaced by a single symbol according to the *piezoelectric contraction* (106),

$$\begin{aligned} xx = 1 \quad yy = 2 \quad zz = 3 \\ yz = zy = 4 \quad xz = zx = 5 \quad xy = yx = 6 \end{aligned}$$

The resulting d_{ij} tensor can be expressed as a 3x6 matrix that operates on the $\mathbf{EE}$ vector to yield the polarization $\mathbf{P}$,

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = 2 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_z E_y \\ 2E_z E_x \\ 2E_x E_y \end{bmatrix}. \quad (4.43)$$

For a centrosymmetric medium, all elements of the d_{ij} matrix vanish. For the non-centrosymmetric crystal systems, the non-vanishing elements of the d_{ij} matrix are determined according to point-group symmetry. For instance, ZnO crystallizes in the wurtzite structure, which has $6mm$ point-group symmetry. Taking the z -direction to be the principle optical axis (the c -axis), the corresponding d_{ij} matrix for ZnO is (106),

$$d^{(6mm)} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix}. \quad (4.44)$$

Further, $d_{15} = d_{24}$ and $d_{31} = d_{32}$. Thus, symmetry has reduced the 27-component second-order nonlinear susceptibility to only three distinct, non-zero terms. The form of $d^{(6mm)}$ also displays some intuitively expected results. Since it is the polarity/anisotropy of the z -axis (c -axis) in ZnO that is responsible for broken inversion symmetry, it is not surprising that the x and y axes (or any two directions orthogonal to the c -axis) are completely interchangeable. It is also not surprising to find a non-zero $d_{33}=d_{zzz}$ component (all electric fields polarized along the c -axis, which in ZnO is found to be the largest of the three non-zero terms (106).

4.3. SHG at surfaces

4.3.1. Second-order nonlinear interactions at surfaces

We have just seen that second-order nonlinear optical processes are forbidden in the bulk of centrosymmetric media. However, at surfaces, grain boundaries, and interfaces inversion symmetry is broken and second-order nonlinear optical processes become dipole-allowed. Interfacial discontinuities occur over a thickness of only a few atomic layers, but can contribute sizably to the total nonlinear susceptibility. The near-surface region is usually modeled as an infinitesimally thin film, to which a local nonlinear susceptibility $\chi_{ijk}^{(2)surf}$ is assigned (107). The total second harmonic response of an interface includes the surface dipole term and the bulk dipole term (in non-centrosymmetric media), as well as a bulk non-local term which contains contributions from both the electric quadrupole and magnetic dipole response. The bulk non-local response is non-local in the sense that it depends not only on the value $\mathbf{E}(\mathbf{r})$ at a specific point in space, but also on the value $\mathbf{E}(\mathbf{r})$ in other locations within the crystal through the term $\nabla \mathbf{E}$. For SHG in reflection off an interface, the complete form of the second-order polarization is given by (108),

$$P_i^{(2)}(2\omega) = \chi_{ijk}^{(2)bd} E_j(\omega) E_k(\omega) + \chi_{ijkl}^{(2)bnl} E_j(\omega) \nabla_k E_l(\omega) + \chi_{ijk}^{(2)surf} E_j(\omega) E_k(\omega), \quad (4.45)$$

where the superscripts *bd*, *bnl*, and *surf* stand for *bulk dipole*, *bulk non-local*, and *surface*, respectively. Again, the first term (*bd*) vanishes in centrosymmetric materials. The three nonlinear susceptibility terms $\chi^{(2)}$ in (4.45) contain, in principle, different elements. For instance, in ZnO the *bd* and *bnl* terms reflect the hexagonal symmetry of the bulk lattice, whereas $\chi_{ijk}^{(2)surf}$ may reflect the rectangular symmetry of the (10 $\bar{1}$ 0) surface.

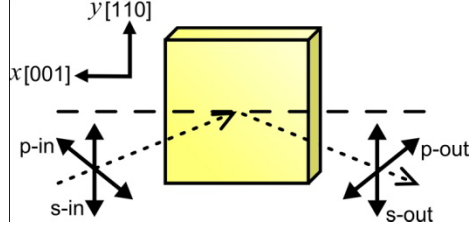


Figure 4.7 Definition of the coordinate system used to describe the nonlinear susceptibility of the TiO₂ rutile(110) surface. The x-coordinate runs along the [001] direction in the surface plane; the y-coordinate runs along the $[\bar{1}10]$ direction in the surface plane; the z-coordinate is the surface-normal $[110]$ direction.

When dealing with the surface nonlinear susceptibility, one often describes the elements of the susceptibility matrix in terms of a coordinate system defined relative to the surface normal direction. In this coordinate system, the z-axis is the surface normal and x and y lie in the surface plane. The $\chi_{zzz}^{(2)surf}$ element of the surface nonlinear susceptibility tensor, which is derived from interfacial discontinuity in the surface-normal direction, is often the strongest contributor (101). The term $\chi_{zzz}^{(2)surf}$ is not to be confused with $\chi_{zzz}^{(2)bd}$; these contributions differ in their physical meaning and do not even reflect the same crystal direction since they are defined within completely different coordinate systems. For SHG at an azimuthally isotropic interface containing an infinite number of mirror planes perpendicular to the surface ($C_{\infty v}$ symmetry) – such as a liquid or amorphous glass surface – there are three independent nonzero terms in the surface nonlinear susceptibility tensor. Following the piezoelectric contraction defined earlier (Eq. (4.43)), we write (109),

$$\chi_{ijk}^{(2)surf} \{C_{\infty v}\} = \begin{bmatrix} 0 & 0 & 0 & 0 & \chi_3 & 0 \\ 0 & 0 & 0 & \chi_3 & 0 & 0 \\ \chi_2 & \chi_2 & \chi_1 & 0 & 0 & 0 \end{bmatrix}, \quad (4.46)$$

where $\chi_2 = \chi_{zzx} = \chi_{zyy}$, $\chi_1 = \chi_{zzz}$, and $\chi_3 = \chi_{yyz} = \chi_{zyz} = \chi_{xxz} = \chi_{xzx}$. Surface susceptibility tensors can also be defined for each exposed facet of a centrosymmetric crystal. Kobayashi *et al.* (110)(111) experimentally determined the non-vanishing components of $\chi_{ijk}^{(2)surf}$ for the (110) surface of rutile TiO₂. Defining their surface coordinate system as shown in Figure 4.7, they found three non-vanishing elements,

$$\chi_{ijk}^{(2)surf} \{ \text{TiO}_2(110) \} = \begin{bmatrix} 0 & 0 & 0 & 0 & \chi_{xxz} = \chi_{xzx} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{bmatrix}, \quad (4.47)$$

with $\chi_{xxz} = \chi_{xzx}$ being the largest in magnitude and originating from hyperpolarizability of the Ti-O zigzag bonds running along the [001] direction (111).

Typically, the phase-matching considerations presented in Section 4.2.2 are not of concern when discussing surface SHG because the interaction volume is so small (a few atomic layers thick, with length comparable to the wavelength of light) compared to the coherence length, even for highly dispersive materials like TiO_2 . However, a peculiar situation can arise when the fundamental beam approaches an interface from within the medium with larger refractive index. As the angle-of-incidence (defined with respect to the surface normal) is increased, the transmitted wave leaves the other side of the interface at shallower and shallower angles. At the critical angle, the fundamental beam is totally reflected back into the high-index medium; however, there is also an imaginary component to the field – the “transmitted” wave – which propagates along the interface completely within the surface plane. The real internally reflected beam undergoes nonlinear conversion as if it has the same substantially enhanced interaction length, L , as the imaginary wave propagating along the surface. If the fundamental and second harmonic fields of the imaginary wave are phase-matched in the surface plane, then the SHG generated in reflection can be many orders of magnitude larger than the SHG intensity that would be obtained in transmission or reflection or even total internal reflection at other angles, as demonstrated originally by Bloembergen & Lee (104) and re-produced in Figure 4.8. Even if the phase-matching is poor, total internal reflection at the critical angle can still offer greatly enhanced SHG intensities due simply to the long effective interaction length (remember that $I^{(2\omega)} \propto L^2$). Consequently, it is advantageous from a practical spectroscopy perspective (signal-to-noise ratio improves as the square root of signal intensity) to reflect off of an interface from the high-index side. This trick is commonly employed by those studying the nonlinear optics of liquid-liquid or liquid-air interfaces (109), but is not always possible at interfaces with semiconductor or metal samples because the solid often absorbs strongly at operating wavelengths.

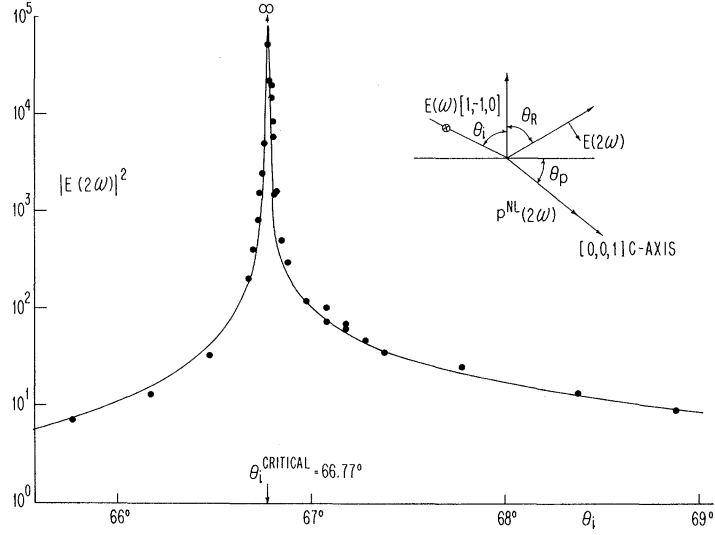


Figure 4.8 From Fig. 2 in Bloembergen & Lee (104). At the critical angle for total internal reflection, SHG can be enhanced by many orders of magnitude. The data here were collected by approaching the surface of a KH_2PO_4 crystal from within a high-index liquid, 1-bromonaphthalene, with fundamental polarization and crystal orientation set for optimum phase matching in the surface plane.

4.3.2. Electric-field-induced second harmonic response (EFISH)

A particularly useful property of the surface second harmonic response is its sensitivity to interfacial electric fields. When an electron transfers from an adsorbate (such as a molecular chromophores or quantum dot) to a bulk semiconductor substrate (such as TiO_2), it leaves behind a positively charged electron vacancy and carries with it a negative charge. This interfacial charge separation establishes an electric field in the surface-normal direction as shown in Figure 4.9, which can be detected with SHG. This unique capability of SHG to detect interfacial electric fields offers the ability to follow the evolving charge separation process in time. Indeed, SHG has been used to follow interfacial fields at metal/electrolyte interfaces (86) and at buried interfaces in field-effect transistors (84).

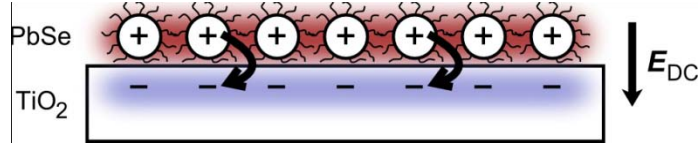


Figure 4.9 Illustration of interfacial charge separation at a quantum dot (PbSe) – semiconductor (TiO₂) interface. Separation of charge across the interface established an electric field oriented in the surface-normal direction that can be detected with SHG.

The electric field-induced second harmonic (EFISH) response at the surface of a centrosymmetric material was first discovered by Lee, Chang, & Bloembergen in 1967 (112). SHG, in general, is highly sensitive to slowly varying or dc electric fields because of the potential for such fields to perturb the symmetry of the medium (108). Phenomenologically, the EFISH response is treated as a four-wave mixing process modulated by an effective fourth-rank nonlinear susceptibility tensor $\chi_{eff}^{(3)}(2\omega = \omega + \omega + 0)$ that contains contributions from both the surface and the bulk (84, 108). The total second-order nonlinear (NL) polarization within the semiconductor given by Eq. (4.45) now includes an extra term, $\chi_{eff}^{(3)} : \mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(0)$. The total nonlinear polarization is then,

$$\begin{aligned} \mathbf{P}^{NL}(2\omega) &= \mathbf{P}^{bd}(2\omega) + \mathbf{P}^{bnl}(2\omega) + \mathbf{P}^{surf}(2\omega) + \mathbf{P}^{EFISH}(2\omega) \\ &= \epsilon_0 \left[\chi_{bd}^{(2)}(2\omega) : \mathbf{E}(\omega)\mathbf{E}(\omega) + \chi_{bnl}^{(2)} : \mathbf{E}(\omega)\nabla\mathbf{E}(\omega) + \dots \right], \end{aligned} \quad (4.48)$$

$$= \epsilon_0 \left[\chi_{surf}^{(2)}(2\omega) : \mathbf{E}(\omega)\mathbf{E}(\omega) + \chi_{eff}^{(3)} : \mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(0) \right]$$

where the superscripts *bd*, *bnl*, and *surf* refer to bulk dipole, bulk non-local, and surface dipole contributions, respectively. For centrosymmetric media such as rutile TiO₂, the *bd* term vanishes due to inversion symmetry. In the absence of a dc electric field, the *bnl* and *surf* contributions may be of comparable magnitude, but can be separated by careful control of geometry and polarization (102). Such work has been done, for example, for the rutile (110) surface of TiO₂ and it was determined that the surface dipole contribution dominates the SHG response – particularly for the geometry depicted in Figure 4.7 with *p*-polarized light (111). In this case, the total nonlinear polarization reduces to surface dipole and EFISH contributions, $\mathbf{P}^{NL}(2\omega) = \mathbf{P}^{surf}(2\omega) + \mathbf{P}^{EFISH}(2\omega)$.

The reflected SHG field can be divided into the sum of background (surface dipole response when $E^{(dc)} = 0$) and EFISH contributions (113),

$$\begin{aligned} \mathbf{E}^{(2\omega)} &= \mathbf{E}_0^{(2\omega)} + \mathbf{E}_{EFISH}^{(2\omega)} \\ &\propto \chi_{surf}^{(2)} (E^{(dc)} = 0) : \mathbf{E}^{(\omega)} \mathbf{E}^{(\omega)} + \chi_{eff}^{(3)} : \mathbf{E}^{(\omega)} \mathbf{E}^{(\omega)} \mathbf{E}^{(dc)}. \end{aligned} \quad (4.49)$$

For the purpose of clarity, we have neglected the linear and nonlinear Fresnel factors. The experimentally observed SHG intensity is,

$$\begin{aligned} I^{(2\omega)} &= \left| \mathbf{E}_0^{(2\omega)} + \mathbf{E}_{EFISH}^{(2\omega)} \right|^2 \\ &= \alpha \left| \chi_{surf}^{(2)} \right|^2 \left(I^{(\omega)} \right)^2 + \beta \left(\chi_{surf}^{(2)*} \chi_{eff}^{(3)} + \chi_{surf}^{(2)} \chi_{eff}^{(3)*} \right) \left(I^{(\omega)} \right)^2 E^{(dc)} + \gamma \left| \chi_{eff}^{(3)} \right|^2 \left(I^{(\omega)} \right)^2 \left(E^{(dc)} \right)^2 \end{aligned} \quad (4.50)$$

where α , β , and γ are constants that depend on geometry, χ^* is the complex conjugate of χ , and $I^{(\omega)}$ is the incident laser field intensity. For the case of rutile TiO_2 (110), which exhibits a large background SHG signal in the absence of an external electric field under the geometry depicted in Figure 4.7 (i.e. $\chi_{surf}^{(2)} \square \chi_{eff}^{(3)}$), the third term in Eq. (4.50) can be neglected. Under such conditions, the observed SHG intensity varies linearly with the electric field strength,

$$\begin{aligned} I^{(2\omega)} &\approx I_0^{(2\omega)} + \Delta I^{(2\omega)} \\ &\approx I_0^{(2\omega)} + \eta \left(I^{(\omega)} \right)^2 E^{(dc)}, \end{aligned} \quad (4.51)$$

with η containing nonlinear susceptibilities and geometric factors. If we take the charge-separated interface in Figure 4.9 to be a parallel plate capacitor, then the electric field strength at the interface due to charge separation is,

$$\begin{aligned} E^{(dc)} &\equiv E^{sep} = \frac{1}{\epsilon_r \epsilon_o} \frac{2Q^{sep}}{A}, \\ &\propto Q^{sep} \end{aligned} \quad (4.52)$$

where Q^{sep} is the amount of separated charge. As a result, we expect the EFISH signal to scale approximately linearly with Q^{sep} ,

$$\Delta I^{(2\omega)} \propto Q^{sep}. \quad (4.53)$$

Consequently, electron transfer dynamics can be extracted directly from the time-resolved SHG data.

4.4. Experimental implementation

4.4.1. Optical layout

The TR-SHG setup built for studying interfacial electron transfer is illustrated schematically in Figure 4.10. A home-built 78 MHz Ti:sapphire oscillator (830 nm, 35 fs, 50 nm bandwidth at FWHM, 200 mW) with peak-to-peak stability better than 0.01% seeds a regenerative amplifier operated at 250 kHz (Coherent RegA 9050). The output of the amplifier is compressed (810 nm, 50 fs, 30 nm bandwidth at FWHM, $\pm 0.1\%$ peak-to-peak), attenuated, and then split into two equal intensity beams. One beam (the pump) passes through a variable-length delay line before recombining with the other beam (the probe) on the sample surface. The polarization state of each beam is independently controlled with quartz waveplates and long-wave pass filters are placed immediately in front of the cryostat (in which the sample is mounted) to remove any residual 405 nm light generated in the waveplates or other optical components. Typically, the pump and probe beams are cross-polarized to avoid coherent artifacts when the two pulses are overlapped in time. The uncoated 1.5 mm thick cryostat windows are made from Suprasil II, a high-quality amorphous silica glass transparent at 405 nm and exhibiting negligible second order nonlinear susceptibility at normal incidence. The pump and probe beams are softly focused non-collinearly at a mutual angle of $\sim 3^\circ$ onto the sample surface. The projection of the beam on the sample at 45° incidence is a $260\text{ }\mu\text{m} \times 360\text{ }\mu\text{m}$ ellipse, as measured by the knife-edge technique. Typically, the laser power is kept sufficiently low to maintain a spatially averaged fluence of less than 1 mJ/cm^2 for both pump and probe pulses, but higher fluencies are easily attainable. The entire laser system is housed within a light-tight enclosure to avoid detection of spurious 405nm light from elsewhere in the room.

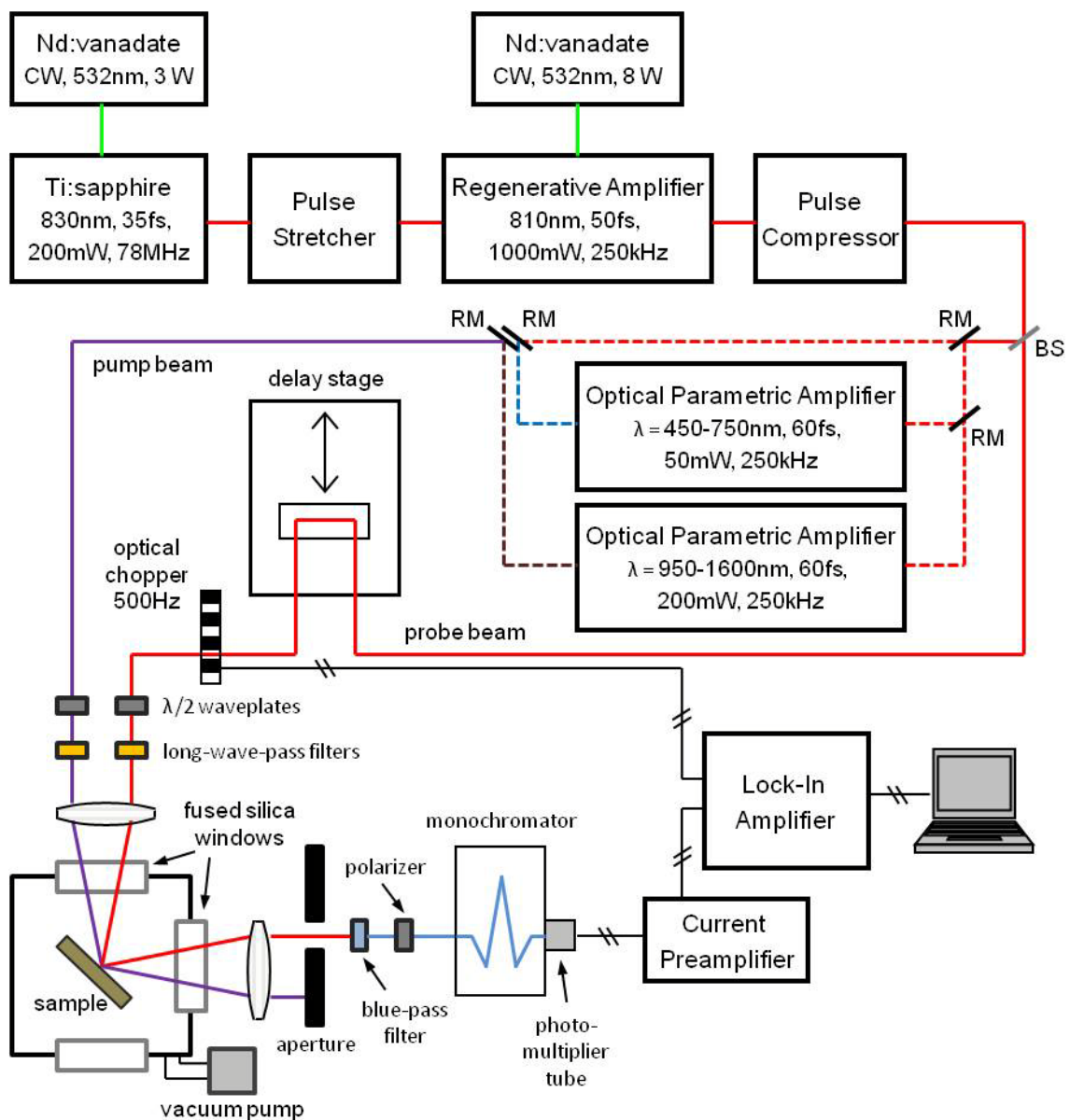


Figure 4.10 Schematic of the optical setup for time-resolved second harmonic generation (TR-SHG) built by the author. Colored lines indicate the path of laser light; dashed lines are optional paths the beams may take in various embodiments of the experimental setup; the purple line represents any arbitrary wavelength of light. Thin black lines with hashes denote electronic data pathways. The sample is housed within a portable controlled-atmosphere cryostat (Janis ST-300) and laser light is introduced through high-quality fused silica windows with negligible nonlinear susceptibility. $\lambda/2$ waveplates control the linear polarization state of the input beams and a Glan-Thompson polarizing prism selects which polarization of the SHG signal is detected. SHG photon detection is accomplished with a photomultiplier tube (Hamamatsu R4220P) whose output is fed through a current preamplifier to a lock-in amplifier that is frequency- and phase-locked to an optical chopper placed in the probe beam path. A personal computer records the data and coordinates movement of the delay stage. BS=beamsplitter; RM=removable mirror.

For two-color measurements (variable wavelength pump, 810 nm probe), a portion of the amplifier output is sent to a double-pass optical parametric amplifier (Coherent OPA 9850 or 9450) for conversion to shorter wavelengths in the visible (OPA 9450) or longer wavelengths in the near- or mid-infrared (OPA 9850). The remaining 810 nm light is used for the probe beam, as above.

By conservation of momentum, second harmonic (SH) light generated from the sample surface is collinear with each reflected beam. When pump and probe pulses are overlapped on the sample in space and time, a third nonlinear signal at the sum of the two frequencies (sum-frequency, SF) is generated at a wave vector in between the two reflected SH signals, as shown in . This SF signal is equivalent to the cross-correlation of the pump and probe laser pulses and provides a convenient mechanism for optimizing spatial overlap, minimizing pulse width, and calibrating “time zero” at the sample surface.

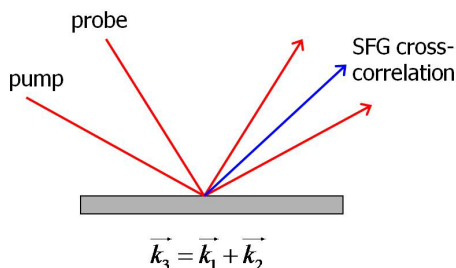


Figure 4.11 When the pump and probe pulses are overlapped on the sample surface in space and time, photons from one beam can combine with photons from the other to generate new photons at the sum frequency. By conservation of momentum, these sum-frequency photons reflect off the surface at a wave vector in between the two individually reflected beam. The temporal profile of this sum-frequency generation (SFG) signal is equivalent to the cross-correlation of the two beams and offers a convenient mechanism for optimizing spatial overlap and time resolution.

4.4.2. Data acquisition

For the laser power and focusing conditions typically used, the reflected fundamental light is $\sim 10^{10}$ times more intense than the SH light propagating collinearly with it. We use a combination of dichroic mirrors (Layertec), color glass filters (CVI Melles Griot), dispersion gratings (Oriel Cornerstone 130 monochromator), and a large-work function photomultiplier tube (Hamamatsu R4220P) to achieve the desired spectral filtering. A Glan-Thompson polarizing prism is used to select only the p- or s-polarized

component of the reflected SH light. The signal from the PMT is amplified and fed to a lock-in amplifier (Stanford Research SR850), which is phase- and frequency-locked with a 500 Hz optical chopper placed in the probe beam path (to distinguish the SH light associated with the probe beam from ambient 405 nm light or scattered SH light associated with the pump). A desktop computer records data from the lock-in amplifier and controls the motorized linear delay stage (Newport – 0.1 μm per step/0.67 fs time resolution). Because of the excellent stability of the laser system ($\pm 0.1\%$ peak-to-peak rms as measured on an oscilloscope), shot-to-shot normalization is usually not necessary. The primary noise source in these measurements is Poisson noise arising from the natural sampling statistics of counting discrete photons. The signal-to-noise ratio (SNR) improves as $\sqrt{N}$, where N is the total number of photons collected. The 250 kHz repetition rate of the laser system is ideal for femtosecond nonlinear optics at the surface of centrosymmetric media. The small second-order nonlinear susceptibility of these materials and the quadratic dependence of SHG signal intensity on laser pulse fluence means that, at conservative laser intensities, only a few SH photons are collected per laser pulse. The high repetition rate of the 250 kHz system (as compared to the 1 kHz rate of a typical regenerative amplifier) means that adequate SNRs can be obtained over shorter lengths of data collection time. The 250 kHz repetition rate is also desirable over the native ~ 80 MHz rate of the oscillator because shot-to-shot waiting times longer than ~ 0.1 μs are usually necessary to allow the system to completely relax back to the ground state before photo-exciting again. The $(250 \text{ kHz})^{-1} = 4 \text{ } \mu\text{s}$ period between laser pulses is an ideal compromise between fast data collection and ensuring full system relaxation.

A typical TR-SHG waveform takes about one hour to collect and is the result of averaging ~ 20 scans at 300 time points per scan. Occasionally, higher-resolution data is collected and is usually the average of ~ 80 scans collected over the course of about five hours. We choose to collect and average many scans instead of dwelling at each time point for an extended period of time so that we can detect (and ensure that we have avoided) changes to the TR-SHG waveform over the course of the experiment.

4.4.3. Demonstration of instrument capability

As a demonstration of the quality of data that can be obtained with our TR-SHG instrument, we show in Figure X the ultrafast nonlinear optical response of the GaAs(100) surface following photoexcitation of the bulk band gap. The rise and recovery of the overall SHG signal intensity is due to ultrafast screening of the near-surface electric field (resulting from band-bending at the GaAs(100) surface) by free charge carriers created by the excitation pulse. The oscillations in the SHG signal are due to coherent excitation of GaAs bulk coherent longitudinal optical (LO) phonons (114).

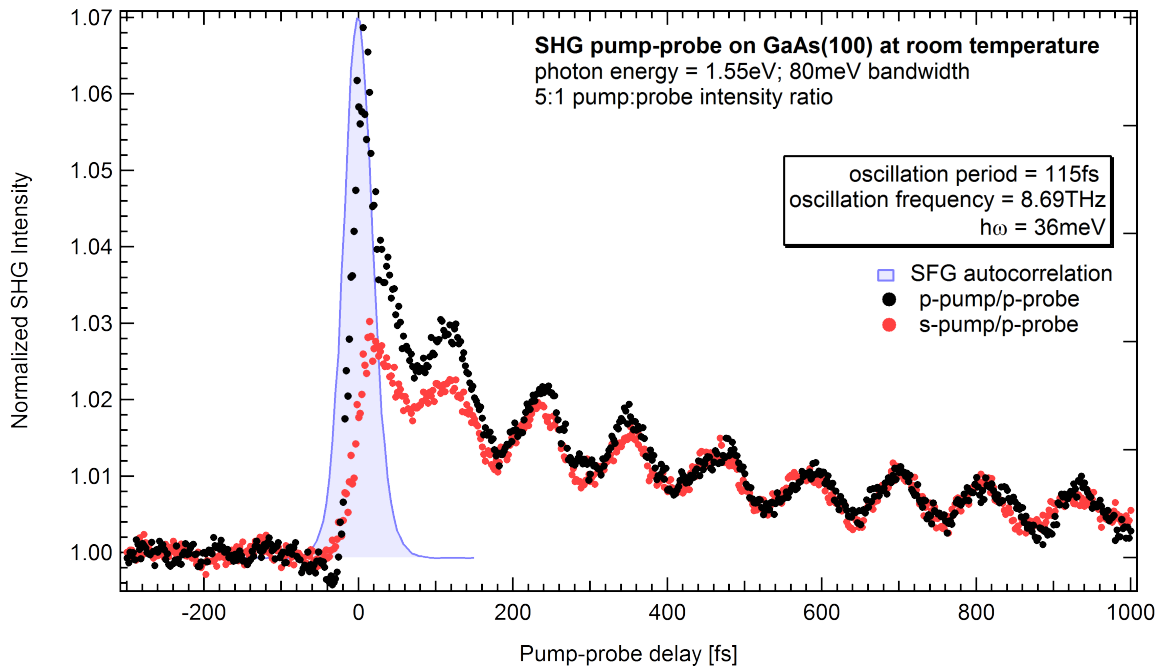


Figure 4.12 TR-SHG response of the GaAs(100) surface following photoexcitation with 820 nm light at room temperature. Oscillations in the data are due to coherent vibration of the GaAs bulk LO phonon (114). The blue area is the instrument response function.

Chapter 5

Hot Electron Dynamics at the ZnO ($10\bar{1}0$) Surface

The chapter has been published as:

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In this chapter, we use femtosecond time-resolved two-photon photoemission spectroscopy (TR-2PPE) to study the dynamics of electrons excited at the ZnO ($10\bar{1}0$) surface. Efficient relaxation of hot electrons within the Γ valley of the bulk conduction band results in sub-30fs lifetimes for electron energies greater than 0.1 eV above the conduction band minimum (CBM). These relaxation rates, which are among the fastest observed in any semiconductor over the same energy range, are consistent with the emission of longitudinal optical (LO) phonons resulting from strong Fröhlich coupling. For energy at or below the CBM, the excited electron lifetime increases exponentially with decreasing energy to as long as 1 ps. Dynamics in this region can be described by electronic relaxation within a quasi-continuum of defect-derived surface states whose density decreases exponentially into the band gap. Deliberately increasing defects on the ZnO ($10\bar{1}0$) surface drastically decreases the lifetime of electrons in this energy region. Existence of these states is consistent with observed upward band-bending and Fermi level pinning at the ($10\bar{1}0$) surface.

5.1. Introduction

ZnO, a direct-gap wide band gap semiconductor, is a remarkably versatile material with applications ranging from catalysis to optoelectronic devices to other emerging technologies featuring easily-synthesized anisotropic nanostructures (115, 116). ZnO nanoparticle films (117, 118) and nanowire arrays (13, 16, 18) have been used in lieu of TiO_2 in dye- and quantum dot-sensitized solar cells as well as in hybrid organic/inorganic bulk heterojunction photovoltaic devices because ZnO has a similar band gap (3.4 eV) and electron affinity (4.2 eV) to TiO_2 , a semiconductor used widely in dye-sensitized solar cells (11). Due to the intrinsic anisotropy of the wurtzite unit cell, ZnO nanowires grow in the c -axis direction. Consequently, the side facets of these nanowires belong to the $\{10\bar{1}0\}$ family of planes, also referred to as the prism face of ZnO. Additionally, the $(10\bar{1}0)$ surface is the most stable of the low-index ZnO surfaces (119) and likely constitutes a large fraction of the surface area in sintered ZnO nanoparticle films. As a result, the majority of charge separation and recombination events occur at the $(10\bar{1}0)$ or equivalent surfaces in optoelectronic and photovoltaic devices. Details on ZnO surface structure and properties are available in an excellent book chapter (120) and a recent review article (121).

For applications in optoelectronics and solar cells, it is important to understand the dynamics of excited electrons in ZnO and at its surfaces, particularly the predominant $(10\bar{1}0)$ surface. Developing this understanding requires the application of time-domain techniques capable of elucidating excited state electron dynamics with femtosecond resolution. Time-resolved two-photon photoemission (TR-2PPE) spectroscopy (59, 122, 123), a surface-sensitive technique that offers simultaneous energy and time-domain characterization of electronic excited states at solid surfaces, is well-suited for obtaining this information. TR-2PPE is a pump-probe technique particularly useful for tracking interfacial electron dynamics. In this approach, the first photon excites an electron from an occupied state into an unoccupied interfacial state (e.g., across the ZnO band gap in

the present study). After a variable time delay, the second photon ionizes the electron for detection, with time, energy, and momentum resolution. TR-2PPE has been successfully applied in the past to probe excited electron dynamics at metal (124) and semiconductor (97) surfaces.

We report in this chapter a TR-2PPE study of the ZnO ($10\bar{1}0$) surface. Our study reveals that the hot electron cooling rates in ZnO are among the fastest observed in any semiconductor at the same electron energies above the conduction band minimum (CBM) (125-128). We show that this is due to long-range Fröhlich coupling responsible for longitudinal optical (LO) phonon emission in polar semiconductors. Additionally, we find longer lifetimes for electrons in a continuum of defect-derived surface states (SS) located in the vicinity of the CBM whose density-of-states (DOS) decreases exponentially into the band gap. Existence of these surface states is consistent with the observed upward band-bending and Fermi level pinning at the ($10\bar{1}0$) surface. While our experiments provide no direct evidence that these defect states are stable in ambient or an aqueous environment, the nature and location of these states is remarkably similar to near-band edge acceptor states which have been assumed in modeling of solar cells featuring ZnO photoanodes and in the interpretation of electron transport and recombination data in these devices (129, 130).

5.2. Experimental methods

Laser light was generated by a commercial mode-locked Ti:sapphire oscillator (Coherent Mira, 76 MHz, ~700-900 nm) pumped by a Nd:vanadate solid state laser at 532 nm (Coherent Verdi). Tunable wavelength Ti:sapphire fundamental emission (typically 840-850 nm, ~60 fs, 8 nJ for this experiment) was frequency tripled in beta barium borate (BBO) and lithium triborate (LBO) crystals (Inrad) to obtain pulses in the near UV (~4.4 eV, < 70 fs, 0.5 nJ). Prism pairs were used for group velocity dispersion compensation both before and after harmonic generation. The UV pulses were then split into two equal intensity beams. One beam passed through a variable delay stage before both beams were focused non-collinearly onto the sample through a $f=0.5\text{m}$ focal length

lens. The two beams converge at a mutual angle of $\sim 2^\circ$. Spatial alignment of the two beams on the sample was aided by ZnO visible fluorescence and the use of a CCD camera. Both pump and probe pulses were p-polarized and incident on the sample surface with an angle of 60° from surface normal. Since this is near the Brewster's angle for the vacuum/ZnO interface, greater than 99% of pump and probe intensity was absorbed by the sample. Under these focusing conditions, the projection of the beam on the sample was a $330 \mu\text{m} \times 660 \mu\text{m}$ ellipse, resulting in a total pulse fluence of $0.3 \mu\text{J}/\text{cm}^2$. Taking the real part of the refractive index to be 1.9 and the absorption coefficient to be 0.018 nm^{-1} at $h\nu = 4.4 \text{ eV}$ for ZnO (131, 132), we calculate a photo-generated electron density of $\sim 5 \cdot 10^{16} \text{ cm}^{-3}$ near the surface.

Unintentionally doped single crystal ZnO ($1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ mm}$) oriented in the $[10\bar{1}0]$ direction (polished) was purchased from MTI Corp. The hydrothermally grown sample was transparent and yellowish in color. The vendor reported *n*-type character with a resistivity of $\rho = 500\text{-}1000 \Omega\cdot\text{cm}$. Using the well known relationship $\rho = (q_e \cdot \mu_n \cdot N_D)^{-1}$ (133) and a ZnO mobility value of $\mu_n = 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (115, 134), we calculate a room-temperature donor concentration of $3.1\text{-}6.2 \cdot 10^{13} \text{ cm}^{-3}$ (hereafter $\sim 5 \cdot 10^{13} \text{ cm}^{-3}$). The crystal was mounted on a sample manipulator and was cooled by liquid nitrogen and heated resistively through a Ta backplate. The clean $(10\bar{1}0)$ surface was prepared by several cycles of Ar^+ ion sputtering (1 keV, $0.7 \mu\text{A}$) for 15 minutes followed by annealing at 850 K for 10-30 min (119). The final annealing step was always less than 15 min to prevent migration of sub-surface metal ions to the surface, as observed by Diebold and coworkers (119, 135). Annealing in oxygen ($P_{\text{O}_2} = 3 \cdot 10^{-6} \text{ torr}$, followed by flash anneal in vacuum to remove residual adsorbed oxygen) was found to have no effect on either the work function or the lifetime of excited carriers. Surface quality was verified by low energy electron diffraction (LEED), which yielded sharp diffraction spots in a rectangular pattern characteristic of the $(10\bar{1}0)$ surface. The orientation of the LEED pattern indicated that the plane of laser incidence is parallel to the $[0001]$ direction.

All experiments were conducted under ultrahigh vacuum with a base pressure $< 2 \cdot 10^{-10} \text{ torr}$. Photoelectrons were collected at normal emission with a VG-100AX

hemispherical analyzer with energy resolution of approximately 35 meV. The sample was biased -1.6 V relative to the spectrometer to increase detection sensitivity. Raw electron kinetic energy data are collected relative to the spectrometer Fermi level (calibrated via a metal sample). Both the spectrometer and the ZnO sample (minus the applied bias) are in contact with the same grounding point, allowing for accurate measurement of the sample work function. The work function of the ZnO (10 $\bar{1}0$) surface was found to change with time. Leaving the freshly annealed sample in the dark for one hour at background pressure resulted in a ~ 0.3 eV decrease in the surface work function. This finding is consistent with the previous observations of Jacobi *et al.* on the healing of near-surface oxygen vacancy defects by oxygen atom diffusion from the surface (136). The work function may also change due to background H₂O adsorption; on other metal oxide surfaces, e.g., TiO₂, the work function was found to decrease by over 1 eV with monolayer adsorption (137). Note that Jacobi *et al.* also found that the time-dependent decrease in surface work function was accelerated by He-I UV radiation (136). Such a photo-induced change in surface work function was not observed for the much lower photon energies used here. Though these work function changes were found not to influence hot electron lifetimes, the sample was flashed periodically to 700 K to desorb any residual adsorbates immediately before each 2PPE measurements.

5.3. Results and discussion

5.3.1. 2PPE spectrum

A ZnO energy level diagram indicating the initial and intermediate states probed in this experiment is shown in Figure 5.1. The shaded region near the valence band maximum (VBM) represents the accessible initial states that may result in two-photon photoemission with $h\nu = 4.4$ eV; the shaded region near the conduction band minimum (CBM) represents the accessible intermediate states that may be transiently populated by pumping from one of the initial states. The value given for the O 2p surface resonance (at the $\bar{\Gamma}$ point of the surface Brillouin zone) is taken from angle-resolved photoemission

(ARPES) measurements resonance (138, 139). The Zn 4s surface resonance at the $\bar{\Gamma}$ point is calculated to lie somewhere in the range 1.5-2.5eV above the CBM (140-142) and is not accessible in this experiment.* Attempts to induce two-photon emission by a two-color IR pump/UV probe (or vice versa) optical configuration yielded completely featureless 2PPE spectra because of the low probability of excitation from occupied states within the band gap of this single crystal sample.

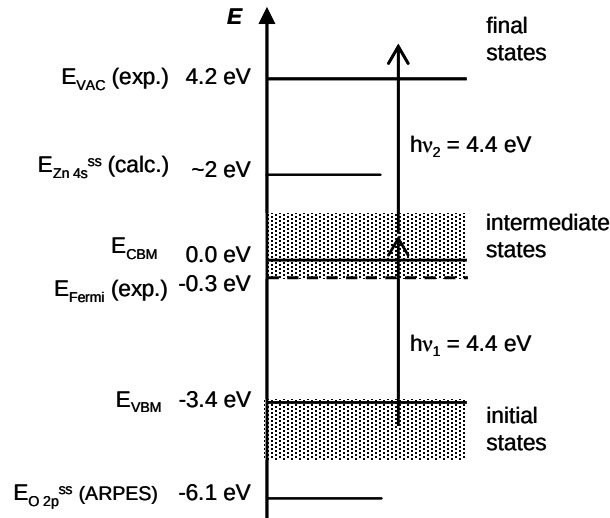


Figure 5.1 Energy diagram depicting two-photon photoemission from ZnO in a UV-UV pump-probe experiment with 4.4 eV photon energy. The shaded regions represent the accessible initial and intermediate states near the top of the valence band and bottom of the conduction band, respectively. Final states are free-electron-like states above the vacuum level (E_{VAC}). Arrows correspond to photon absorption. The location of the occupied O 2p surface resonance (138, 139) and the unoccupied Zn 4s surface resonance (140-142) at the $\bar{\Gamma}$ point of the surface Brillouin zone are included for reference. CBM=conduction band minimum; VBM=valence band maximum; SS=surface state.

A typical 2PPE spectrum taken at 120 K and 4.38 eV photon energy is shown in Figure 5.2. All spectra shown in this chapter are displayed on an intermediate state scale referenced to either the Fermi level or the CBM. We assign the peak at the low energy end of the spectrum, which appears in all spectra, to the free exciton (FX), based on its

* To access the Zn 4s surface resonance, the use of photon energy greater than ~4.4eV would be required, which is prohibited due to intense single-photon emission resulting in the formation of a space-charge region above the sample surface.

long lifetime (see Section 5.3.3) and the energetic position of this peak relative to the Fermi level and to the vacuum level (see below). The FX peak position and the known exciton binding energy (115) of 60 meV are used to calibrate the surface CBM, which is marked by an arrow 0.23 ± 0.05 eV above the Fermi level in Fig. 2. Corroboration for the assignment of the FX peak and the CBM comes from the measured electron affinity, $\chi = E_{VAC} - E_{CBM}$, where E_{VAC} is the *surface* vacuum level. For photoemission experiments on semiconductors, electron affinity is a better reference among individual samples and between research labs than the work function, $\Phi = E_{VAC} - E_{Fermi}$, because sample charging, surface band-bending, and photovoltage shifts (143) can lead to artificial drifting of Φ . The electron affinity is independent of these effects and remains an autonomous point of comparison. The measured electron affinity based on the FX and CBM assignments is $\chi = 4.20 \pm 0.05$ eV, which is in nearly exact agreement with data obtained from angle-resolved photoemission experiments (138, 139). Additional evidence for correct assignment of the FX and CBM comes from the high-energy edge in the 2PPE spectrum. The highest energy feature in the spectrum should result from photon absorption by an electron in an initial state near the valence band maximum (VBM). This absorption event produces an intermediate state electron at energy $E_{VBM} + 1h\nu = E_{CBM} - E_{gap} + 1h\nu = 0.94$ eV above the CBM, which is marked with another arrow in Figure 5.2. The small tail above this energy can be attributed to phonon-assisted transitions and defect states above the VBM extending into the band gap, which have also been observed in ultraviolet photoelectron spectroscopy (UPS) measurements conducted in our lab on Zn (10 $\bar{1}$ 0) (not shown).

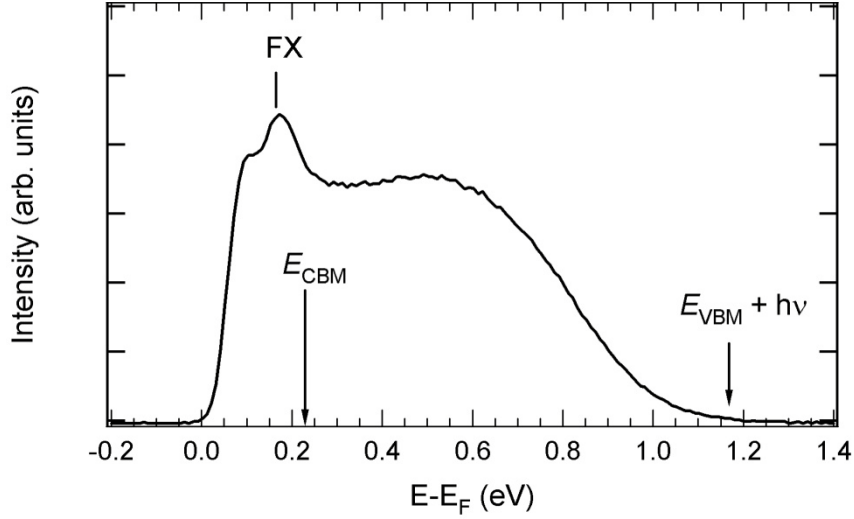


Figure 5.2 2PPE spectrum on an intermediate state energy scale referenced to the Fermi level. The spectrum was collected at 120 K and 4.38 eV photon energy. The feature labeled “FX” is attributed to photoemission from the free exciton state. CBM is assigned according to the FX binding energy (60 meV) (115). The arrow at $E_F + 1.17$ eV indicates the energy of an electron promoted from the top of the valence band.

5.3.2. Surface band-bending and photo-voltage shift

We have taken 2PPE spectra with different laser power and show in Figure 5.3 a set of power-dependent 2PPE spectra taken at room temperature with $h\nu = 4.38$ eV. The inset in Figure 5.3 shows a log-log plot of the integrated photoelectron emission intensity versus the time-averaged photon flux, f [photons $\text{cm}^{-2} \text{s}^{-1}$]. The slope of the solid line drawn through the data is 2. The key message from this power-dependence is that the *entire* spectrum scales with photon flux squared, verifying that all spectral features are results of two-photon processes and that lower-energy features cannot be attributed to one-photon emission of electrons normally occupying the conduction band or shallow trap states just below the CBM. This point is critically important for understanding the interpretation of time-resolved data presented in the next section of this article.

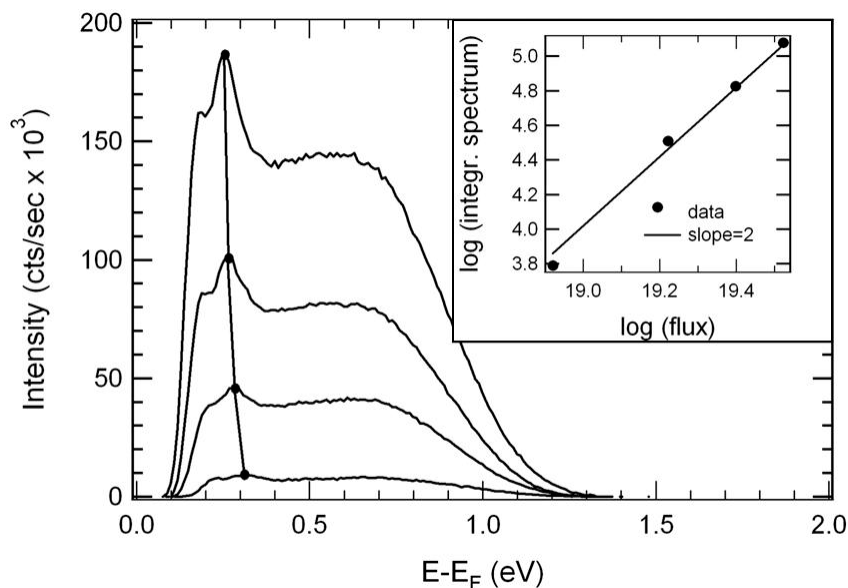


Figure 5.3 Dependence of the 2PPE spectrum on laser intensity. The spectra here were collected at room temperature with 4.38 eV photon energy. In order of increasing intensity, the spectra correspond to time-averaged photon fluxes of 0.8, 1.7, 2.5, and $3.3 \cdot 10^{19}$ photons $\text{s}^{-1} \text{cm}^{-2}$. Ordinates are included to emphasize relative photoemission intensity. Spectra are plotted vs. intermediate state energy referenced to the bulk Fermi level (E_F) to indicate the shift of the entire spectrum toward lower energy with increasing laser power. The behavior is characteristic of surface photovoltage effects and indicative of *n*-type (upward) band-bending at the surface. INSET: logarithm of the integrated spectrum vs. logarithm of flux density; a line of slope = 2 is included for reference. The scaling of photoemission intensity with photon flux density indicates that *all* features in the spectrum result from two-photon absorption.

Careful inspection of the spectra in Figure 5.3 reveals a photon flux-dependent shift in energy of the entire 2PPE spectrum relative to the bulk Fermi level. This behavior is characteristic of a surface photovoltage (SPV) shift (143-145) and indicates *n*-type (upward) band-bending at the ZnO surface. Briefly, under equilibrium (dark) conditions, bands bend upward at the surface due to charging of surface acceptor states within the projected fundamental gap, forming a space charge region (SCR) near the surface. As light is absorbed within this region, the photogenerated electron-hole pairs separate due to the potential gradient within the SCR. Minority carriers (holes) are accelerated toward the surface while majority carriers (electrons) are accelerated away from the surface into the bulk. This separation of charge results in a flattening of the bands, with higher excitation density resulting in greater band-flattening. Since photoemission spectroscopy is most sensitive to the sample surface, this effect will manifest itself as a downward shift

of the photoemission spectrum relative to the Fermi level (145). In Figure 5.3, this shift appears as an apparent movement of the entire spectrum toward lower energies with increasing laser power.

Hecht and coworkers pointed out that the magnitude of the SPV shift should be temperature-dependent (145). In an *n*-type material with low doping density (such that tunneling through the SCR is not important), the restoring current depends on the diffusion of electrons up the potential gradient back to the surface. At the surface, electrons can recombine with holes that have accumulated there and restore the bands to their equilibrium (bent) position. The diffusivity of both electrons and holes increases with temperature, resulting in smaller SPV shifts at higher temperatures. Indeed, we found that for the same incident photon flux, this temperature-dependent effect resulted in a SPV shift of -40 ± 8 meV on ZnO (10 $\bar{1}0$) when the temperature is decreased from 300K to 120K (not shown).

The magnitude of the SPV shift provides an estimate of the equilibrium surface potential, V_s . At room temperature and with lowest laser power (closest to dark equilibrium conditions), the Fermi level is “pinned” at 0.37 ± 0.05 eV below the CBM at the surface; at 120K and with highest laser power (nearly flat-band conditions), the Fermi level is pinned at 0.23 ± 0.05 eV below the CBM at the surface. Neglecting temperature-dependent shifting of the bulk Fermi level, we may conclude that $|V_s| \geq 0.14 \pm 0.07$ eV. These observations are in general agreement with Heiland and co-workers, who observed Fermi level pinning on freshly-cleaved ZnO prism faces in the range 0.25-0.35 eV below the CBM (120) and surface potentials around -0.12 V for ZnO prism faces annealed to 670K in UHV (146). The nature and origin of the surface states leading to band-bending at the (10 $\bar{1}0$) surface is discussed in Section 5.3.5.

5.3.3. Two-pulse correlation measurements

Figure 5.4 shows data from a typical two-pulse correlation (TPC) measurement, where the photoemission intensity at a given energy is recorded as a function of delay between the pump and probe pulses. Since both pump and probe pulses are at the same wavelength, “positive” or “negative” delay corresponds to the same pump-probe

condition and the TPC curve is symmetric. The data are fit to the model proposed by Ogawa and Petek (147), wherein the TPC photoemission intensity is considered to be the sum of three components. The first component is a constant baseline due to two-photon photoemission induced by each of the two individual pulses. The second component is a coherent two-photon photoemission process wherein the increased laser field intensity due to temporal overlap of the two pulses directly couples the initial and free-electron-like final states, without ever populating a real intermediate state; this component is equivalent to the two-pulse autocorrelation (AC). The third component is due to an incoherent two-photon photoemission pathway wherein real intermediate states are populated. Electrons occupying these intermediate states may absorb an additional photon, leading to photoemission, or undergo scattering events and decay to lower-lying states. The intermediate state lifetimes are extracted through modeling of this third component.

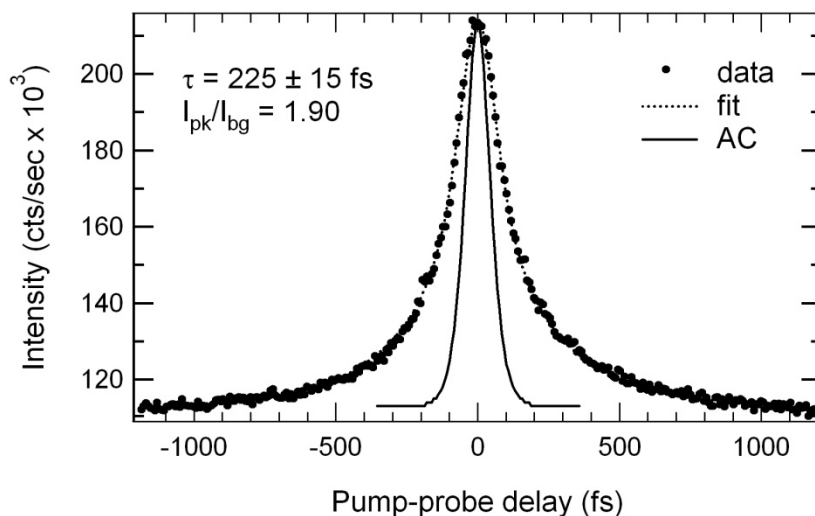


Figure 5.4 Example two-pulse correlation (TPC) curve, from which the lifetime (τ) of the transiently populated intermediate state at a given energy may be extracted by fitting to the model described in the text. The solid line is the laser pulse autocorrelation (AC) obtained from the model fit. The AC width is 102 fs; single pulse FWHM is 66 fs. Ordinates are included to emphasize peak-to-background intensity ratio (I_{pk}/I_{bg}).

The three additive contributions to the TPC intensity are modeled, respectively, as a constant background, a sech^2 AC (coherent component), and a convolution of the AC

with a symmetric exponential decay (incoherent component). In fitting the experimental data, the relative intensities of the three contributions are allowed to vary independently. Due to the relatively large number of fitting parameters, a stochastic fitting algorithm called “differential evolution” is used.* To maintain consistency, the AC width obtained from fitting TPC at high electron energies, where the intermediate state lifetime is much less than the laser pulse width, was fixed when fitting lower-energy data. Based on comparison of simulated TPC curves to experimental measurements, we estimate that lifetimes as short as 30 fs can be reliably determined with our instrument. It is worth noting that the model described here does not separately account for indirect population of intermediate states by electron decay from higher-energy states. We will show later (section 5.7) that even when re-population by decay from higher energy states is important, the *apparent* lifetime as measured in a TPC experiment may still appear single-exponential.

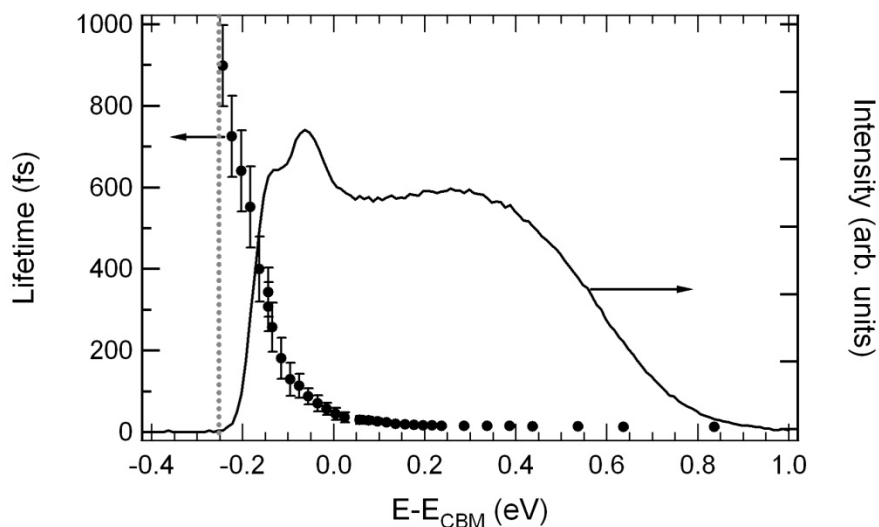


Figure 5.5 Intermediate state lifetimes (solid circles, left axis) extracted from the two-pulse correlation (TPC) measurements plotted against energy referenced to the conduction band minimum (CBM). The 2PPE spectrum (solid line, right axis) is included for reference. The dotted vertical line at -0.23 eV indicates the Fermi level. The data were collected at 120 K and 4.38 eV photon energy.

* IGOR code for the genetic optimization algorithm was obtained from <http://motofit.sf.net>. The code is based on algorithms found in (210).

In Figure 5.5, a comparison is shown of hot electron lifetime vs. intermediate state energy collected at 120K; the kinetic energy spectrum is included for reference. Above the CBM, hot electron lifetimes are less than 50 fs and appear to depend weakly on energy. Below the CBM, a strong energy dependence of lifetimes in the hundreds of femtoseconds is observed. While the lifetimes observed below the CBM are significantly longer than those observed above the CBM, electrons in these intermediate states below the CBM are still orders of magnitude shorter-lived than the expected lifetime of a free exciton in ZnO (115). Teke *et al.* studied time-resolved photoluminescence (PL) of free and donor-bound excitons in ZnO over a range of temperature and sample preparation conditions (148). They found the decay to be biexponential, with a fast component ranging from ~ 100 -400 ps (attributed to non-radiative recombination) and a slow component > 1 ns (the radiative lifetime of the FX). The lifetimes observed in the 2PPE data below the CBM are 2-3 orders of magnitude less than even the *fast* component of exciton annihilation. Furthermore, the strong energy dependence of the 2PPE lifetime data in Figure 5.5 suggests that these sub-picosecond transients are not associated with exciton annihilation. Sub-picosecond dynamics below the CBM are instead attributed to electronic relaxation within a continuum of defect derived surface states below the band edge. Detailed motivation for this assignment is presented in Section 5.3.5.

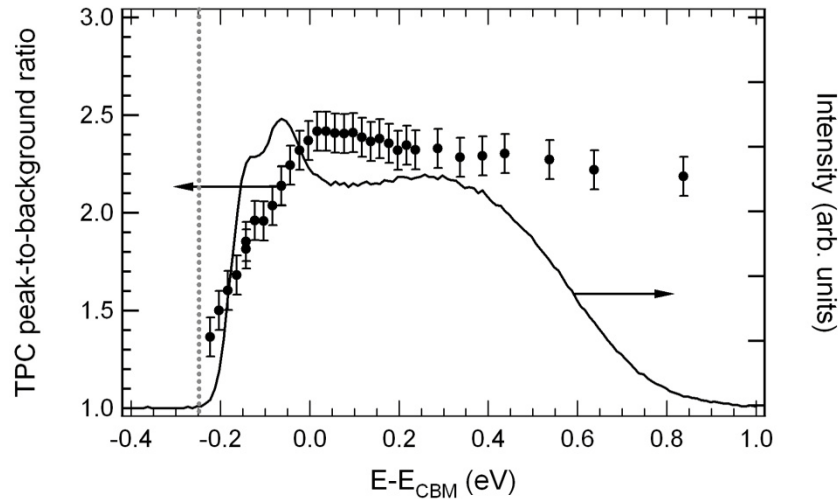


Figure 5.6 Peak-to-background ratio (solid circles, left axis) of the two-pulse correlation measurement (TPC) plotted against energy referenced to the conduction band minimum (CBM). The 2PPE spectrum (solid line, right axis) is included for reference. The dotted vertical line at -0.23 eV indicates the Fermi level. The data were collected at 120 K and 4.38 eV photon energy.

Ogawa and Petek pointed out that the phase coherence loss in the generation of a hot-electron population during a TPC measurement is equivalent to the autocorrelation of femtosecond laser pulses having a random phase component (147). Accordingly, the theoretical peak-to-background ratio in a TPC measurement is 3:1 (149). Because the two beams are non-collinearly focused on the sample, their spatial intensity profiles can never completely overlap. As a result, observed TPC peak-to-background ratios will always be less than 3. In Figure 5.6, TPC peak-to-background ratios as a function of intermediate state energy are shown. Above the CBM the peak-to-background ratio is roughly constant at ~ 2.4 . Below the CBM, peak-to-background ratios monotonically decrease with decreasing intermediate state energy. This behavior indicates that below the CBM, there is an additional background component in the photoelectron intensity. This background component has the following characteristics: (1) it is constant (or at least approximately constant) over the time scale for the TPC measurement (< 10 ps); (2) its intensity is not influenced by coherence between the pump and probe pulses; and (3) it must originate from a two-photon process, as explained in the discussion accompanying Fig. 3. These indicators suggest that the origin of the background contribution is a long-lived (> 100 ps) excited state that cannot be directly (resonantly) populated by the laser pulse – i.e., it is due to the bulk exciton. The excitonic features in the 2PPE kinetic energy spectrum (c.f. Figure 5.2) are not directly excited by the laser pulse. Because the photon energy (4.4 eV) is larger than the ZnO band gap (3.4 eV) by 1 eV, photoexcited electron-hole pairs are formed far from the Γ point. In this region of the Brillouin zone, group velocities $v_g = \partial\omega/\partial k$ of the electron and hole states are sufficiently different to de-stabilize any exciton directly excited far from the band minimum (150). Consequently, the free exciton observed in the 2PPE spectrum results from the coupling of electrons and holes separately generated near their respective band minima. As a result, the intensity of the exciton feature in the 2PPE spectrum is insensitive to coherence between the pump and probe pulses.

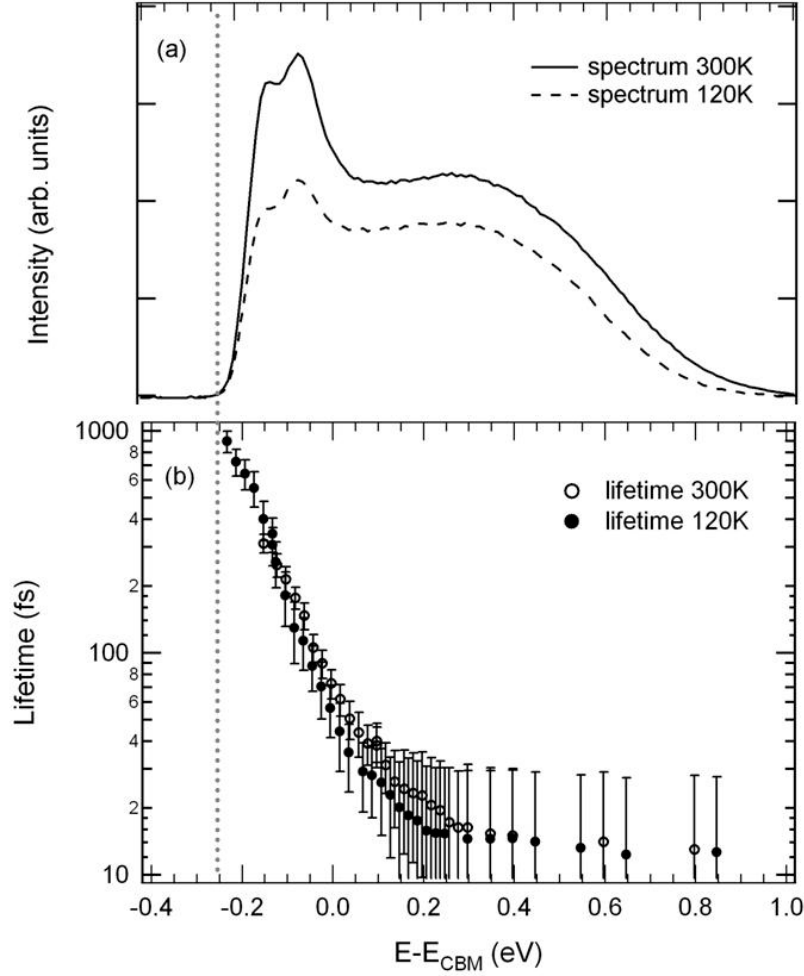


Figure 5.7 (a) 2PPE spectra at 300 K (solid line) and 120 K (dashed line) plotted against intermediate state energy referenced to the conduction band minimum (CBM). (b) Electron lifetimes at 300 K (open circles) and 120 K (solid circles) plotted against energy referenced to the CBM. The dotted vertical line at -0.23 eV indicates the Fermi level at 120 K. The energy scale has been shifted to correct for the temperature-dependent photovoltage shift. All data were collected on the same sample with 4.38 eV photon energy.

The temperature dependence of hot electron lifetimes is shown in Figure 5.7. The lifetime data and corresponding 2PPE spectrum at 300 K have been shifted in energy to account for the temperature-dependent SPV effect described earlier. The dotted vertical line indicates the Fermi level at 120 K. The data in Figure 5.7(b) are plotted on a log scale to emphasize the trend below the CBM and to better-resolve the dynamics of the short-lived states above the CBM. The lifetime trends at 300 K and 120 K are very similar and the difference appears to be within experimental uncertainty of the

measurement (which is considerable at higher electron energies due to the limited time resolution of the instrument).

Because of the large ZnO band gap (3.4 eV) and electron affinity (4.2 eV), and the low probability of pumping from occupied states within the band gap, a monochromatic UV-pump/UV-probe 2PPE configuration was required (see Figure 5.1). Consequently, the shape of the 2PPE spectrum in Figure 5.2 is dominated by coherent two-photon photoemission. This limitation of our laser instrument, combined with the ultrafast (< 30 fs) relaxation of hot electrons in ZnO, prohibits measurement of the time-dependent energy relaxation of the entire nonequilibrium electron population (151). Correspondingly, the ensuing discussions of hot electron relaxation within the conduction band focus exclusively on the ultrashort hot electron lifetime.

5.3.4. *Ultrafast hot electron cooling in the conduction band*

The generally accepted model for the relaxation of hot electrons in bulk semiconductors consists of two processes whose relative importance is dictated by their characteristic timescales (36, 125, 152). First, the nonequilibrium population of hot electrons undergoes carrier-carrier scattering, resulting in a transient, thermalized hot electron distribution characterized by a hot electron temperature T_e that is greater than the lattice temperature. Second, the transient hot electron population relaxes to the lattice temperature by phonon emission. Following excitation by femtosecond laser pulses, this carrier thermalization process occurs on the order of 10^2 fs (125, 126, 153) and is at least one order of magnitude longer than the lifetimes observed above the CBM in ZnO (see Figure 5.7). We believe that, because of the low laser pulse energy used in the present study (oscillator only) and the relatively short hot electron lifetimes observed, hot electron cooling by phonon emission may occur before significant electron-electron thermalization in ZnO.

Due to the finite escape depth of photoelectrons, the 2PPE signal comes from only the top-most surface region (a few nm). Consequently, a possible mechanism for 2PPE signal decay is the diffusion of hot electrons away from the surface (into the bulk). To investigate the role of the near-surface electric field due to surface charging in aiding electron transport away from the surface, we conducted self-consistent carrier dynamics

simulations of electron and hole concentrations near the surface during femtosecond laser pulse excitation (see Section 5.5). Our simulations show that, under experimental conditions relevant to our study, electron transport into the bulk occurs on a timescale of ~ 10 ps. Consequently, this mechanism cannot be responsible for the 2PPE signal decay. We can also rule out the scattering of electrons into and out of surface resonances, as studied extensively in other semiconductors (90, 97, 151, 154) because no surface resonances are observed in the 2PPE spectrum within this energy range and because no such resonances are expected to lie within the projected energy region of the conduction band under investigation here (140-142).

The hot electrons probed in this investigation are confined to the Γ valley of bulk ZnO (it would take an extra ~ 1 eV of photon energy to populate the next-highest lying valley in ZnO) (140). Intra-valley relaxation due to electron-phonon scattering occurs efficiently in polar semiconductor via the Fröhlich interaction (sometimes called polar optical scattering), which describes the coupling of electrons to polarization waves associated with longitudinal optical (LO) phonons (155). This type of electron-phonon coupling, which favors scattering events involving small changes in electron momentum (as is the case for intra-valley decay of hot electrons), has been shown to be the dominant mechanism of hot electron relaxation in other polar semiconductors such as GaAs (152, 156) and InP (151). Simple analytic expressions for the total Fröhlich scattering rate as a function of energy E above the CBM may be obtained within the parabolic and isotropic band approximation. The corresponding phonon emission rate is given by (157),

$$\frac{1}{\tau} = \frac{e^2 \omega \sqrt{m_{eff}}}{4\pi \epsilon_0 \hbar \sqrt{2}} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right] \frac{1}{\sqrt{E}} \ln \left[\frac{\sqrt{E} + \sqrt{E - \hbar \omega}}{\sqrt{E} - \sqrt{E - \hbar \omega}} \right] \cdot [n_{BE}(\omega, T) + 1] \quad (5.1)$$

where τ is the hot electron lifetime, ω is the phonon frequency,^{*} m_{eff} is the electron effective mass, and ϵ_∞ and ϵ_s are the optical-frequency and static dielectric constants,

^{*} We take the LO phonon band to be dispersionless, which is a good approximation in ZnO since the total bandwidth of the LO phonon branch is less than 6 meV (211). Further, only phonons near the zone center take part in polar optical scattering since the magnitude squared of the Fröhlich interaction Hamiltonian scales as Q^{-2} , where Q is the magnitude of the phonon wave vector.

respectively. The factor $n_{BE}(\omega, T)$ is the Bose-Einstein occupation probability of a phonon with energy $\hbar\omega$ at temperature T ,

$$n_{BE} = \frac{1}{e^{\hbar\omega/k_bT} - 1} \quad (5.2)$$

All phonon scattering processes, regardless of the interaction potential, scale as n_{BE} or $n_{BE} + 1$ for phonon absorption or emission, respectively (155). For a LO phonon energy of 72 meV in ZnO, we should expect to see only a ~6.5% increase in hot electron lifetimes going from 300K to 120K, which is well within the experimental uncertainty. Thus, the lack of significant temperature dependence in Figure 5.7 is consistent with a decay process involving LO phonons.

Equation (5.1) predicts that hot electrons excited greater than 0.1 eV above the CBM in ZnO should exhibit lifetimes shorter than 10 fs, which is consistent with our experimental observation of lifetimes shorter than the limit of time resolution of our instrument (~30 fs). In Table 5.1, a comparison of calculated LO phonon emission rates among several polar semiconductors is made, taking into account a first-order correction for non-parabolic dispersion due to inter-band coupling (see Section 5.6 for further details).^{*} The expected hot electron lifetimes in the ionic wurtzite semiconductors ZnO and GaN are significantly shorter than those in the more covalent zincblende GaAs and InP. The stronger Fröhlich coupling in the wurtzite materials is due primarily to the large difference between their static and high-frequency dielectric constants, which in turn reflects the relative contribution of nuclear and electronic polarization to the screening of electric fields within these materials. In ZnO and GaN, the electric fields induced by ion movement within the lattice are strong relative to the compensating polarization of surrounding electrons, resulting in longer-range interactions between hot electrons and LO phonons and correspondingly shorter hot electron lifetimes. The weaker temperature dependence of LO phonon emission rates in the wurtzite materials reflects the comparatively large LO phonon energy. Similar behavior is expected in other metal oxides as well. A 2PPE study of the clean rutile (110) surface of TiO₂ showed hot

^{*} Relevant material properties were taken from (212) and references therein.

electron cooling faster than could be resolved with the authors' 10-fs laser pulses (128), consistent with a decay pathway dominated by strong Fröhlich coupling.

Table 5.1 Calculated inverse emission rate (in femtoseconds) of a LO phonon by an electron excited 0.5 eV above the conduction band minimum. The calculation includes a first-order correction for non-parabolic dispersion due to interband coupling, as detailed in Section 5.6.

	ZnO	GaN	GaAs	InP
300 K	6.7 fs	10.9 fs	189 fs	186 fs
120 K	7.2 fs	11.2 fs	246 fs	225 fs

An important consideration when evaluating the role of electron-phonon scattering in cooling of a laser-excited hot electron population is the screening of the electron-phonon interaction by other charge carriers (158-160). There is a critical carrier density N_c below which the phonon emission rate is independent of carrier density, but above which the phonon emission rate significantly decreases with increasing carrier density. Yoffa determined that there is a general trend among critical carrier densities in direct-gap polar semiconductors (159). If a value is known for one semiconductor then the value for another can be determined with the knowledge that,

$$N_c \propto \epsilon_s m_{eff} \omega^3 \quad (5.3)$$

Taking $N_c^{GaAs} = 5 \cdot 10^{17} \text{ cm}^{-3}$ (158), the critical carrier density in ZnO is then $N_c^{ZnO} = 1 \cdot 10^{19} \text{ cm}^{-3}$, which is over two orders of magnitude greater than the carrier density obtained in our investigation ($n = 5 \cdot 10^{16} \text{ cm}^{-3}$). Thus, carrier screening of the electron-phonon interaction should not play a role in this experiment – a conclusion that is supported by the observed ultrafast lifetimes. It is worth noting, however, that carrier densities close to N_c can be easily obtained during studies of ultrafast dynamics in semiconductors using amplified laser systems. Wen *et al.* summarized a number of recent femtosecond pump-probe studies of hot electron dynamics in ZnO thin films and nanostructures (161). Hot electron thermalization and cooling times have been reported over the range of 0.2-2.0 ps, reflecting the important role that super-critical carrier

densities can play in screening electron-phonon interactions, as well as other factors specific to nanostructures, such as hot phonon effects (36).

While the preceding analysis seems to support the conclusion that polar optical scattering is the cause of the ultrafast decay dynamics observed at energies greater than 0.1 eV above the CBM, we cannot completely rule out the influence of electron-hole interactions or surface defect scattering. Further, Eq. (5.1) represents a simplified single-electron picture of polar optical scattering; full treatment requires consideration of the entire non-equilibrium distribution and realistic density of states (151). However, the trends predicted by the analytic model have been reproduced experimentally. Using the same experimental technique (2PPE), hot electron lifetimes in ZnO and TiO₂ (128) are measured to be shorter than 30 fs and 10 fs, respectively, while lifetimes in GaAs (126) and InP (151) are found to be hundreds to several hundreds of femtoseconds.

Hot electron cooling within 0.1 eV of the CBM represents the transition from LO phonon emission to other types of electron-phonon scattering events involving lower-frequency phonon modes. These processes have characteristically slower scattering rates, and hot electron lifetimes grow correspondingly longer as high-energy phonon emission becomes impossible due to unavailability of electronic accepting states. The presence of surface states below the band minimum does not offer additional density of accepting states for fast polar optical scattering since scattering from bulk bands into surface states is a form of inter-valley scattering, which favors short-range interactions with large wave vector phonons (97).

5.3.5. *Electron dynamics below the conduction band minimum*

Below the conduction band minimum (CBM) lifetimes increase rapidly from ~60 fs at the CBM to ~1000 fs at the Fermi level. We argued earlier (in Section 5.3.3) that dynamics observed in this energy region must be attributed to electronic states isoenergetic with, but separate from, the much longer-lived bulk free excitons and other associated excitonic states. We turn our attention now to the origin of these dynamics.

A reasonable estimation of the equilibrium width of the surface space charge region (SCR) can be made by invoking the depletion approximation, wherein the SCR is assumed to be a region of constant charge density equal to the donor density, N_D , which

was identified earlier as $\sim 5 \cdot 10^{13} \text{ cm}^{-3}$. For a surface potential of -0.3 V, the SCR width is 2.3 μm , which is substantially larger than the optical absorption depth (56 nm) (131) or the photoelectron mean-free-path (a few nm). Thus, the potential does not vary considerably across the sample depth probed in a 2PPE experiment. One may argue that laser-excited carrier concentrations might be large enough to substantially alter the band-bending potential near the surface within the timescale of the TPC measurement. Under such circumstances, electrons photoemitted from near the CBM might appear at different energies in the 2PPE spectrum depending on the depth from which they originated. Carrier dynamics simulations (see Section 5.5) showed that the laser intensities used in this 2PPE study are not strong enough to induce significant changes to the potential profile near the ZnO surface on a femtosecond time scale. Therefore, the possibility of conduction band electrons appearing below the surface CBM in the 2PPE spectrum can be eliminated. The observed short-lived electrons appearing below the surface CBM in the 2PPE spectrum must come from electronic states within the band gap.

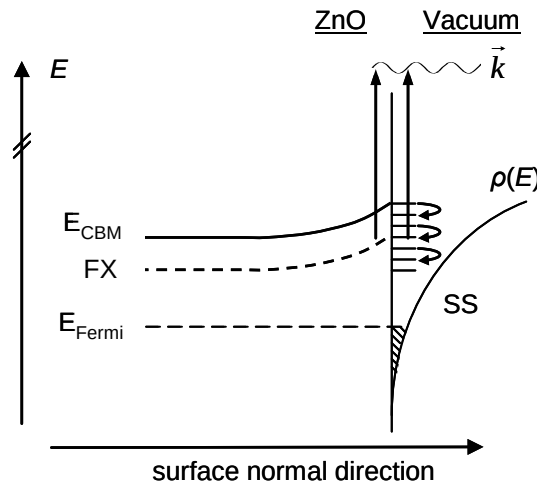


Figure 5.8 Depiction of electronic relaxation within a quasi-continuum of surface states (SS) below the conduction band minimum (CBM), which appear at the same energy in the 2PPE spectrum as features related to bulk excitons (vertical arrows depict photoemission). The strong energy-dependence of intermediate state lifetime below E_{CBM} is explained by an exponentially decreasing density of SS with decreasing energy. The presence of these defect-derived SS is the cause of band-bending and Fermi level pinning at the $(10\bar{1}0)$ surface. FX=free exciton.

The relaxation mechanism responsible for electron dynamics below the CBM is illustrated in Figure 5.8. There exists a quasi-continuum of surface states (SS) near the conduction band edge and the lifetime data below the CBM in Figure 5.5 & Figure 5.7 reflect the time scale for electronic relaxation within this SS manifold. These short-lived SS are in the same energy range as the long-lived FX or associated excitonic states, as shown in Figure 5.8. The decreasing peak-to-background ratio in Figure 5.6 indicates that the density of these SS decreases with decreasing energy below the CBM. The density-of-states (DOS) distribution in the SS manifold can be estimated more precisely from the energy dependent electron lifetime. We show in Section 5.7 that lifetimes increasing exponentially with decreasing energy below the CBM (as shown in Figure 5.5 & Figure 5.7) are consistent with an exponentially decreasing DOS over the same range of electron energies. We further show analytically that for an exponential distribution of states, TPC curves may still exhibit single-exponential decay dynamics, even when re-population of states by decay of electrons from higher-energy states is considered. Following this analysis, the data in Figure 5.5 are well represented by an exponential distribution of states below the CBM,

$$\rho(E) = \rho_0 \exp\left(\frac{E - E_{CBM}}{m_c}\right), \quad (5.4)$$

where m_c reflects the average depth of the distribution (129). A fit to the data in Figure 5.5 reveals an average trap depth of $m_c = 0.11 \pm 0.01$ eV.

The high-energy edge of the SS distribution is not well-characterized, but appears to overlap energetically with the CBM, as evidenced by the continuous increase of the electron lifetime across the CBM (c.f. Figure 5.5). In the vicinity of the CBM, the electron lifetime extracted from the TPC measurement is a DOS-weighted average of contributions from electrons residing in both extended conduction band states and isoenergetic surface states. Consequently, the lifetime data will be smoothly varying across this energetic region. Smoothly varying DOS across the band edge is also observed near the VBM in UPS measurements taken in our lab on the same ZnO (162). The continuous increase of the electron lifetime across the FX peak is also expected, since we have argued that within the timescale of these TPC measurements, the only

contribution of the FX to the TPC curve is an added constant background component (Section 5.3.3). The relatively short 1 ps lifetime of electrons occupying SS just above the Fermi level (as compared to electrons at the CBM which may live for nanoseconds) is attributed to SS-mediated electron-hole recombination.

The presence of near-band edge SS with acceptor character has been inferred previously from a variety of experiments. Gatos and co-workers performed surface photovoltage spectroscopy measurements on the ZnO prism faces in high vacuum and obtained results that could only be explained by a continuous spectrum of SS extending from 1.5 eV below the CBM up to the band edge (163). Heiland and Luth performed surface photoconductivity measurements that revealed surface band-bending and Fermi level pinning at 0.25-0.35 eV below the CBM, implying the presence of acceptor states spanning this energy range at the surface (120). The band gap surface states observed in the present study are not due to the large density of Zn 4s dangling bond states (DBs) on the $(10\bar{1}0)$ surface; *ab initio* calculations have predicted the DBs are at energies located > 1 eV above the CBM (140-142). We attribute states observed below the CBM in this study to surface defects, such as step-edges, kinks, or vacancies, as has been suggested previously (136, 164). 2PPE data collected on surfaces that were made intentionally defective support this interpretation. For example, lifetime measurements made on the same sputtered sample before and after the annealing step are compared in Figure 5.9. Lifetimes below the CBM decrease dramatically moving from the nearly perfect (annealed) surface to the defective surface. As argued in Section 5.7, decay rates within the SS manifold are proportional to the density of SS. By increasing surface DOS through added defects, decay rates increase and electron lifetimes correspondingly decrease.

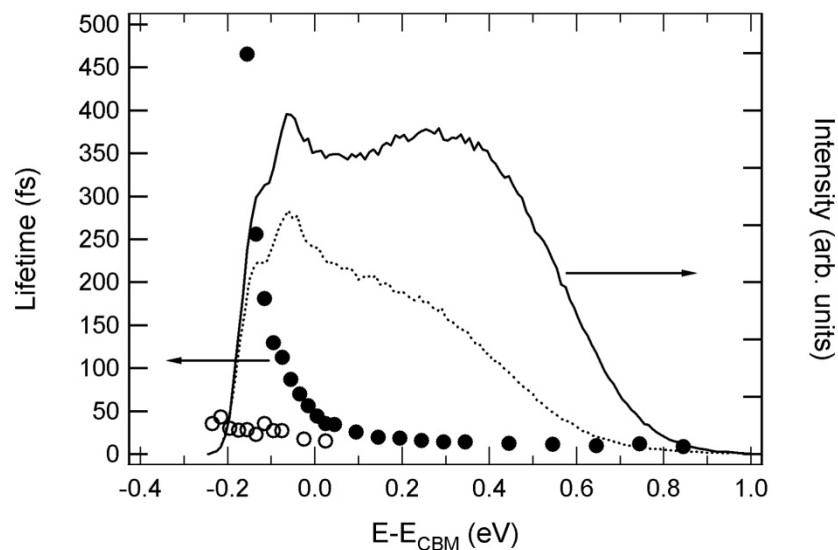


Figure 5.9 Comparison of intermediate state lifetimes for the annealed surface (solid circles, left axis) and the defective surface (open circles, left axis). Defects were intentionally introduced by Ar^+ ion sputtering without subsequent annealing. 2PPE spectra corresponding to the annealed surface (solid line, right axis) and the defective surface (dotted line, right axis) are included for reference. The data were collected at 120 K and 4.38 eV photon energy and the energy scale of the defective surface data has been shifted to correct for the defect-induced photovoltage shift.

Further evidence that defects are responsible for Fermi level pinning at the ZnO ($10\bar{1}0$) surface comes from the defect-induced shift of the 2PPE spectrum, shown in Figure 5.10.* Filling additional and deeper trap states at the surface leads to increased surface charging. As a result, the Fermi level is pinned further within the gap, away from the CBM. The spectra shown in Figure 5.10 exemplify this behavior. The defective surface 2PPE spectrum is shifted 0.13 ± 0.01 eV higher in energy relative to the annealed surface spectrum, indicating that the Fermi level is pinned deeper within the gap at the defective surface.

* Note that absolute photoemission intensities should not be compared across spectrum measurements due to variations in laser power and sample manipulator position.

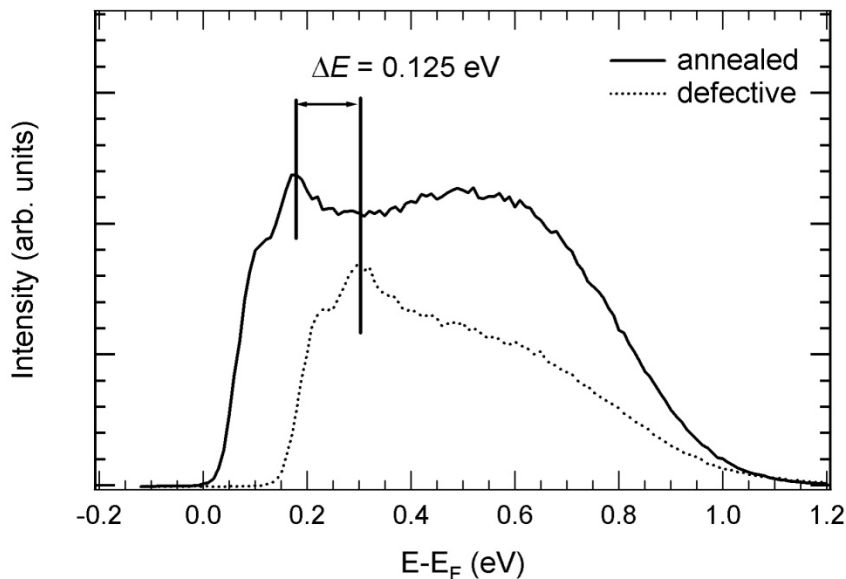


Figure 5.10 Shift of the 2PPE spectrum relative to the bulk Fermi level after introduction of additional surface defects. The defective surface 2PPE spectrum (dotted line) is shifted 0.125 ± 0.010 eV higher in energy relative to the annealed surface spectrum (solid line), indicating that the Fermi level is pinned deeper within the gap. Defects were intentionally introduced by Ar^+ ion sputtering without subsequent annealing. The data were collected at 120 K and 4.38 eV photon energy.

The diffusivity of electrons in ZnO or TiO_2 sintered nanoparticle films is known to increase with increasing photoinjected charge density (129). This is thought to be due to the filling of deep trap levels in an exponential distribution of states below the CBM, allowing other electrons occupying higher energy states to move more freely. In characterizing the distribution of trap states in nanoparticle thin films, the parameter $\alpha = kT/m_c$ is most commonly used (129). At 300K, the m_c parameter obtained for our clean ZnO surface corresponds to $\alpha = 0.24 \pm 0.02$. This is remarkably similar to the value $\alpha = 0.27 \pm 0.05$ obtained indirectly from capacitance measurements on ZnO nanoparticle films used in dye-sensitized solar cells (130). While our experiments provide no direct evidence that defect states observed on the ZnO (10 $\bar{1}$ 0) surface in UHV are stable to atmospheric exposure and a water environment, the similarity in α obtained by these two very different experimental techniques suggests that the band-edge surface states characterized in this 2PPE study may be related to those responsible for electron trapping and transport in nanoparticle thin films and nanowire arrays. Other experiments performed under ambient conditions have shown that annealing ZnO nanoparticle films

and nanowire arrays dramatically improves their conductivity (165). These findings, when considered in light of the results of the 2PPE study here, suggest that the trap states that influence electron transport in dye-sensitized solar cells reside on the surfaces of the ZnO nanoparticles and nanowires used to assemble these cells.

5.4. Conclusions

Femtosecond time-resolved two-photon photoemission (TR-2PPE) spectroscopy was used to investigate the relaxation of hot electrons at the ZnO (10 $\bar{1}$ 0) surface. Hot electron lifetimes shorter than 30 fs are observed for conduction band electrons excited greater than just 0.1 eV above the conduction band minimum (CBM). These ultrafast relaxation times are attributed to emission of longitudinal optical (LO) phonons via the Fröhlich interaction, which is shown to be a very efficient decay pathway in ZnO, a polar semiconductor with strong ionic character. Additionally, we find a continuum of defect-derived surface states (SS) located in the vicinity of the CBM whose lifetime increases exponentially into the band gap. We show that these exponentially increasing electron lifetimes are consistent with an exponentially decreasing density of surface states within the band gap. Our study reveals upward band-bending at the (10 $\bar{1}$ 0) surface and Fermi level pinning within this surface state continuum ($\sim$ 0.3 eV below the CBM). Comparison to other experiments performed under ambient conditions suggests that these defect-derived surface states on ZnO (10 $\bar{1}$ 0) may share common origins as those responsible for carrier trapping observed in electron transport in ZnO nanoparticle films and nanowire arrays.

5.5. Finite element simulations of charge-carrier diffusion

In order to investigate the role of surface band-bending in accelerating electrons away from the ZnO surface during a 2PPE experiment, we conducted self-consistent simulations of electron and hole dynamics during femtosecond laser pulse excitation.

Specifically, we solved the time dependent electron and hole drift-diffusion equations simultaneously with Poisson's equation in one dimension. Solutions to the coupled partial differential equations and relevant boundary conditions were found using the finite element method as implemented in the COMSOL Multiphysics® package. Note that these simulations apply exclusively to conduction band electrons near the band minimum which have already undergone thermal relaxation via phonon emission.

The ZnO sample is treated as a semi-infinite slab, with $z = 0$ at the surface and $z > 0$ in the bulk. In the one-dimensional approximation, Poisson's equation (SI unit system) is,

$$\frac{\partial^2 V(z,t)}{\partial z^2} = -\frac{\rho(z,t)}{\varepsilon}, \quad (5.5)$$

where ε is the permittivity of ZnO and $\rho(z,t)$ is the charge density, given by,

$$\rho(z,t) = e(p(z,t) - n(z,t) + N_d). \quad (5.6)$$

In Eq. (5.6), p and n are the concentration of holes and electrons, respectively, N_d is the concentration of ionized donors, and e is the magnitude of the electron charge (defined so that e is positive). Substitution of electron and hole fluxes into their respective continuity expressions leads to the well-known drift-diffusion equations,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial z} \left(\mu_n n \frac{\partial V}{\partial z} - D_n \frac{\partial n}{\partial z} \right) = G(z,t), \quad (5.7)$$

and,

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial z} \left(-\mu_p p \frac{\partial V}{\partial z} - D_p \frac{\partial p}{\partial z} \right) = G(z,t), \quad (5.8)$$

where the diffusivity, $D_{n,p}$, and mobility, $\mu_{n,p}$, are related through the Einstein relation,

$$\frac{D_{n,p}}{\mu_{n,p}} = \frac{k_b T}{e}. \quad (5.9)$$

In Eqs. (5.7) & (5.8), $G(z,t)$ is the electron-hole pair generation rate in the bulk ($z > 0$). Over the short time scales we are interested in (< 50 ps), bulk recombination may be neglected. The rates of electron and hole generation are equal and are described by

spatiotemporal variation of femtosecond laser pulse absorption. If a sech^2 pulse shape is assumed, then the rate of bulk generation is given by (97),

$$G(z, t) = \alpha f (1 - R) e^{-\alpha z} \frac{0.88}{W} \text{sech}^2 \left(\frac{1.76t}{W} \right), \quad (5.10)$$

where α is the absorption coefficient, f is the photon flux (photons per pulse divided by irradiated area), R is the reflection coefficient of the vacuum/ZnO interface at the particular angle of incidence, W is the temporal width (FWHM) of the laser pulse, and the term $0.88/W$ is the normalization constant that arises from integration of the sech^2 function.

The variation of electron and hole concentrations in space and time are found by simultaneously solving Eqs. (5.5), (5.7), & (5.8) with the application of appropriate initial and boundary conditions. Initial electron and potential distributions are calculated as follows: Before each laser pulse (@ $t = 0$), $p(z)$ is set to zero ($p(z) \approx 0$ at equilibrium) and $n(z)$ is found from the Boltzmann relation,

$$n(z) = N_d \exp \left[\frac{e \cdot V(z)}{k_b T} \right], \quad (5.11)$$

where $V(z) < 0$ for an n -type material exhibiting upward band bending. Equation (5.11) is solved simultaneously with Poisson's equation to yield initial conditions for $n(z, t=0)$ and $V(z, t=0)$. For $t > 0$, boundary conditions for solution of Poisson's equation are,

$$@ z = 0, \quad V = V_s, \quad (5.12)$$

and,

$$@ z = \infty, \quad \frac{\partial V}{\partial z} = 0. \quad (5.13)$$

From the 2PPE data we are able to assign a maximum constant surface potential of $V_s = -0.3$ V. Boundary conditions for electrons are,

$$@ z = 0, \quad J_n = -r_n \quad (5.14)$$

and,

$$@ z = \infty, \quad n = N_d ; \quad (5.15)$$

for holes,

$$@ z = 0, \quad J_p = -r_p , \quad (5.16)$$

and,

$$@ z = \infty, \quad p = 0 . \quad (5.17)$$

In Eqs. (5.14)–(5.17), $J_{n,p}$ is the flux of electrons or holes at the surface and $r_{n,p}$ is the surface electron/hole capture rate. The surface capture rate is often expressed phenomenologically through a surface recombination velocity, i.e. $r_p = v_p \cdot p$, but more detailed expressions may be derived if specific information about the surface states participating in surface recombination is known (166).

The most important result of our simulation is that the laser intensities used in this 2PPE study are not strong enough to induce significant changes to the potential profile near the ZnO surface within the timescale of interest for a two-pulse correlation (TPC) measurement (< 10 ps). Because the width of the SCR ($\sim 2 \mu\text{m}$) is much greater than the escape depth of photoelectrons ($\sim$ a few nm), the observed short-lived (sub-picosecond) electrons appearing below the surface CBM in the 2PPE spectrum must come from electronic states within the band gap, and the possibility of conduction band electrons from deeper within the sample appearing in the 2PPE spectrum below the surface CBM can be eliminated. Further, we find that no dynamics observed in our 2PPE experiment (at any electron energy probed) can be explained by diffusion of electrons away from the surface. For $r_{n,p} = 0$ (no surface capture of electrons or holes) and the doping and laser focusing conditions corresponding to our 2PPE experimental conditions, our simulations show that diffusion of electrons into the bulk occurs on a ~ 10 ps time scale, which is much longer than any dynamics observed in our 2PPE investigation (c.f. Figure 5.7). However, we do find that when doping levels are higher than in our unintentionally doped ZnO sample (e.g., $N_d >> 10^{14} \text{ cm}^{-3}$), timescales for electron drift into the bulk can be sub-picosecond. For the reasonable scenario where $N_d = 10^{16} \text{ cm}^{-3}$ and $V_s = -0.3 \text{ V}$, electron concentration at the surface decays with an exponential decay constant of ~ 400 fs because of the strong surface electric field which accelerates electrons into the bulk.

Therefore, drift of electrons away from the surface *must* be considered when analyzing TR-2PPE measurements made on intentionally doped semiconductor samples.

5.6. Calculation of the Fröhlich scattering time

The following derivation of the Fröhlich scattering rate expression, including inter-band coupling, is adapted from references (156, 167, 168). We begin by considering an electron in initial state $|k\rangle$ in a polar semiconductor with ion cores in initial state $|c\rangle$. From Fermi's Golden Rule, the transition probability per unit time from initial state $|k, c\rangle$ to final state $|k', c'\rangle$ due to a perturbation Hamiltonian H' is given by,

$$W(k, c \rightarrow k', c') = \frac{2\pi}{\hbar} |\langle k, c | H' | k', c' \rangle|^2 \delta[E(k', c') - E(k, c) \pm \hbar\omega], \quad (5.18)$$

where the delta function implies conservation of energy in the transition. If the perturbation is due to a polarization wave, then the interaction Hamiltonian is,

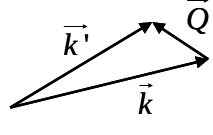
$$H' = e \int |\Psi_k(r)|^2 \phi(r) d^3r \quad (5.19)$$

where the product $e|\Psi_k(r)|^2$ is the electron charge density and $\phi(r)$ is the electric potential associated with the polarization of the crystal. With the help of quantum field theory, the matrix elements for phonon creation (emission) and annihilation (absorption) can be derived,

$$|\langle k, c | H' | k', c' \rangle|^2 = \frac{2\pi e^2 \hbar \omega}{4\pi \epsilon_0 V Q^2} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_\infty} \right] G(k, k') \cdot [n_{BE}(\omega, T) + 1] \quad (\text{emission}) \quad (5.20)$$

$$|\langle k, c | H' | k', c' \rangle|^2 = \frac{2\pi e^2 \hbar \omega}{4\pi \epsilon_0 V Q^2} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_\infty} \right] G(k, k') \cdot n_{BE}(\omega, T) \quad (\text{absorption}), \quad (5.21)$$

where ω is the LO phonon frequency, V is the volume of the crystal, $Q = |\vec{k}' - \vec{k}|$ is the magnitude of the phonon wave vector,



$$(5.22)$$

ϵ_s and ϵ_∞ are the static and high-frequency dielectric constants, respectively, and $G(k, k')$ is the overlap integral between the initial and final electron states. For s-states and parabolic bands, $G(k, k') \rightarrow 1$. The factor $n_{BE}(\omega, T)$ is the Bose-Einstein occupation probability of a phonon with energy $\hbar\omega$ at temperature T ,

$$n_{BE} = \frac{1}{e^{\hbar\omega/k_B T} - 1}. \quad (5.23)$$

Equations (5.20) and (5.21) contain the phonon wave vector dependence mentioned previously. The magnitude squared of the matrix element scales as $1/Q^2$, meaning that the interaction favors small changes in electron momentum. The total scattering rate $1/\tau$ is obtained by plugging Eq. (5.20) or (5.21) into (5.18) and integrating over all final states k' (167),

$$\frac{1}{\tau} = \frac{V}{(2\pi)^3} \int_0^\infty dk' \int_0^\pi d\varphi \int_0^{2\pi} d\theta \cdot W(k, k') \cdot k'^2 \cdot \sin\varphi. \quad (5.24)$$

Here, V is the volume of the crystal and φ is the angle between $\vec{k}$ and $\vec{k}'$. The total scattering rate assuming parabolic bands is given by (157),

$$\frac{1}{\tau} = \frac{e^2 \omega \sqrt{m}}{4\pi\epsilon_0 \hbar \sqrt{2}} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right] \frac{1}{\sqrt{E}} \ln \left[\frac{\sqrt{E} + \sqrt{E - \hbar\omega}}{\sqrt{E} - \sqrt{E - \hbar\omega}} \right] \cdot [n_{BE} + 1] \quad (\text{emission}) \quad (5.25)$$

$$\frac{1}{\tau} = \frac{e^2 \omega \sqrt{m}}{4\pi\epsilon_0 \hbar \sqrt{2}} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right] \frac{1}{\sqrt{E}} \ln \left[\frac{\sqrt{E} + \sqrt{E + \hbar\omega}}{\sqrt{E} - \sqrt{E + \hbar\omega}} \right] \cdot n_{BE} \quad (\text{absorption}). \quad (5.26)$$

Ehrenreich (169) showed that when the band gap is much larger than the spin-orbit splitting, the conduction band dispersion relation (below other minima) can be expanded in the form,

$$\frac{\hbar^2 k^2}{2m_{eff}} = \gamma(E) = E \left[1 + \alpha E + \beta E^2 + \dots \right]. \quad (5.27)$$

Note that as $\alpha, \beta, \dots \rightarrow 0$ we recover the parabolic band dispersion relation. He deduced from a similar relationship that the coefficients in the expansion can be calculated as,

$$\alpha = \frac{1}{E_g} \left(1 - \frac{m_{eff}}{m_0} \right)^2 \quad (5.28)$$

$$\beta = -\frac{2}{E_g^2} \frac{m_{eff}}{m_0} \left(1 - \frac{m_{eff}}{m_0} \right)^3. \quad (5.29)$$

For ZnO, $\alpha=0.153 \text{ eV}^{-1}$ and $\beta=-0.018 \text{ eV}^{-2}$. If second and higher order terms are neglected (a fine approximation in ZnO, given the value of β), we are left with,

$$\gamma(E) = E(1 + \alpha E). \quad (5.30)$$

The overlap integral $G(k, k')$ now becomes,

$$G(k, k') = (a_k a_{k'} + c_k c_{k'} \cos \varphi)^2, \quad (5.31)$$

where φ is the angle between $\vec{k}$ and $\vec{k}'$, and the coefficients a_k and c_k are given by,

$$a_k = \left[\frac{1 + \alpha E(k)}{1 + 2\alpha E(k)} \right]^{1/2} \quad (5.32)$$

$$c_k = \left[\frac{\alpha E(k)}{1 + 2\alpha E(k)} \right]^{1/2}. \quad (5.33)$$

Substituting (5.31) into (5.20) or (5.21) and plugging into (5.18), then integrating over all final states k' , we obtain the total probability per unit time that an electron with wave vector $\vec{k}$ will be scattered by an LO phonon,

$$\frac{1}{\tau} = \frac{e^2 \omega \sqrt{m_{eff}}}{4\pi \epsilon_0 \hbar \sqrt{2}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \frac{(1 + 2\alpha E')}{\gamma^{1/2}(E)} F_0(E, E') \cdot N_0(\omega, T), \quad (5.34)$$

where,

$$E' = \begin{cases} E + \hbar \omega & \text{absorption} \\ E - \hbar \omega & \text{emission} \end{cases} \quad (5.35)$$

$$N_0(\omega, T) = \begin{cases} n_{BE}(\omega, T) & \text{absorption} \\ n_{BE}(\omega, T) + 1 & \text{emission} \end{cases} \quad (5.36)$$

and,

$$F_0(E, E') = C^{-1} \left(A \ln \left| \frac{\gamma^{1/2}(E) + \gamma^{1/2}(E')}{\gamma^{1/2}(E) - \gamma^{1/2}(E')} \right| + B \right), \quad (5.37)$$

with,

$$A = \left[2(1 + \alpha E)(1 + \alpha E') + \alpha \{ \gamma(E) + \gamma(E') \} \right]^2 \quad (5.38)$$

$$B = -2\alpha \cdot \gamma^{1/2}(E) \cdot \gamma^{1/2}(E') \left[4(1 + \alpha E)(1 + \alpha E') + \alpha \{ \gamma(E) + \gamma(E') \} \right] \quad (5.39)$$

$$C = 4(1 + \alpha E)(1 + \alpha E')(1 + 2\alpha E)(1 + 2\alpha E'). \quad (5.40)$$

If we take $\alpha = 0$, equation (5.34) reduces to equations (5.25) and (5.26).

5.7. An analytic model for the relaxation of charge carriers within an exponential density-of-states

Here we present a general model for the relaxation of electrons within a continuum of states below the conduction band minimum (CBM), considering decay into lower-lying acceptor states as well as re-population due to electrons relaxing from higher-energy states. We go on to show that the exponential dependence of electron lifetime on the electronic state energy, as observed in two-pulse correlation (TPC) measurements (c.f. Figure 5.7), is consistent with an exponential distribution of states below the CBM. We use this result to calculate the average trap energy from electron relaxation dynamics in the vicinity of the CBM.

Consider the population and depopulation of [surface] states with energy between E_j and $E_j + \delta E$ by electrons. Let $n(E_j)$ be the number of electrons (per cm^2) occupying states within this energy range, and let $\rho(E_j)\delta E$ be the number of states (per cm^2) within this range. Fermi's Golden Rule dictates that the probability of an electronic transition to

a state with given energy is proportional to the density of accepting states. Therefore, the rate of change of electron population $n(E_j)$ is given by,

$$\frac{dn(E_j, t)}{dt} = \sum_{E_i > E_j} k_{ij} n(E_i, t) \rho(E_j) \delta E - \sum_{E_i < E_j} k_{ji} n(E_j, t) \rho(E_i) \delta E, \quad (5.41)$$

where k_{ij} is the rate constant for transitions from a state with energy E_i to a state with energy E_j , and k_{ij} contains, among other parameters, the matrix element for the transition. The first term on the right-hand-side (RHS) of Eq. (5.41) represents the population of states with energies between E_j and $E_j + \delta E$ by electrons relaxing from all states with energies $E_i > E_j$. The second term on the RHS of Eq. (5.41) represents the depopulation of states with energies between E_j and $E_j + \delta E$ by electrons decaying into all states with energy $E_i < E_j$. In writing Eq. (5.41) we have implicitly assumed that saturation effects are unimportant, i.e. $\rho(E_j) \delta E \gg n(E_j)$. For a continuum of states Eq. (5.41) is re-written as an integral-differential equation,

$$\frac{dn(E_j, t)}{dt} = \int_{E_j}^{E_c} k_{ij} n(E_i, t) \rho(E_j) dE_i - \int_{-\infty}^{E_j} k_{ji} n(E_j, t) \rho(E_i) dE_i, \quad (5.42)$$

where E_c is the energy at the CBM. Since electronic transitions within the surface state (SS) manifold are phonon-assisted, only states within an energy range $E_j + \sigma$ will contribute to the population of states at energy E_j , where the parameter σ reflects the bandwidth of available phonon modes. Similarly, only states having energies within $E_j - \sigma$ will serve as acceptors for decay from states at energy E_j . If we assume that the rate coefficient for transition between states i and j is independent of energy within the neighborhood of σ around E_j , then $k_{ij} \rightarrow k_d$, and the rate equation becomes,

$$\frac{1}{k_d} \frac{dn(E_j, t)}{dt} = \rho(E_j) \int_{E_j}^{E_j + \sigma} n(E_i, t) dE_i - n(E_j, t) \int_{E_j - \sigma}^{E_j} \rho(E_i) dE_i. \quad (5.43)$$

Equation (5.43) is straightforward to solve numerically if assumptions are made about $\rho(E)$ and the initial conditions on $n(E)$. One would proceed by solving the differential equation at highest energy first, so that the first term on the RHS is zero, then continue by solving the differential equation again at all lower energies so that a full

profile of $n(E, t)$ is developed. However, it is perhaps more enlightening to seek analytic solutions for $n(E, t)$ when suppositions about $\rho(E)$ can be made. If $\rho(E)$ is exponentially distributed in energy below the CBM,

$$\rho(E) = \rho_o e^{-(E_c - E)/m_c}, \quad (5.44)$$

then Eq. (5.43) becomes,

$$\begin{aligned} \frac{1}{k_d \rho_o} \frac{dn(E_j)}{dt} &= e^{-(E_c - E_j)/m_c} \int_{E_j}^{E_j + \sigma} n(E_i) dE_i - n(E_j) \int_{E_j - \sigma}^{E_j} e^{-(E_c - E_i)/m_c} dE_i \\ &= e^{-(E_c - E_j)/m_c} \int_{E_j}^{E_j + \sigma} n(E_i) dE_i - n(E_j) m_c e^{-(E_c - E_j)/m_c} [1 - e^{-\sigma/m_c}], \end{aligned} \quad (5.45)$$

where we have stopped writing the time dependence of $n(E)$ explicitly. If σ is small, then the integral over higher-energy states can be approximated by $n(E_j) \cdot \sigma$ and Eq. (5.45) becomes,

$$\begin{aligned} \frac{1}{k_d \rho_o} \frac{dn(E_j)}{dt} &= -n(E_j) \cdot e^{-(E_c - E_j)/m_c} \cdot [m_c (1 - e^{-\sigma/m_c}) - \sigma] \\ &= -n(E_j) \cdot e^{-(E_c - E_j)/m_c} \cdot C(\sigma), \end{aligned} \quad (5.46)$$

where $C(\sigma)$ is a constant that depends on σ and m_c . Expanding the term $e^{-\sigma/m_c}$ in a Taylor series,

$$e^{-\sigma/m_c} = 1 - \frac{\sigma}{m_c} + \frac{\sigma^2}{2m_c^2} - \dots, \quad (5.47)$$

and keeping terms up to second order in σ / m_c , we find that $C(\sigma)$ reduces to,

$$C(\sigma) \approx \frac{\sigma^2}{2m_c}. \quad (5.48)$$

Rearranging (5.46), we obtain,

$$\frac{dn(E_j)}{dt} = -\frac{n(E_j)}{\tau_j}, \quad (5.49)$$

where,

$$\tau_j = \frac{2m_c e^{(E_c - E_j)/m_c}}{k_d \rho_o \sigma^2} \quad (5.50)$$

The solution of Eq. (5.49) is simply,

$$n(E_j, t) = n_o(E_j) \cdot e^{-t/\tau_j} \quad (5.51)$$

where the experimentally observed apparent lifetime, τ_j , of an electron residing in a state with energy E_j is given by Eq. (5.50). Thus, for an exponential distribution of states below the CBM, electron populations at all energies are expected to follow single-exponential decay dynamics where the lifetime increases exponentially with decreasing SS energy. Additionally, the parameter m_c , which describes the average depth of the SS distribution, is uniquely determined by a fit of the TPC lifetime, τ_j , to the form $\tau_j \propto \exp[(E_c - E_j)/m_c]$.

Chapter 6

Structure and Optical Properties of Electronically-Coupled Arrays of PbSe Quantum Dots

Portions of this chapter have been published as:

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W.A. Tisdale, K.J. Williams, B.A. Timp, D.J. Norris, E.S. Aydil, and X.-Y. Zhu, “Hot-Electron Transfer from Semiconductor Nanocrystals”, *Science* **328**, 1543 (2010).

In this Chapter, we detail the changes that occur when two-dimensional arrays of colloidal PbSe quantum dots (QD) are subjected to chemical treatment with either hydrazine (HYD) or 1,2-ethanedithiol (EDT). We determine, using atomic force microscopy (AFM), that these treatments lead to a significant reduction in inter-QD spacing, consistent with removal of the native long-chain oleic acid ligands that coat the surface of each PbSe QD. Fourier transform near-infrared (FT-NIR) spectroscopy reveals large red-shifting of the first optical transition energy that cannot be explained by solvatochromism alone. These red-shifts are attributed to strong and tunable electronic coupling between neighboring QDs in the chemically treated 2D arrays. Further, we find that the electronic coupling in these 2D QD assemblies is an order of magnitude larger

than in 3D assemblies, which is likely due to decreased “geometric frustration” within the 2D film. Finally, we show that treatment of the QD film with either EDT or hydrazine reveals a rich assortment of ultrafast dynamical processes in highly excited PbSe QDs that can be followed with time-resolved nonlinear optical techniques. These dynamics include the temperature-dependent relaxation of hot charge carriers and coherent excitation of a previously-unidentified PbSe surface phonon mode at $75 \pm 10 \text{ cm}^{-1}$. These findings have implications for the use of PbSe QD films in optoelectronic devices, such as photodetectors (170) and solar cells (22, 75, 76).

6.1. Introduction

The processing of electronic materials using solution-based techniques such as roll-to-roll transfer, dip coating, spin coating, or inkjet printing can offer significant cost savings compared to traditional vacuum-based techniques and will be necessary for the realization of low-cost large-area flexible electronics. Colloidal semiconductor nanocrystals, or quantum dots, are attractive solution-processable materials because of the ease with which their electronic and optical properties can be tuned and their chemistry can be manipulated (171). The use of solution-cast quantum dot solids in electronic and optoelectronic devices requires high charge carrier mobility, which is determined by the electronic exchange coupling energy between neighboring quantum dots (172-175). However, the presence of long-chain surface ligands, which are required for synthesis, colloidal stability, and electronic passivation, leads to poor conductivity in QD films due to weak inter-QD electronic coupling resulting from the large separation distance between neighboring nanocrystal cores.

For PbSe QDs, a popular strategy for increasing the conductivity of deposited films has been the exchange or removal of native oleic acid (OA) capping ligands by post-deposition chemical treatment of the QD film (175-177). Talapin & Murray were the first to show that hydrazine (N_2H_2), a powerful nucleophile and reducing agent, is an effective chemical species for increasing the conductivity of PbSe QD films (175). Law *et al.* corroborated these findings to some extent, but also showed that hydrazine leads to

only partial removal of the surface ligands (176). Later, Luther *et al.* showed that a short-chain dithiol such as 1,2-ethanedithiol (EDT) could be used to quantitatively substitute for oleic acid on the surface of PbSe QDs, resulting in a QD film that is both strongly coupled (due to short inter-QD separation) and electronically passivated (177). In this Chapter, we summarize our own studies into the structural, optical, and ultrafast nonlinear optical changes that take place when thin films of PbSe QDs supported on SiO₂ and TiO₂ are treated with hydrazine or EDT.

6.2. Sample preparation

Colloidal PbSe nanocrystals were synthesized based on methods developed by Murphy *et al.* (178) and Luther *et al.* (177). In a typical synthesis, PbO (2.5 g), oleic acid (OA, 9 mL), and 1-octadecene (35 mL) were placed in a three-neck round-bottom flask. The reaction flask was then degassed to <40 mTorr while stirring vigorously and purging with dry nitrogen gas. The degassing process was repeated three times. The reaction vessel was heated to 180 °C under nitrogen and was maintained at that temperature for approximately 1 hr while the precursor solution turned optically clear. Meanwhile, a solution of Se dissolved in trioctylphosphine (TOPSe; 1.0 M, 21 mL total volume) was prepared and loaded into syringes inside a nitrogen glovebox. 15 mL of cold (0°C) anhydrous toluene was loaded into separate syringes. The TOPSe precursor was removed from the nitrogen glovebox and immediately injected into the reaction vessel. The temperature of the reaction solution was maintained at 150 °C during nanocrystal growth. UV/visible/near-infrared absorption measurements (Cary 5E) were used to monitor nanocrystal growth. Once the desired nanocrystal size was obtained (growth time varied from 30 s to 10 min), the heat source was removed from the reaction vessel and 15 mL of anhydrous toluene was swiftly injected into the vessel. The reaction vessel was rapidly cooled to room temperature using an ice bath. The reaction product was cannulated from the reaction vessel into a Schlenk flask and transferred into the nitrogen glovebox. All post-synthesis methods necessary to prepare clean nanocrystal dispersions were carried out in the nitrogen glovebox. The PbSe nanocrystals were precipitated out of the growth

solution using a mixture of anhydrous methanol, butanol, and 200 proof ethanol (1:1:2, respectively) and isolated after centrifuging. The supernatant was discarded and the nanocrystals were re-dispersed in dry hexane. Precipitation with 200 proof ethanol followed by re-dispersion in dry hexane was repeated three times. The final product was a solution (variable concentration) of oleic acid-capped PbSe nanocrystals (OA-PbSe) in hexane.

Nanocrystal size was determined by the energy of the first peak in the optical absorption spectrum as calibrated by Dai *et al.* (179). The first exciton absorption energies for the OA-capped nanocrystals used in this study were 0.62 eV (2010 nm), 0.67 eV (1860 nm), 0.70 eV (1770 nm), 0.71 eV (1740 nm), 0.80 eV (1540 nm), 0.84 eV (1470 nm), 0.90 eV (1380 nm), 0.97 eV (1270 nm), 1.12 eV (1110 nm), and 1.14 eV (1080 nm) corresponding to nanocrystal diameters of 6.7 nm, 6.1 nm, 5.8 nm, 5.7 nm, 5.0 nm, 4.7 nm, 4.4 nm, 4.0 nm, 3.4 nm, and 3.3 nm, respectively. The same peak positions sized according to the work of Moreels *et al.* (180) would yield nanocrystal diameters of 7.6 nm, 6.7 nm, 6.2 nm, 6.1 nm, 5.0 nm, 4.7 nm, 4.2 nm, 3.6 nm, 2.9 nm, and 2.8 nm, respectively. Selected optical absorption spectra are shown in Figure 6.1.

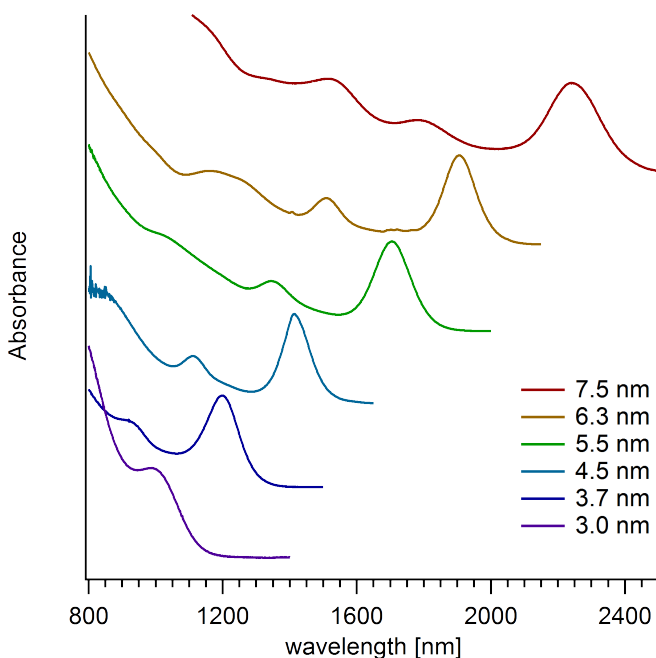


Figure 6.1 Optical absorption spectra for selected sizes of OA-capped PbSe nanocrystals dispersed in CCl_4 . The spectra have been offset for clarity. Nanocrystal diameter was determined

by the position of the lowest-energy absorption feature according to the sizing curve of Dai *et al.* (179).

Single crystal rutile TiO₂ was purchased from MTI Corporation (Richmond, CA). The <110> oriented crystals were 10 mm x 10 mm square, 1 mm thick, and mechanically polished on both sides. In-plane crystallographic orientation was determined by optical birefringence at 532 nm. Atomically flat surfaces were obtained by successive rinsing with 0.2 M NaOH then deionized water, followed by immersion in 1 M HCl under UV irradiation (254 nm) for 30 min and finally rinsing with deionized water and acetone in air (181).

Laser quality fused silica flats were purchased from CVI Melles Griot (Albuquerque, NM). The 15 mm diameter x 1 mm thick circular substrates were cleaned by sonication in acetone followed by immersion in 1 M HCl then rinsing with deionized water in air.

All PbSe QD films were prepared in a controlled atmosphere argon glovebox to prevent PbSe oxidation. Clean substrates were rinsed with distilled hexane before partial submersion in the OA-PbSe/hexane solution followed by withdrawal at a constant velocity of 1 cm/s. Desired coverage of the TiO₂ substrate was achieved by varying the concentration of the OA-PbSe/hexane solution (typically ~5 mg/mL) and verified by atomic force microscopy (AFM). The dip-coating process yielded samples that were optically uniform over a large area in the center of the substrate with drying lines visible at the top of the sample and along the edges.

Dried OA-PbSe films were submerged in a solution of 1 M hydrazine (HYD) in acetonitrile for 20 min at room temperature then dried under argon. The HYD concentration was chosen following the work of Law *et al.*, who showed removal of oleic acid without change in nanocrystal size or chemical reduction of PbSe (176). The reaction time was chosen based on the continuous red shift of the first absorption peak during the first 10-15 min of HYD treatment followed by saturation of the red-shifted peak position with increasing duration of HYD treatment (see Section 6.5).

Following the work of Luther *et al.* (177), dried OA-PbSe films were submerged in a solution of 0.1 M 1,2-ethanedithiol (EDT) in acetonitrile for 30 seconds at room temperature then dried under argon.

For laser experiments, each sample was clamped to a cold finger inside a Janis ST-300 liquid helium cryostat. To prevent exposure of the sample to ambient atmosphere, the cryostat was loaded and sealed inside the argon glovebox. The cryostat was evacuated to less than 1 mTorr base pressure for at least one hour using a liquid nitrogen-cooled cryopump before making measurements.

6.3. Experimental methods

Atomic force microscopy was carried out on a humidity-controlled (<5% RH) Agilent 5500 scanning probe microscope with a ~100-micron (X-Y range) scanner operated in open loop. A silicon tip integrated with a rectangular, uncoated silicon cantilever (Applied Nanostructures, <10 nm radius of curvature, 3 N/m nominal spring constant, resonance frequency of 67.30 kHz, and quality factor of ≈ 140) was used in AC mode so as to place the oscillator in the net attractive regime (diagnosed via the phase signal) at a drive frequency (67.53 kHz) above resonance and a set point amplitude of approximately 95% of the free oscillation amplitude (≈ 15 nm; i.e., low kinetic energy, low tip-sample dissipation). This minimal-perturbation configuration was generally needed for successful imaging, to avoid capillary transfer of nanoparticles to the AFM tip, as readily occurred at ambient humidity and/or in a net repulsive regime (i.e., “true tapping”, achieved at higher free-oscillation amplitude, lower set point or lower drive frequency).

We use Fourier transform infrared (FTIR) and near-infrared (FT-NIR) spectroscopy in multiple total internal reflection geometry for spectroscopic characterization of PbSe nanocrystal films on TiO₂. Large rutile single crystals oriented <110> and mechanically polished on both sides were purchased from Princeton Scientific Corporation (Princeton, NJ). These 1 mm thick crystals were cut to 32 mm x 10 mm with a polished 45° bevel on both ends to be used as ATR-FTIR waveguides. PbSe nanocrystal films were prepared on the exposed (110) surface as described. Measurements were carried out inside a nitrogen glovebox using a Nicolet 6700 FTIR-NIR spectrometer with either an InGaAs (FT-NIR) or liquid nitrogen-cooled mercury-

cadmium-telluride (FTIR) detector. Periodic interference fringes in the absorption spectrum due to strong TiO₂ birefringence were removed by narrowband Fourier filtering.

X-ray photoelectron spectroscopy (XPS) was used for compositional analysis of treated samples and to check for Pb oxidation following laser irradiation. Spectra were collected at room temperature in an ultrahigh vacuum spectrometer equipped with a hemispherical electron energy analyzer (Phi 5400). A Mg K_α ($h\nu = 1253.6$ eV) anode operated at 200 W was used as the X-ray source. The X-ray incidence angle was 5° from surface normal and photoelectrons were collected at 55° from surface normal. A sealed transfer vessel was used for transporting samples from the glovebox to the XPS loading chamber air-free. Due to the high resistivity of the TiO₂ substrates, some modest sample charging was observed (less than 2 eV). To correct for this effect, energy scales were referenced to the Ti 2p binding energy of 458.6 eV (182).

Details of the TR-SHG experimental setup are available in Chapter 4. Briefly, the sample is mounted in a controlled atmosphere liquid helium cryostat with fused silica windows. We use 50fs pulses of 810 nm (1.53 eV) light both to photoexcite (pump) the nanocrystals and detect (probe) the second harmonic response. The intensity of reflected second harmonic light at 405 nm ($I^{(2\omega)}$) was recorded as a function of time delay between the pump and probe pulses. The polarization (p or s) of the fundamental was controlled and that of the second harmonic independently detected to isolate specific components of the nonlinear susceptibility tensor. The pump and probe beams are softly focused non-collinearly at a mutual angle of ~3° onto the sample surface. The projection of the beam on the sample at 45° incidence is a 260 μm × 360 μm ellipse, as measured by the knife-edge technique. The laser power is kept sufficiently low to maintain a spatially averaged fluence of less than 1 mJ/cm² for both pump and probe pulses. For all samples at all temperatures, the time-resolved second harmonic (TR-SH) response is observed to be independent of pump beam polarization. Unless otherwise indicated, all TR-SH data shown here were collected with orthogonally polarized pump and probe beams to minimize coherent artifacts near $t = 0$ (particularly scattered SF light). A typical TR-SHG waveform takes about one hour to collect and is the result of averaging ~20 scans at 300 time points per scan.

A pump laser fluence of 1 mJ/cm^2 corresponds to an average photoexcitation of one electron-hole pair per nanocrystal for the smallest PbSe nanocrystals used. We have investigated the power dependence of the SH response to laser fluences as low as 0.03 mJ/cm^2 . Only the magnitude of the SH response changes; the dynamics and overall shape of the TR-SH response function are unchanged. We also routinely check the TR-SH response at multiple locations on the sample surface. Again, the magnitude of the response varies due to spatial variation in PbSe surface concentration, but the dynamics are unchanged. Dynamics are also invariant with storage of the sample within the cryostat for days at a time or transferring the sample back to the glovebox for later re-evaluation.

Due to the quadratic dependence of SHG intensity on incident laser power, it is desirable to use high laser fluences in order to obtain large signal-to-noise ratios. However, high laser power can damage the PbSe nanocrystals and the TR-SH response under high intensity light may not reflect dynamics under the low excitation conditions characteristic of solar radiation. To assess the effects of prolonged laser irradiation, we continuously monitor the TR-SH waveform during data collection. For the chemically-treated PbSe films investigated here, the only variations in the TR-SH waveform we observe over the course of hours are small changes in the magnitude of the signal due to drifting laser power.

Fused silica, an insulating amorphous SiO_2 glass, is used as the substrate supporting PbSe QD films in the TR-SHG studies. Silica has a vanishingly small nonlinear susceptibility such that nearly all SHG intensity is attributable to the QDs. Additionally SiO_2 has a band gap much too large to allow QD-substrate electronic coupling. All TR-SHG data collected on QD-covered SiO_2 substrates exhibit a broad (500-800 fs FWHM) symmetric peak in intensity centered at $t = 0$ that is due to efficient sum-frequency (SF) generation of light scattered from the nanocrystal film and internally reflected off the back surface of the SiO_2 substrate (104, 109). The intensity of this scattered SF component increases substantially following treatment with HYD or EDT due to changes in the nanocrystal film morphology as observed via AFM. The data shown in this chapter have had this SF component removed for clarity.

The oxidation of PbSe nanocrystals in air is well documented (177). When the PbSe surface becomes oxidized, peaks in the XPS spectrum due to core level

photoemission from oxygen-bound Pb will appear 1.0 eV higher in binding energy than the selenium-bound Pb (183). To be sure that laser irradiation does not lead to photo-oxidation of the PbSe surface under the residual atmosphere within the cryostat (base pressure < 1 mTorr), we measured the XPS spectrum of a 1 ML HYD-treated film after one day's worth of laser experiments (Fig. S5). The sample was transferred to a sealed vessel inside the glovebox for air-free transfer to the XPS vacuum chamber. The Pb 4f peaks are Gaussian in shape without detectable asymmetry toward higher binding energies, indicating that the PbSe surface is free from oxidation

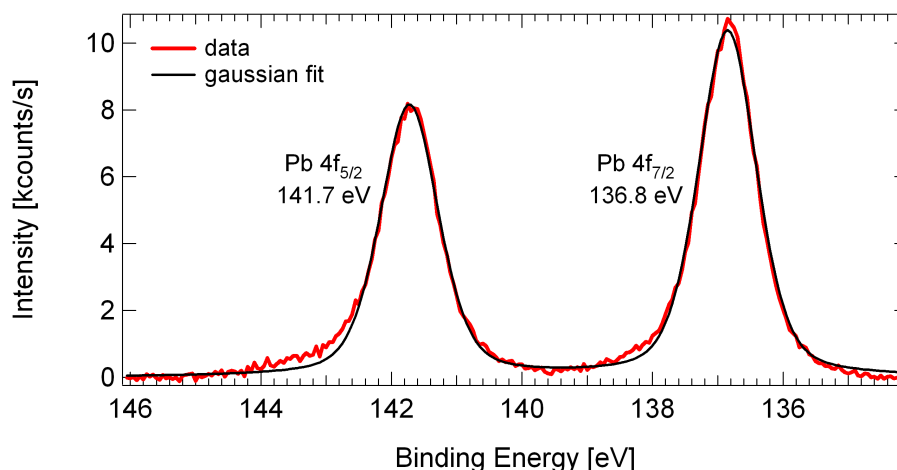


Figure 6.2 XPS spectrum in the vicinity of Pb 4f core level photoemission. The sample is 1 ML PbSe nanocrystals on TiO₂ (110) treated with HYD. This spectrum was collected after typical daily TR-SHG measurements. Following laser experiments, the sample was transferred to a sealed vessel inside the glovebox for air-free transfer to the XPS vacuum chamber. The XPS spectrum shows two Gaussian peaks without significant asymmetry toward higher binding energies, indicating that the PbSe surface is free from oxidation. A linear background has been subtracted.

6.4. Film morphology and structural rearrangement

In Figure 6.3, atomic force micrographs of a submonolayer of PbSe QDs on a (110) TiO₂ surface taken before and after the hydrazine exposure (3 min.) are shown. Before exposure (Figure 6.3a), the surface is characterized by a network of two-dimensional islands. The magnified image (Figure 6.3b) clearly reveals hexagonally

close-packed domains with an inter-QD distance of 10 ± 1 nm. This is also the height of the islands, as shown by the blue histogram in Figure 6.3e. The inter-QD distance and the island height is consistent with the diameter of the QDs ($d = 6 \text{ nm} \pm 5\%$) plus a 2 nm surface layer due to the oleic acid ligands. After hydrazine exposure, the AFM image (Figure 6.3c) reveals two effects. First, as shown by the red histogram in Figure 6.3e, the island height decreases to 6 ± 1 nm, which is identical to the size of bare QDs (*i.e.*, without their surface ligands). Second, individual QDs can no longer be resolved in the images. Both effects would be expected if the oleic acid ligands were removed and the inter-QD separation decreased. The removal of the oleic acid is also verified below by vibrational spectroscopy (see Section 6.5). Instead of individual QDs, the magnified image (Figure 6.3d) shows larger domains (lateral size 20-40 nm) that are separated by boundaries. This behavior is consistent with two-dimensional densely packed islands of QDs that suddenly lose their surface ligands while exhibiting limited mobility on the substrate. In such a case, the large islands break up into domains. Our data would then suggest that these domains correspond to 2D aggregates of 10-100 closely packed bare QDs. We estimate that the surface coverage of these 2D aggregates in our sample is $\sim 20\text{-}30\%$ of a monolayer (ML).

Note that after hydrazine treatment, we also see a broadening of the height distribution (Figure 6.3e). This is consistent with the presence of more disorder in the 2D assemblies and the break-up of large islands as oleic acid capping molecules are removed. For small domains on the order of or smaller than the tip size, convolution of tip shape with the topography of the 2D aggregates (including some individual QDs) tends to smear out and broaden the height distribution in a topographical AFM image.

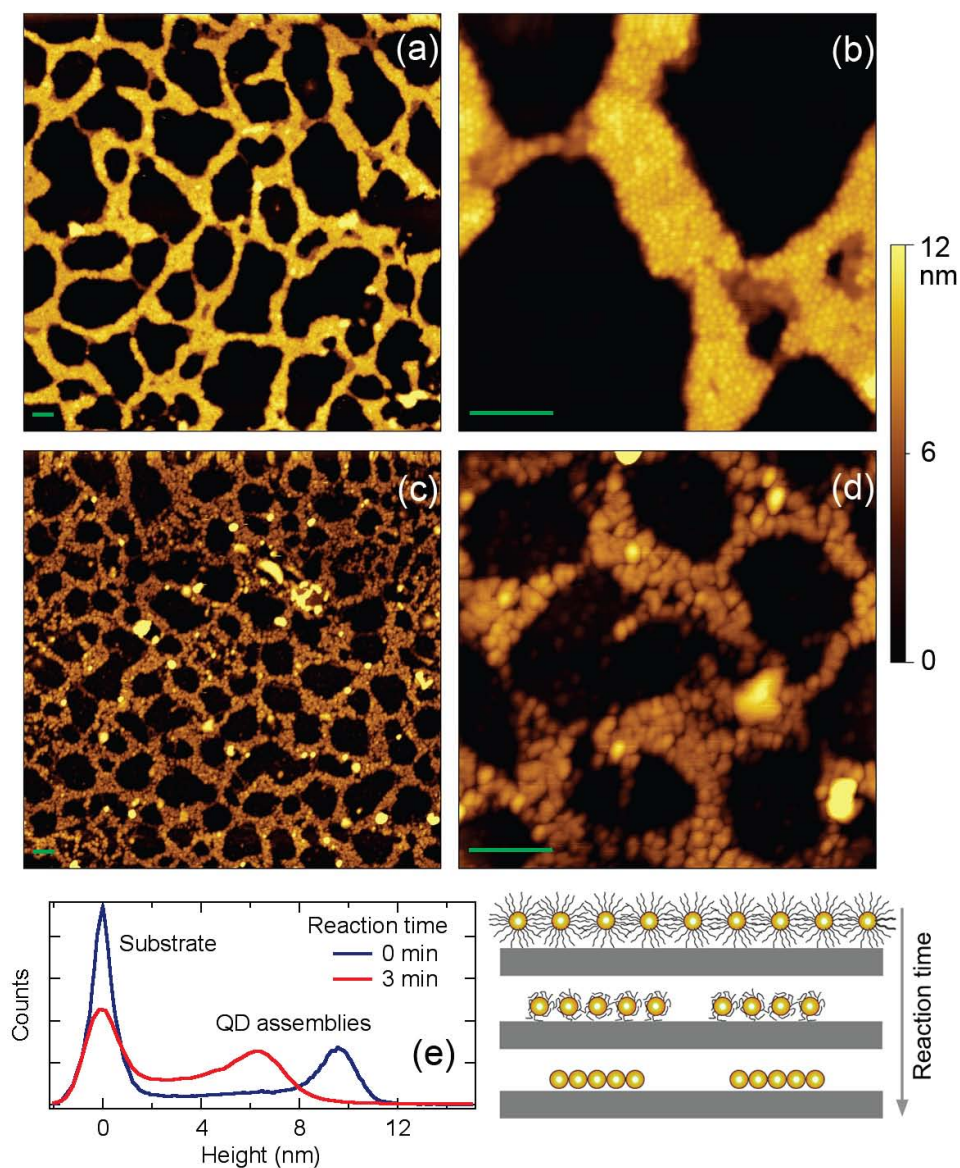


Figure 6.3 Attractive-regime AC-mode atomic force microscopy (AFM) images of sub-monolayers of PbSe QDs assembled on TiO₂(110): (a) and (b) as-deposited QDs with oleic acid surface ligands; (c) and (d) after exposure to 1M hydrazine in acetonitrile for 3 min. (b) and (d) are magnified scans of (a) and (c), respectively. All green scale bars are 100 nm. (e) A height histograms of images (a) and (c). The cartoon illustrates proposed morphology changes with reaction time. Note that the surface coverage of QDs in (a) and (c) are slightly different due to variations in the dip-coating process.

6.5. Chemical composition, solvatochromism, and strong electronic coupling

A great deal of information can be obtained from ATR-FTIR spectra of these films. The hydrazine exposure induces two major changes. First, the C-H stretch at $\sim 2920\text{ cm}^{-1}$ (362 meV) disappears (Figure 6.4a), consistent with removal of oleic acid. The residual and poorly resolved C-H stretch that remains may be attributed to background contaminants, as it is also present in the spectrum from a clean TiO_2 surface. Second, a systematic red-shift in the first exciton peak with increasing hydrazine exposure time is observed (Figure 6.4b). For ~ 0.2 ML of 6 nm PbSe QDs on TiO_2 , this peak shifts from 5650 cm^{-1} (700 meV) to 5000 cm^{-1} (620 meV) after 10 minutes of exposure to 1 M hydrazine in acetonitrile. This shift is independent of the nature of the substrate surface, as a nearly identical shift is observed for the same coverage of PbSe QDs assembled on the SiO_2 terminated Si surface. However, the red-shift is not observed when the starting coverage of PbSe QDs is significantly lower, as shown in Figure 6.4c for 0.02 ML after hydrazine exposure for 70 minutes. Finally, the magnitude of the red-shift depends on the size of the QDs. For smaller QDs of $d = 4$ nm, the maximum red-shift is almost twice as large as that of $d = 6$ nm. Note that hydrazine treatment of the 0.2 ML samples also increase the absorbance at energies higher than the first exciton transition (Figure 6.4b). This has been observed before for multilayer PbSe thin films and was attributed to enhanced electronic exchange coupling between QDs (176, 177), although changes in light scattering may also play a role.

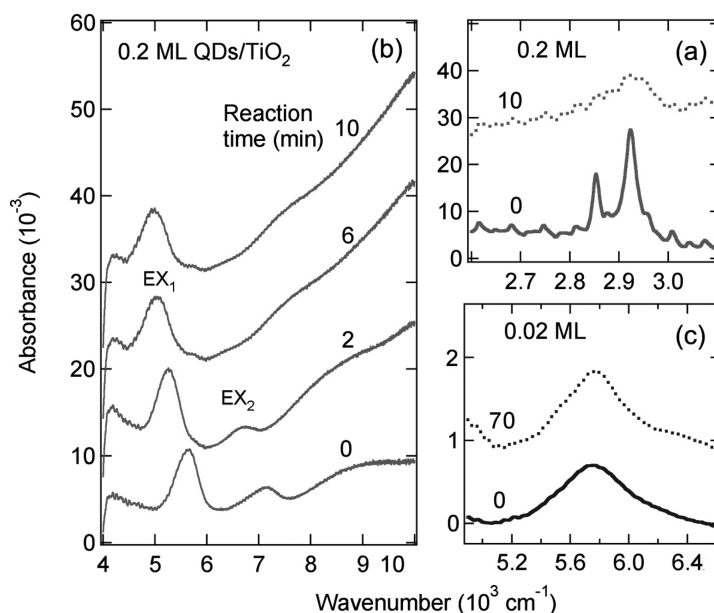


Figure 6.4 (a) ATR-FTIR spectra in the C-H stretch region of a ~ 0.2 ML film of oleic-acid-capped PbSe QDs on TiO_2 before (solid line) and after (dotted line) exposure to 1M hydrazine in acetonitrile for 10 minutes. (b) ATR-FTIR spectra in the exciton region (EX_1 and EX_2 label the first and second exciton transitions, respectively) of the same surface as a function of reaction time in 1 M hydrazine in acetonitrile. (c) ATR-FTIR spectra of ~ 0.02 ML oleic acid capped PbSe QDs on TiO_2 (solid) and after exposure to 1M hydrazine in acetonitrile for 70 minutes (dotted).

The left panel in Figure 6.5 summarizes the observed shift of the first exciton transition energy as a function of reaction time for ~ 0.2 ML of 4 nm QDs on TiO_2 (grey triangles), ~ 0.2 ML of 6 nm QDs (red circles on TiO_2 and green diamonds on SiO_2 -terminated silicon), and ~ 0.02 ML of 6 nm QDs on SiO_2 (squares). For the low surface coverage (0.02 ML), the exciton transition energy does not change with hydrazine exposure time. For the high surface coverages (0.2 ML), the exciton transition energy as a function of exposure time can be described well by an exponential decay (solid curves) for both sizes and most of the shifting occur within the first 10 minutes of reaction time. In contrast to peak position, the linewidth of the first exciton absorption peak only change slightly following hydrazine treatment ($\leq 10\%$ increase), as shown in the right panel for 6 nm PbSe QDs.

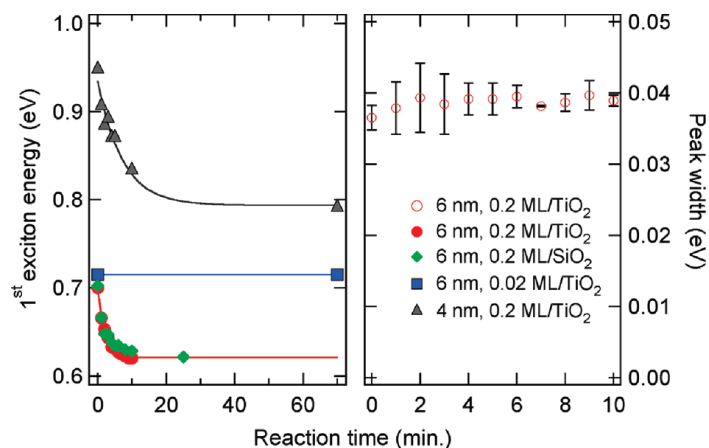


Figure 6.5 Right: width of the first exciton absorption peak as a function of the exposure time to 1 M hydrazine for 0.2 ML of 6 nm QDs on TiO₂. Left: Energy of the first exciton transition as a function of the exposure time to 1M hydrazine in acetonitrile for the indicated surface coverage and QD diameter (red: 0.2 ML of 6 nm QDs, blue: 0.02 ML of 6 nm QD, grey: 0.2 ML of 4 nm QDs) on SiO₂ (green) and TiO₂ (all other colors).

When the OA-capped PbSe QD film is exposed to 0.1 M 1,2-ethanedithiol (EDT) in acetonitrile, similar red-shifting of the first exciton transition energy is observed. However, the magnitude of the red-shift is consistently less than the hydrazine-induced red-shift by more than half. In Figure 6.6, a comparison is made between hydrazine and EDT treatments for similar-sized PbSe QDs. After exposure to hydrazine the first exciton peak shifts to the red by $\sim 660 \text{ cm}^{-1}$ (82 meV). If instead of hydrazine the OA-capped PbSe QD film is exposed to EDT, the red-shift is only $\sim 210 \text{ cm}^{-1}$ (26 meV). Additionally, composition analysis by X-ray photoelectron spectroscopy (XPS, not shown) clearly indicates the presence of sulfur within the EDT-treated film. In contrast, XPS analysis of hydrazine-treated films shows no detectable presence of nitrogen left behind. This collection of evidence suggests that the action of hydrazine is to strip away the oleic acid ligands leaving behind a nominally bare QD surface, whereas the action of EDT is to substitute for the oleic producing a thiol-passivated QD surface with a thin ligand shell (Figure 6.7).

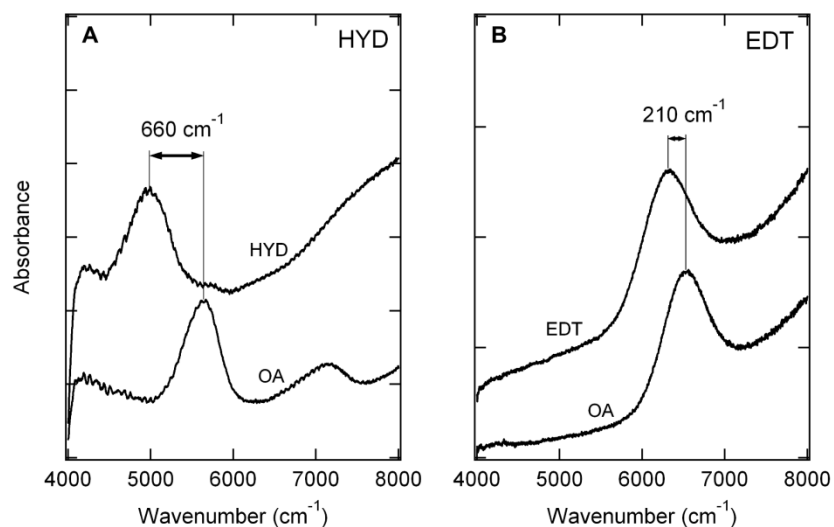


Figure 6.6 Dependence of the first exciton peak position on chemical treatment. (A) 5.8 nm PbSe nanocrystals capped with the native oleic acid (OA) ligands and after exposure to 1.0 M hydrazine (HYD) in acetonitrile for 10 min. The first exciton peak shifts 660 cm^{-1} (82 meV) toward the red following HYD treatment. (B) 5.0 nm PbSe nanocrystals capped with the native OA ligands and after exposure to 0.1 M 1,2-ethanedithiol (EDT) in acetonitrile for 30 s. The first exciton peak shifts only 210 cm^{-1} (26 meV) toward the red following EDT treatment.

For thicker QD films, the red-shift of the first exciton transition energy is much smaller. Figure 6.8 shows FTIR spectra for a 20 nm thick film of PbSe QDs (diameter slightly less than 6 nm) deposited on the SiO_2 -terminated Si surface. With increasing time of hydrazine exposure, we see up to 80% loss of oleic acid ligands for a total reaction time of 60 minutes (left panel). The first exciton transition red-shifts by a total of 204 cm^{-1} (25 meV), right panel. This red-shift is a factor of 3-4 smaller than that for the submonolayer coverage.

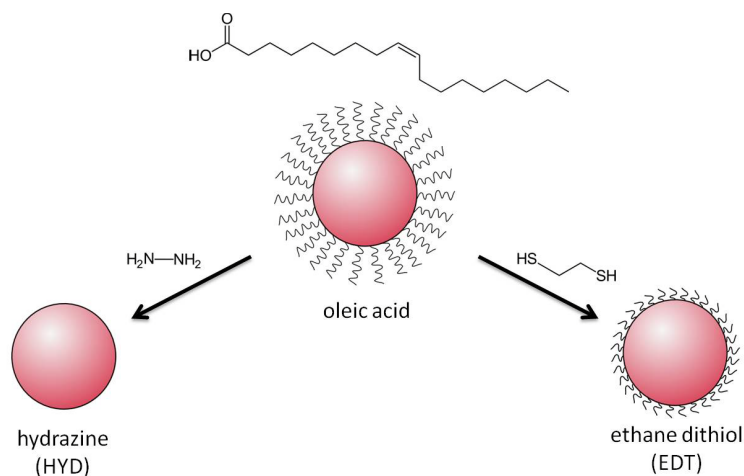


Figure 6.7 Schematic comparison of the hydrazine and EDT treatments. As-prepared, our PbSe QDs are covered with a layer of long-chain oleic acid ligands. After treatment with hydrazine, the oleic acid ligands are stripped leaving a nominally bare QD surface. In contrast, EDT substitutes for the native oleic acid ligands resulting in the presence of a thin ligand shell.

There are several possible explanations for the red-shift of the first exciton transition energy following treatment of the PbSe QD film with hydrazine or EDT. One possibility is that the chemical treatment causes QD growth, resulting in smaller confinement energies and a correspondingly narrower effective band gap. This explanation can be eliminated because growth of one QD can only occur at the expense of another. Such a ripening mechanism would lead to a broadening of the first exciton transition, which is not observed. The absorption spectrum retains its sharp excitonic features, indicating that a monodisperse QD population remains after chemical treatment. Law *et al.* also arrived at the same conclusion following their studies of hydrazine treatment of PbSe nanocrystals (176). A second possible explanation, which would account for the large difference in the magnitude of the red-shift between monolayer and multilayer QD films, involves strong QD-substrate electronic interactions. This, too, can be eliminated as a possibility because the magnitude of the red-shift is independent of substrate material. This is particularly significant for the case of SiO₂, where PbSe electron and hole energy levels reside deep within the SiO₂ band gap, negating the possibility of strong adsorbate-substrate electronic interactions. Further, we observe no red-shift for isolated QDs (Figure 6.4c), suggesting that the interaction responsible for the red-shift is between neighboring QDs.

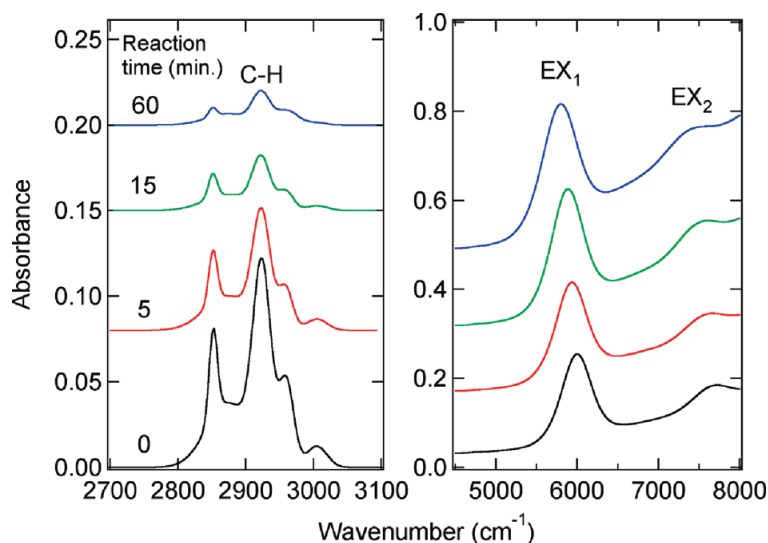


Figure 6.8 ATR-FTIR spectra for a 20 nm thick film of oleic-acid-capped PbSe QDs (~6 nm diameter) on SiO₂ as a function exposure time to 1M hydrazine in acetonitrile for 0-60 minutes. The panel on the left shows the C-H stretch region; the panel on the right shows the region near the first (EX₁) and second (EX₂) exciton transitions. The red-shift for this thicker film (~200 cm⁻¹; 25 meV) is 3-4 times smaller than what is observed in monolayer films for similar QD sizes.

A third possible explanation for the red-shift of the first exciton transition energy is *solvatochromism*. Solvatochromism, or the dependence of the energy of an optically excited state on the dielectric constant of the solvent, can qualitatively account for most of our observations, including the direction of the shift, size dependence, the absence of significant broadening of the transition linewidth, and the difference between EDT and hydrazine. As detailed in Section 2.1.3, one contribution to the total energy of a nanocrystal excited state is the electrostatic polarization of the medium outside the nanocrystal by the free charge carriers excited within the nanocrystal. A larger dielectric constant outside lowers the energy of the nanocrystal excited state via increased electrostatic solvation. For the PbSe QD films considered here, the “solvent” is the sea of QDs surrounding each individual nanocrystal. As the fraction of organic material ($\epsilon = 2.1$) within the film decreases due to chemical treatment with either EDT or hydrazine, the average dielectric constant of the film approaches that of PbSe ($\epsilon = 23.9$), lowering the energy of the nanocrystal excited state. Additionally, as the ligand shell is removed or its thickness is reduced, the effects of solvatochromism become more

pronounced. Leatherdale & Bawendi showed that the net solvation energy (for charge carriers in the 1S orbital), including dielectric screening by the ligand shell, is (45),

$$\delta = \frac{\pi q^2}{2\epsilon_1\epsilon_0 a} \sum_{l=1}^{\infty} a^{2l+1} A_l \int_0^1 j_0^2(\pi x) x^{2l+2} dx, \quad (6.1)$$

where q is the electron charge, a is the radius of the nanocrystal core, j_0 is a spherical Bessel Function, and the term A_l is given by,

$$A_l = \frac{l+1}{a^{2l+1}} \frac{a^{2l+1}(\epsilon_2 - \epsilon_3)[\epsilon_1 + l(\epsilon_1 + \epsilon_2)] + b^{2l+1}(\epsilon_1 - \epsilon_2)[\epsilon_3 + l(\epsilon_2 + \epsilon_3)]}{a^{2l+1}(\epsilon_1 - \epsilon_2)(\epsilon_2 - \epsilon_3)l(l+1) + b^{2l+1}[\epsilon_2 + l(\epsilon_1 + \epsilon_2)][\epsilon_3 + l(\epsilon_2 + \epsilon_3)]}, \quad (6.2)$$

where $b-a$ is the thickness of the ligand shell, and ϵ_1 , ϵ_2 , and ϵ_3 are the dielectric constants of the nanocrystal core, the ligand shell, and the surrounding solvent, respectively (see Figure 2.5). The total shift of the first exciton transition energy is then,

$$\Delta \equiv \delta_{\text{treated}} - \delta_{\text{OA-capped}}. \quad (6.3)$$

In Figure 6.9, the calculated solvatochromic shift, Δ , is plotted as a function of ligand shell thickness, assuming randomly close-packed spherical QDs (fill factor = 0.64), with organic material filling the voids in the film. Δ becomes significant for ligand shell thicknesses less than 0.5 nm, and is strongly size-dependent for bare QDs. However, we see that solvatochromism can account for, at most, ~25 meV of the red-shift, whereas we observe red-shifts as large as 150 meV (see Figure 6.5). Additionally, solvatochromism cannot explain the large difference between the magnitude of the red-shift in monolayer and multilayer QD films. In fact, we would expect the opposite trend (smaller red-shifts for 2D arrays) because the nanocrystals are incompletely surrounded by other QDs in submonolayer films. Consequently, solvatochromism cannot be the primary reason for the large red-shift of the first exciton transition energy after chemical treatment of the PbSe QD film.

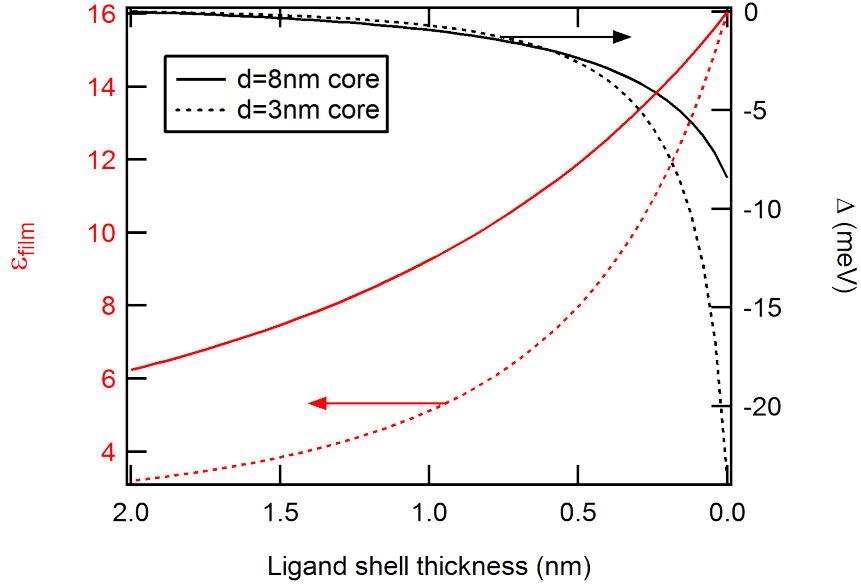


Figure 6.9 Calculated solvatochromic shift of the first exciton transition in a PbSe QD film as a function of ligand shell thickness. The calculation assumes random close-packed spherical QDs (fill factor = 0.64), and the void spaces are assumed to be filled with organic material.

The only possible explanation remaining is that the red-shift of the first exciton transition energy is due to inter-QD electronic coupling. As the ligand shell thickness is reduced, the nanocrystal cores of neighboring QDs come closer together. The electronic exchange coupling energy $V_{ab} = \langle a | \hat{H} | b \rangle$ (between two neighboring QDs a and b) is expected to then increase due to greater spatial overlap of electronic wave functions. For the hexagonally close-packed arrays we have observed with AFM (Figure 6.3), tight-binding theory predicts that nearest-neighbor coupling will result in the formation of electronic energy bands with bandwidth $12V_{ab}$ (68). If both electron and hole levels exhibit similar nearest-neighbor coupling energies (a likely scenario because of the similar electron and hole effective masses in PbSe (184)), the magnitude of the red-shift will be,

$$\Delta = -\left(6V_{ab}^{(e)} + 6V_{ab}^{(h)}\right) \approx -12V_{ab}. \quad (6.4)$$

We expect larger V_{ab} for smaller nanocrystals because the leakage of the wave function outside the nanocrystal core is more extensive, enabling greater spatial overlap (see Section 2.3.4). The difference in the magnitude of the red-shift between monolayer (2D) and multilayer (3D) QD films is attributed to “geometric frustration” in the latter. A

greater amount of structural re-ordering is required to achieve a close-packed configuration in a three-dimensional lattice than in two dimensions. As a result, the band structure of the 3D assembly does not form as completely, reducing the bandwidth of the solid and producing smaller red-shifts.

Equation (6.4) offers a simple way to estimate the nearest-neighbor exchange coupling energy in QD solids. In our hydrazine-treated 2D arrays, we obtain nearest-neighbor coupling energies as large as 7 and 13 meV for 6 nm and 4 nm PbSe QDs, respectively. These values are consistent with the findings of a scanning tunneling microscopy and spectroscopy study of thermally annealed 2D assemblies of PbSe QDs (67). Liljeroth *et al.* observed formation of mini-bands with bandwidths of 50-150 meV. Using the same tight-binding theory, these numbers correspond to $V_{ab}=4-13$ meV. Such strong inter-QD coupling has implications for the nature of charge transport within PbSe QD films, and suggests that a Marcus picture of electron transfer in these systems would be inappropriate (see Section 2.3.5).

6.6. Hot carrier cooling and coherent phonon excitation

Time-resolved second harmonic generation (TR-SHG) has been used to study electron dynamics in a variety of semiconductor systems. Johnson *et al.* detected the ultrafast nonlinear optical response of single ZnO nanowires (not exhibiting quantum size effects) following photoexcitation of the band gap (185). They observed an ultrafast drop in SHG intensity followed by a recovery over the course of ~ 10 ps. They postulated (without explanation or justification) that the “polarizability” of valence band electrons is greater than that of conduction band electrons. The drop in intensity was then attributed to a depletion of the valence band population, so the recovery of the signal corresponded to some fast recombination. The same group also studied the TR-SH response after photoexcitation of the bulk ZnSe band gap; again, they observed a drop in SHG intensity followed by a recovery within $\sim 30-40$ ps (186). Borguet and co-workers have also used TR-SHG to probe electron dynamics at semiconductor surfaces and observed recovery dynamics ranging from sub-picosecond to nanoseconds (85, 89, 187-190). Most notably,

these authors found that the pump-induced change could be *either* positive *or* negative, depending on how the semiconductor surface was prepared (188). While the authors of this work again attributed their results to the “valence band electron hyperpolarizability model”, it seems to us that the dependence of the pump-induced change on surface passivation is striking evidence for an alternative explanation: these transient dynamics are related to near-surface electric fields. At almost any semiconductor surface in dark equilibrium, the Fermi level is pinned somewhere within the band gap, resulting in band-bending and the establishment of a corresponding near-surface electric field. As we have seen (Section 4.3.2), this condition can lead to an electric field-induced second harmonic (EFISH) enhancement of the nonlinear susceptibility. Upon photoexcitation of the band gap, photogenerated charge carriers screen this near-surface field, partially quenching the equilibrium EFISH enhancement. With diffusion, charge trapping, and recombination, the near-surface fields are eventually restored.

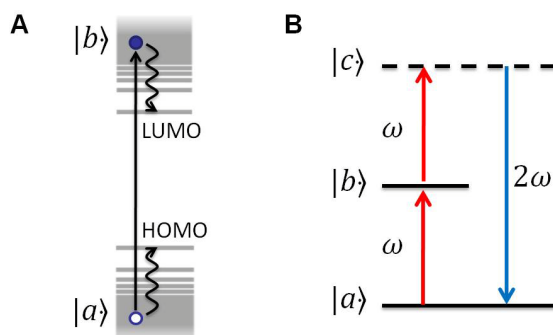


Figure 6.10 (A) Hot carrier relaxation following photoexcitation from occupied state $|a\rangle$ to unoccupied state $|b\rangle$. (B) SHG energy level diagram showing one-photon resonance with the $|a\rangle \rightarrow |b\rangle$ transition. Solid lines indicate real electronic energy levels; the dashed line is a virtual level.

In contrast to the electric field effects likely responsible for transient nonlinear phenomena near bulk semiconductor surfaces, we expect our quantum-sized PbSe nanocrystals to exhibit dynamics that can be described by resonant nonlinear optical phenomena similar to atoms or molecules. For all sizes studied, the probe wavelength (810 nm, or 1.53 eV) is one-photon resonant with a dipole-allowed interband transition $|a\rangle \rightarrow |b\rangle$ within each PbSe QD. Because our pump beam is the same wavelength of light

as the probe, the electronic transition excited by the pump beam involves the same two electronic energy levels. When population is transferred from the ground state to the excited state, $\chi^{(2)}$ decreases in magnitude according to (99),

$$\chi_{ijk}^{(2)}(2\omega, \omega) \propto (\rho_a^{(0)} - \rho_b^{(0)}) \frac{\mu_{ac}^i \mu_{cb}^j \mu_{ba}^k}{\left[([E_c - E_a] - 2\hbar\omega) - i\hbar\gamma_{ca}\right] \left[([E_b - E_a] - \hbar\omega) - i\hbar\gamma_{ba}\right]}, \quad (6.5)$$

where $\rho_a^{(0)}$ is the population in the ground state, $\rho_b^{(0)}$ is the population in the excited state, μ_{nm} is a transition dipole moment, γ_{nm} is a damping rate, and the indices i, j , and k run over the Cartesian coordinates x, y , and z . As the electron relaxes down from the hot electron energy level $|b\rangle$ and the hole relaxes upward from $|a\rangle$, the ground-state population of these states is recovered and $\chi^{(2)}$ increases back to its equilibrium value (Figure 6.10). Consequently, the SHG signal recovery dynamics reflect the timescale for hot carrier cooling within the PbSe QDs.

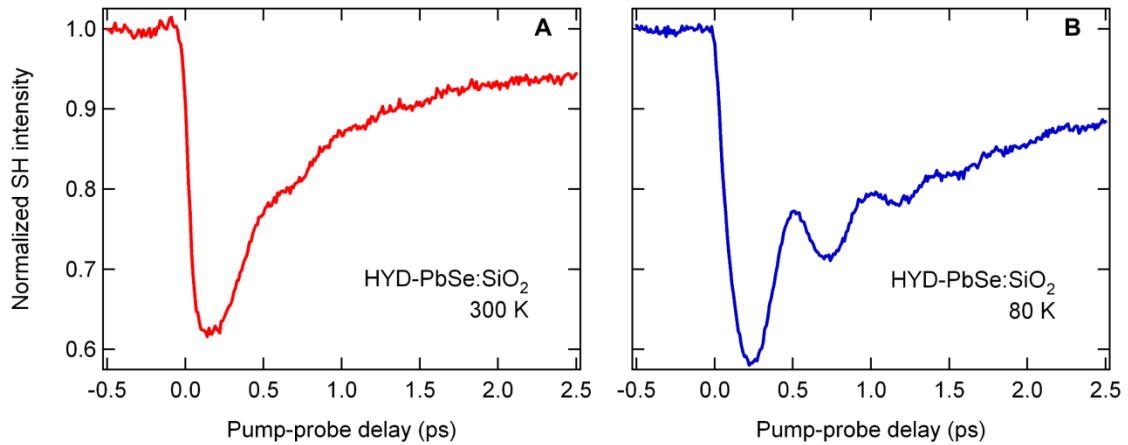


Figure 6.11 TR-SH response of hydrazine (HYD)-treated PbSe nanocrystals ($d = 6.7$ nm) on SiO_2 at (A) 300 K and (B) 80 K. The SH signal recovers faster at 300 K (~ 0.5 ps time constant) than at 80 K (~ 3 ps time constant).

While wavelength-dependent experiments are needed for complete verification, the results we have obtained so far seem to support our theory. The femtosecond time-resolved second harmonic (TR-SH) response of a hydrazine-treated PbSe QD film is shown in Figure 6.11. Upon photoexcitation, there is a sharp drop ($>30\%$) in the SHG intensity, followed by a recovery to the background level over the course of picoseconds.

The TR-SH response of EDT-treated films (Figure 6.12) is nearly identical. We also notice a dependence of the SHG recovery rate on temperature. At 300 K (Figure 6.11A) the SHG signal recovery time constant is ~ 0.5 ps, whereas at 80 K (Figure 6.11B) the time constant is ~ 3 ps. These time constants follow the same temperature trend reported for $1P_e$ to $1S_e$ relaxation in PbSe nanocrystals (47) and are approximately five times faster than the time constants reported for similar sizes, as would be expected for faster relaxation between higher excited states.

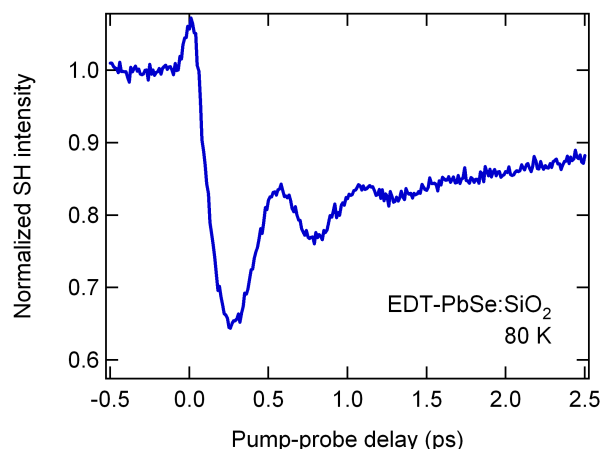


Figure 6.12 TR-SH response of PbSe nanocrystals ($d = 6.7$ nm) on SiO_2 treated with 1,2-ethanedithiol (EDT) at 80 K. The response is similar to that of HYD-treated nanocrystals on SiO_2 .

In addition to the sudden drop in SHG intensity and sub-picosecond recovery, we also notice large oscillations in our time-resolved data at a frequency of $\sim 75 \text{ cm}^{-1}$ (2.2 THz, 9.3 meV). The oscillations are observed with both s- and p-polarized light. Observation of oscillations such as these with TR-SHG is usually indicative of coherent phonon excitation (191). Due to the fast dephasing of these coherent motions, it is difficult to pinpoint the exact frequency with any certainty better than $\pm 10 \text{ cm}^{-1}$. However, within our experimental uncertainty, we observe no systematic dependence of the oscillation frequency on QD size, temperature, chemical treatment, or substrate material (Figure 6.13).^{*} For small crystallites, the acoustic vibrations of the bulk lattice become

^{*} The frequency was determined by fitting the data at later times ($t > 150\text{fs}$) to an exponentially decaying sine wave superimposed on a linear background: $S(t) = a + bt + c \sin(\omega t + \phi)e^{-t/\tau}$.

discretized due to the classical boundary conditions imposed by the finite-sized material. As Lamb derived over a century ago, the lowest-order (and most strongly observed) vibrational mode of a spherical homogeneous elastic body is a spheroidal breathing mode whose frequency varies inversely with particle size, $\omega_a \sim v_l/R$, where v_l is the longitudinal sound velocity and R is the particle radius (192). Ikezawa *et al.* observed the $1/R$ size-dependence for the spherical breathing mode in PbSe QDs with $\omega_a = 10\text{--}40\text{ cm}^{-1}$ for diameters ranging from 7 nm to 2 nm (193). Consequently, the confined acoustic mode can be ruled out as the source of our oscillation. In contrast to the acoustic modes, the optical phonon modes do not exhibit strong size-dependence because the wavelength of these modes (approximately equal to the lattice constant) is much smaller than the size of a nanocrystal (69, 194). The bulk longitudinal optical (LO) and transverse optical (TO) phonons in PbSe have frequencies of 133.1 cm^{-1} and 44.0 cm^{-1} , respectively (195, 196), so they can be ruled out as well. While it is possible that these oscillations are due to a collective motion of the electronically-coupled PbSe QD film, the frequency range and size-independence suggests that these oscillations originate from an as-yet unidentified optical phonon mode – possibly a PbSe surface optical mode.

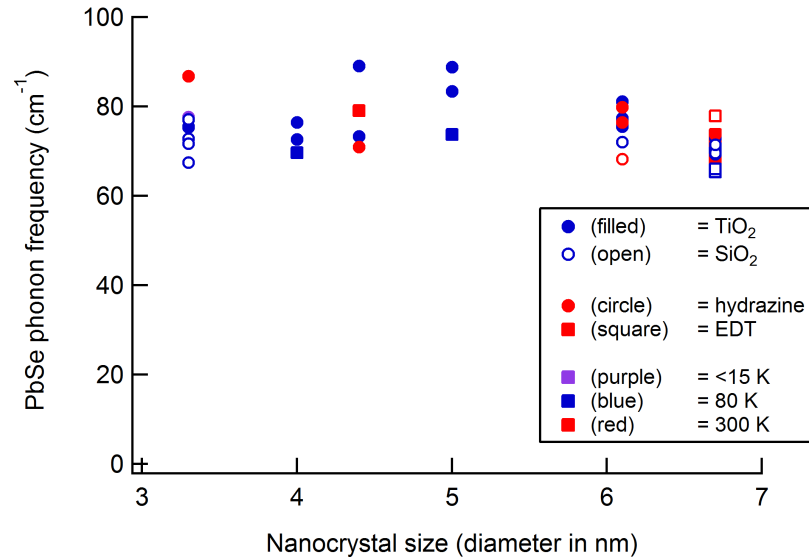


Figure 6.13 Dependence of the coherent phonon frequency on nanocrystal size, temperature, surface chemical treatment, and substrate material. No systematic variation is observed.

In contrast to the rich dynamics observed in hydrazine- or EDT-treated PbSe QD films, no detectable dynamics are observed for QD films still coated with the native oleic acid ligands (Figure 6.14). The fact that OA-capped PbSe nanocrystals do not exhibit either coherent phonon oscillations or a drop in SH intensity upon photoexcitation is intriguing. We also notice that static SH intensities increase by an order of magnitude following treatment of OA-PbSe:SiO₂ samples with either HYD or EDT. While the change in second-order susceptibility may be due to strong inter-nanocrystal electronic coupling, it is also possible that increased SHG intensities are due to charge trapping within the chemically treated film. PbSe crystallizes in the rock salt structure, which is centrosymmetric and bulk-SHG inactive. Local separation of charge within the PbSe nanocrystal film (i.e. by electron or hole trapping at the nanocrystal surface) may “activate” the PbSe core for SHG via electric field-induced symmetry-breaking, increasing static SHG intensities and revealing dynamic processes that would otherwise be hidden from observation.

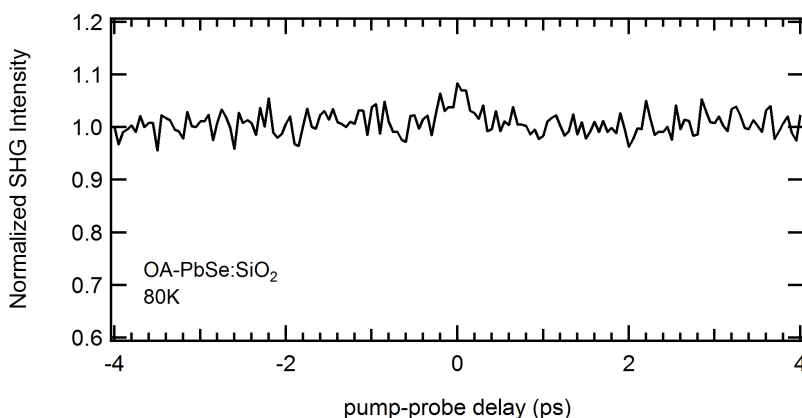


Figure 6.14 TR-SH response of oleic acid (OA) – capped PbSe QDs on silica. Unlike the hydrazine- or EDT-treated samples, the OA-capped QDs exhibit no detectable pump-induced change, aside from a coherent artifact at $t=0$.

6.7. Conclusions

We have used atomic force microscopy, Fourier transform infrared and near-infrared spectroscopy, and time-resolved second harmonic generation to investigate the

changes that occur when two-dimensional arrays of colloidal PbSe quantum dots (QD) are subjected to chemical treatment with either hydrazine (HYD) or 1,2-ethanedithiol (EDT). We have found that the QDs self-assemble into two-dimensional hexagonal close-packed islands on the surface of TiO₂, and that the hydrazine and EDT treatments lead to a significant reduction in inter-QD spacing, consistent with removal of the native long-chain oleic acid ligands that coat the surface of each PbSe QD. Following treatment with hydrazine or EDT, we observe a large (up to 150 meV) red-shift of the first-exciton transition energy that cannot be explained by solvatochromism alone. These red-shifts are attributed to strong and tunable electronic coupling between neighboring QDs in the chemically treated 2D arrays, which strongest coupling observed after hydrazine treatment. Further, we find that the electronic coupling in these 2D QD assemblies is an order of magnitude larger than in 3D assemblies, which is likely due to decreased “geometric frustration” in the 2D film. Finally, we show that treatment of the QD film with either EDT or hydrazine reveals a rich assortment of ultrafast dynamical processes in highly excited PbSe QDs that can be followed with time-resolved nonlinear optical techniques. These dynamics include the temperature-dependent relaxation of hot charge carriers and coherent excitation of a previously-unidentified PbSe surface optical phonon mode at $75 \pm 10 \text{ cm}^{-1}$. These findings have implications for the use of PbSe QD films in optoelectronic devices, such as photodetectors (170) and solar cells (22, 75, 76).

Chapter 7

Hot Electron Transfer from PbSe Nanocrystals

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In typical semiconductor solar cells, photons with energies above the semiconductor band gap generate hot charge carriers that quickly cool before all of their energy can be captured, a process that limits device efficiency. Although fabricating the semiconductor as a quantum dot can slow this cooling, the transfer of hot carriers to electron/hole acceptors has not yet been thoroughly demonstrated. We use time-resolved optical second harmonic generation to observe hot electron transfer from colloidal lead selenide nanocrystals (PbSe NCs) to a titanium dioxide electron acceptor (TiO₂). With appropriate chemical treatment of the nanocrystal surface, this transfer occurs much faster than expected. Moreover, the electric field resulting from sub-50 femtosecond charge separation across the PbSe-TiO₂ interface excites coherent vibrations of the TiO₂ surface atoms, whose motions can be followed in real time.

7.1. Introduction

The maximum theoretical efficiency of a standard silicon solar cell in use today is limited to $\sim 31\%$, in part by the loss of any photon energy that exceeds the semiconductor band gap (9). Absorption of high energy photons creates hot electrons and holes that cool quickly (within ~ 1 picosecond) to the band edges by sequential emission of phonons. There the carriers remain for hundreds of picoseconds or longer before slower processes such as radiative or non-radiative recombination occur. The goal of standard solar cells is to extract these band-edge electrons and holes to produce electrical current. However, due to the initial cooling process, significant solar energy has already been irreversibly lost. If instead, all of the energy of the hot carriers could be captured, solar-to-electric power conversion efficiencies could be increased, theoretically to as high as 66% (37). We can envision the realization of such a hot carrier solar cell in a semiconductor device where scattering among photoexcited electrons and re-absorption of additional photons in the conduction band is faster than hot electron cooling, resulting in a quasi-equilibrium characterized by an electron temperature much higher than the lattice temperature. This is coupled with equally fast hot electron transfer to an electron conductor in a narrow energy window (to minimize additional energy loss in the latter). The same argument applies to the holes.

A potential route to the above hot carrier solar cell is to utilize semiconductor nanocrystals, or quantum dots (30). In these materials, the quasi-continuous conduction and valence energy bands of the bulk semiconductor become discretized due to confinement of the charge carriers. Consequently, the energy spacing between the electronic levels can be much larger than the highest phonon frequency of the lattice, creating a “phonon bottleneck” wherein hot-carrier relaxation is only possible via slower multiphonon emission (36). For example, hot-electron lifetimes as long as ~ 1 ns have been observed in quantum dots grown by molecular beam epitaxy (197). Even in colloidal quantum dots, which are coated with surfactant molecules that provide additional high frequency vibrations for carrier relaxation, long lifetimes have been demonstrated through careful design of core-shell structures and control of interfaces (38). Such slowing of electron relaxation in core-shell quantum dots has recently been shown to allow the tunneling of hot electrons through the shells to surface trap states (53). Due

to their ability to slow electronic relaxation, quantum dots can in principle enable extraction of hot carriers (to electron or hole conductors) before they cool to the band edges, leading to more efficient solar cells (31). However, hot carrier transfer from nanocrystals to an electron or hole conductor has not yet been observed. Here we show that electron transfer from the higher excited states of a colloidal semiconductor nanocrystal (PbSe) to a common electron acceptor (TiO₂) is indeed possible and, with appropriate chemical treatment of the nanocrystal surface, occurs on an ultrafast time scale (<50 fs).

Although heterogeneous electron transfer from molecular chromophores to metal-oxide semiconductors has been probed with femtosecond time-resolved absorption (70), extending this approach to quantum dots has proved challenging. Differentiating between transient spectroscopic signatures of the photoexcited quantum dot, the reduced TiO₂ substrate, and the trap states is difficult (78). Further, to generate adequate signal, porous samples with large surface area but poorly defined interfaces are used. Consequently, reported timescales have spanned from picoseconds to microseconds (19, 78-80).

Optical second harmonic generation (SHG) (107) is a much better technique for studying quantum-dot-to-semiconductor electron transfer because it offers femtosecond time resolution with sufficient sensitivity for well-defined crystalline interfaces. In a centrosymmetric semiconductor such as rutile TiO₂, the second harmonic response originates only from the first few atomic layers near the surface (111). Thus, SHG should be extremely sensitive to changes in the local electronic environment resulting from interfacial electron transfer. Indeed, SHG has been used to probe ultrafast electron transfer at liquid-liquid interfaces (88). We show here that it can also be applied to semiconductor interfaces.

7.2. Hot electron transfer

For fast electron transfer to occur, the nanocrystals should exhibit strong electronic coupling to the substrate. We chose colloidal PbSe quantum dots as they are easy to prepare (175) and are better suited for electron transfer than other possible

materials. In particular, PbSe has an extremely large exciton Bohr radius (46 nm) such that charge carriers in sub-10-nm diameter PbSe quantum dots are subject to strong quantum confinement effects (184), and their electronic wave functions will extend spatially well beyond the nanocrystal surface. This delocalization facilitates electron transfer if the nanocrystals are close to an electron accepting substrate. We chose rutile TiO₂ for this role because it not only is technologically relevant and available as a single crystal, but it also has a very large density of accepting states. Further, the (110) surface of rutile TiO₂ is one of the most studied metal oxide interfaces, and the surface nonlinear susceptibility tensor and the origins of the second harmonic response are known (111).

Each sample consisted of 1 to 2 monolayers of PbSe nanocrystals deposited on atomically flat single-crystalline (110) TiO₂ (Fig. 1A, B). The films were chemically treated with either hydrazine or 1,2-ethanedithiol (EDT) (see Section 7.5) to respectively remove or substitute for the oleic acid initially present on the nanocrystal surface. Both treatments enhance electronic coupling to the TiO₂ substrate and within the film (66, 175-177, 198), but the bare surfaces produced by hydrazine result in stronger coupling (Figure 6.6). However, hydrazine can also leave many dangling bonds at the nanocrystal surface that can presumably act as scattering sites and accelerate electronic cooling within the quantum dot. In contrast, thiols such as EDT passivate the nanocrystal surface and slow hot electron relaxation in colloidal nanocrystals (38).

We tested PbSe nanocrystals ranging in diameter from 3.3 nm to 6.7 nm. As with all strongly confined semiconductor nanocrystals, the energy of excited electron states in PbSe quantum dots increases with decreasing particle size. Thus, we first used ultraviolet photoelectron spectroscopy (UPS), in conjunction with optical absorption, to determine the energy of the lowest excited electronic state in our nanocrystals (see Section 7.6). We found that, regardless of particle size or chemical treatment, this state was always below the TiO₂ conduction band minimum (Figure 7.1C). As a result, electron transfer from PbSe to TiO₂ should only be possible from hot electronic states of the quantum dot (79).

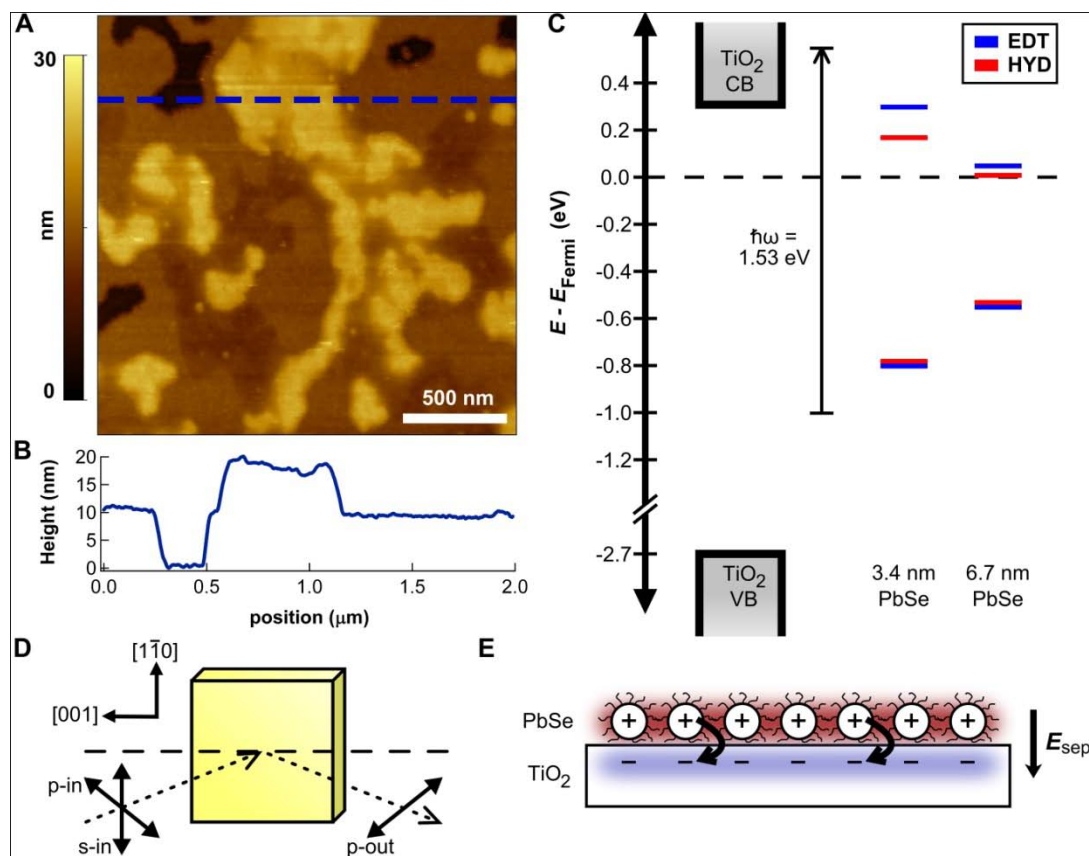


Figure 7.1 (A) Atomic force micrograph showing the morphology of a ~ 1.5 monolayer film of 6.7 nm oleic acid-capped PbSe nanocrystals supported on atomically flat TiO₂. (B) Line height profile corresponding to the dashed blue line in (A). The height of a monolayer (~ 11 nm) is the diameter of a nanocrystal (~ 7 nm) plus the thickness of the passivating organic layer (~ 2 nm) both above and below. (C) Alignment of highest occupied and lowest unoccupied quantum dot energy levels relative to the TiO₂ conduction band edge following chemical treatment of the nanocrystal surface. Alignment is determined by ultraviolet photoelectron and near-infrared absorption spectroscopies and indicates that electron transfer from the lowest excited state of the quantum dot is not energetically possible. The vertical arrow depicts symmetric photoexcitation of the PbSe quantum dots with 810 nm light. Numerical values are available in Table 7.1. VB = valence band; CB = conduction band; EDT = 1,2-ethanedithiol; HYD = hydrazine. (D) Illustration of the crystal orientation and optical polarization used for SHG in reflection from the rutile (110) surface. (E) Schematic representation of the interfacial electric field generated by separation of electrons and holes across the PbSe-TiO₂ interface. Red indicates positive charge density; blue negative charge density.

To study this electron transfer, we used 50 fs pulses of 810 nm (1.53 eV) light both to photoexcite (pump) the nanocrystals and detect (probe) the second harmonic response (see Section 7.5). The intensity of reflected second harmonic light at 405 nm ($I^{(2\omega)}$) was recorded as a function of time delay between the pump and probe pulses. The polarization (p or s) of the fundamental was controlled and that of the second harmonic

independently detected to isolate specific components of the nonlinear susceptibility tensor (Figure 7.1D).

If electron transfer occurs, the separation of electrons and holes across the PbSe-TiO₂ interface generates an electric field, E^{sep} , oriented in the surface normal direction (Figure 7.1E). SHG is highly sensitive to such slowly varying (relative to the optical frequency) electric fields because they can perturb the symmetry of the medium (108). This electric-field-induced second harmonic (EFISH) response has been used to study metal-electrolyte interfaces (86) and buried interfaces in field-effect transistors (84). When an interface already exhibits a large SHG signal, $I_0^{(2\omega)}$, even without an induced interfacial field [*e.g.*, rutile (110) under the p-in/p-out configuration in Figure 7.1D], the change in the SHG intensity, $\Delta I^{(2\omega)}$, due to electron transfer is proportional to E^{sep} as,

$$\Delta I^{(2\omega)} = I^{(2\omega)} - I_0^{(2\omega)} \approx \eta \left(I^{(\omega)} \right)^2 E^{sep}, \quad (7.1)$$

where $I^{(\omega)}$ is the intensity of the probe beam at the fundamental frequency ω , and η contains the dependence on the dielectric function through linear and nonlinear Fresnel factors as well as the wavelength-, polarization angle-, and crystallographic orientation-dependent nonlinear susceptibility (see Chapter 4) (113). If the charge-separated PbSe-TiO₂ interface is treated as a parallel-plate capacitor, then E^{sep} and the corresponding EFISH signal scale approximately linearly with the amount of separated charge. Consequently, electron transfer dynamics may be extracted directly from the time-resolved change in SHG intensity following photoexcitation of the PbSe film.

However, the analysis is complicated by the contribution to the SHG response from the quantum dots themselves. In particular, we expect photoexcitation of the quantum dots to lead to a decrease in SHG intensity, as is observed in molecular chromophores (88) and semiconductor nanowires (185). Indeed, we measure a drop in SHG intensity upon photoexcitation of our PbSe films supported on amorphous silica glass (at all quantum dot sizes, treatments, and temperatures). Because glass has a bandgap too wide to accept electron transfer from our quantum dots, we attribute this reduced intensity to their intrinsic SHG response (see Section 6.6 of Chapter 6).

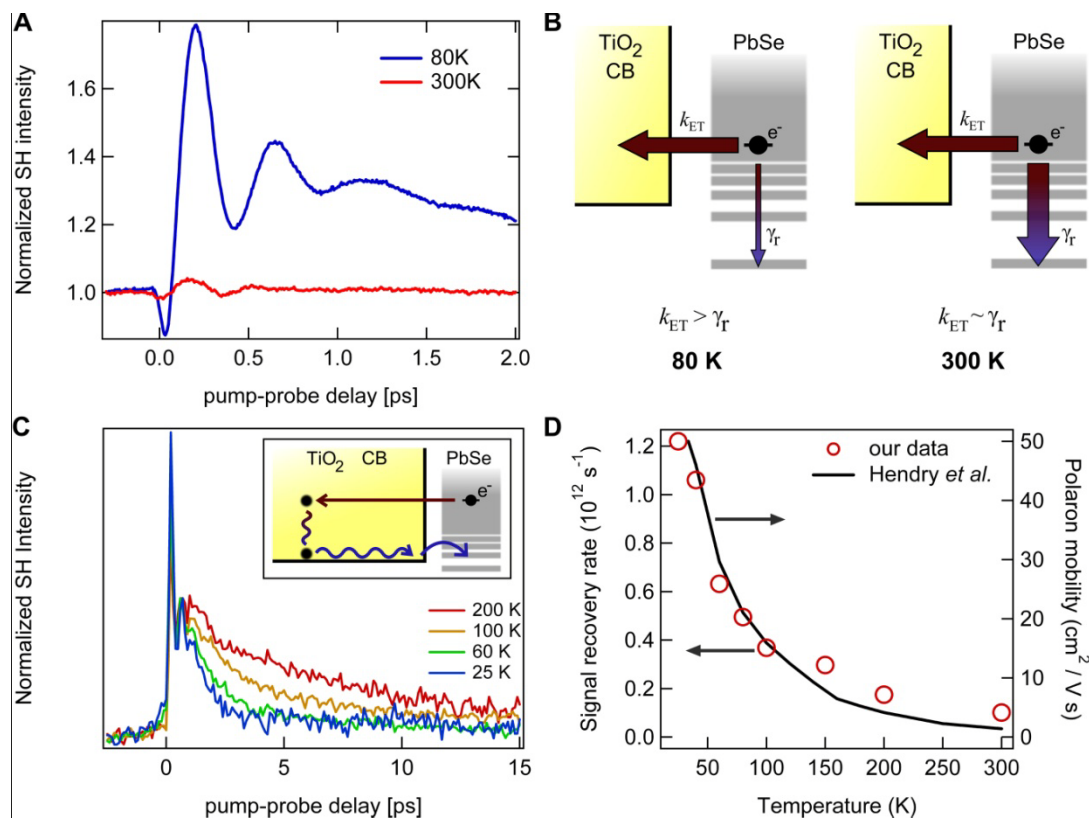


Figure 7.2 (A) Time-resolved second harmonic response of the TiO₂ surface coated with 1.5 monolayers of hydrazine-treated 3.3 nm PbSe nanocrystals. The large rise in SHG intensity is indicative of efficient electron transfer from PbSe to TiO₂. (B) Illustration of the competing pathways of interfacial electron transfer and intra-quantum-dot relaxation. At higher temperatures, hot electron relaxation (γ_r) becomes competitive with interfacial electron transfer (k_{ET}). (C) Temperature-dependent decay of the pump-induced SHG signal enhancement; the absolute intensity has been normalized for pump-induced change to better illustrate the temperature-dependent recovery rate. *Inset:* Cartoon showing ballistic electron injection (straight arrow) followed by phonon scattering and polaronic transport back to the interface (wavy lines) then transfer back to the nanocrystal (curved arrow). (D) Correlation of SHG signal recovery rate (red circles) with the temperature-dependent polaron mobility perpendicular to the *c*-axis in TiO₂ measured previously (199) assuming a temperature-independent polaron effective mass (black line).

In contrast to this drop, we observe a significant rise in SHG intensity after photoexcitation of the quantum dots on TiO₂ at 80 K (Figure 7.2A). This response is consistent with efficient hot electron transfer from PbSe to TiO₂ for several reasons. First, the SHG signal rises on a timescale shorter than the laser pulse (50 fs). Such an ultrafast response would be expected for the strong-coupling limit of electron transfer. Also, because the electronic relaxation time between the first two excited states in similar-sized PbSe quantum dots has been measured as 540 fs at 300 K (47), electron transfer must be

significantly faster than this to outpace the cooling process. Second, the magnitude of the ultrafast SHG response decreases with increasing temperature (Figure 7.2A). As the PbSe quantum dots are warmed to 300 K, the time constant for electron transfer should be largely unaffected in the strong-coupling limit. However, the electronic relaxation rate is known to increase exponentially (47). Thus, at higher temperatures cooling of hot electrons can compete with hot electron transfer (Figure 7.2B). Because cooled electrons cannot transfer to TiO₂ in our samples, accelerated cooling leads to a decrease in SHG signal. As a negative control, we observe no electron transfer when we decrease the pump photon energy to below the threshold necessary to reach the conduction band minimum of TiO₂ (Figure 7.3).

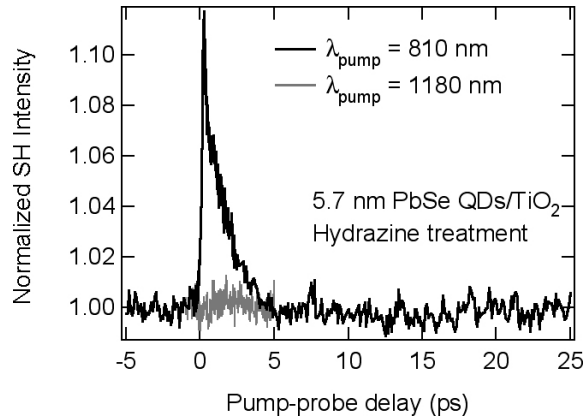


Figure 7.3 SHG response of PbSe nanocrystals ($d = 5.7$ nm) on TiO₂ (treated with hydrazine) at 80 K for two different pump laser wavelengths: $\lambda_{\text{pump}} = 810$ nm (black) and $\lambda_{\text{pump}} = 1180$ nm (grey). The laser power at each wavelength was chosen to maintain an average excitation of 1.0 electron-hole pairs per nanocrystal.

An analysis of the temperature-dependent decay of the pump-induced SHG signal on the ps time scale (Figure 7.2C) is consistent with the temperature-dependence of electron mobility in TiO₂. If an electron transfers from PbSe to a resonant energy level within the TiO₂ conduction band, this electron would have considerable kinetic energy. It would move ballistically into TiO₂ where electron-phonon scattering would bring it to the bottom of the conduction band, forming a polaron (199, 200). The electric field would eventually return the electron back to the TiO₂ surface for recombination with the positively charged nanocrystal and quenching of the EFISH signal (inset to Figure 7.2C).

An alternative interpretation is that the injected electron diffuses deep into bulk TiO₂ and is thus screened, resulting in the decay in SHG signal. In this scenario, recombination occurs on a much longer time scale (between consecutive probe pulses). We favor the former interpretation because simulation on the single crystal TiO₂(110) surface showed an order of magnitude faster time scale (~100 fs) for electron diffusion into the bulk TiO₂, while back electron transfer from the near surface region of TiO₂ to electron acceptors on the surface occurs on ps time scales, in agreement with the SHG decay time observed here (200). Regardless of which mechanism is operative, the decay of the interfacial electric field would be proportional to the mobility of the polaron (see Section 7.9). Previous optical measurements determined this mobility in single-crystalline rutile TiO₂ as a function of temperature (199). The strong correlation between the decay rate of pump-induced SHG signal enhancement and the temperature-dependent polaron mobility (Figure 7.2D) supports the conclusion that we are observing hot electron transfer to delocalized TiO₂ conduction band states.

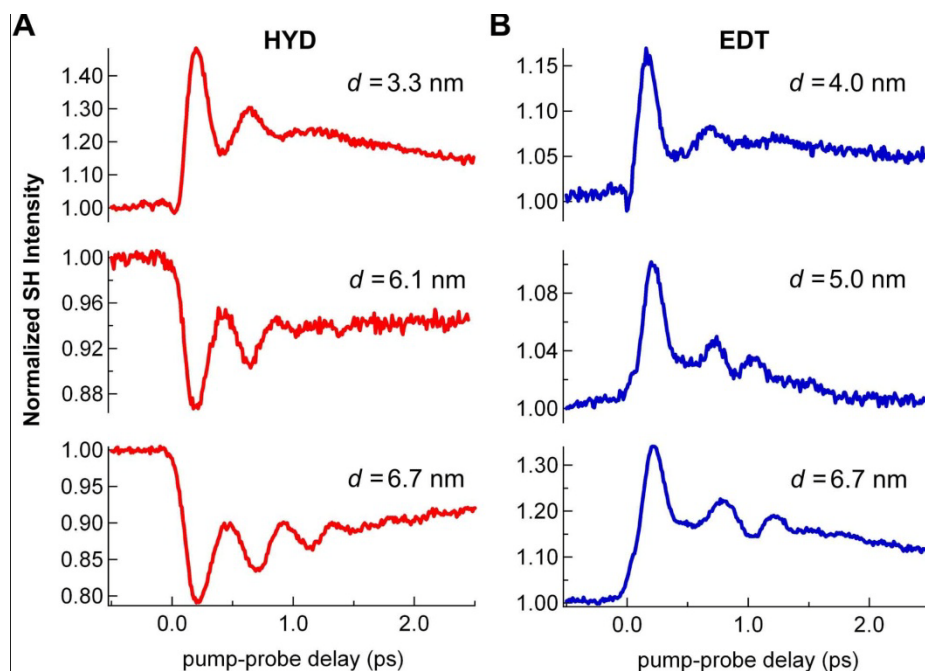


Figure 7.4 Dependence of the time-resolved second harmonic response on nanocrystal size following treatment with (A) hydrazine (HYD) or (B) 1,2-ethanedithiol (EDT). The EDT-treated nanocrystals display efficient hot electron transfer for all sizes studied whereas significant hot electron transfer is only observed for smaller nanocrystals treated with hydrazine.

Further evidence is provided by the influence of nanocrystal size on the SHG response at 80 K. The pump-induced SHG response has two opposite contributions: the positive response from electron transfer to TiO_2 and the negative contribution from photo-excited nanocrystals. In hydrazine-treated samples (Figure 7.4A), only smaller PbSe nanocrystals (3.3 nm) exhibit a signal characteristic of efficient electron transfer. The larger quantum dots (6.1 and 6.7 nm) exhibit a sharp drop in the SHG signal at zero pump-probe delay, indicative of a dominant contribution from photoexcited nanocrystals (Figure 6.11 and Figure 6.12). The electronic state energies in the nanocrystals are size-dependent and these observations are related to which excited states are resonant with the TiO_2 conduction band. In larger nanocrystals, this resonance occurs for highly excited electronic states (above $1P_e$) where ultrafast relaxation makes hot electron transfer less competitive. In smaller nanocrystals, the resonance occurs for the second excited state ($1P_e$) and its relatively long lifetime makes hot electron transfer to TiO_2 more efficient. Further, if the overall hot electron relaxation rate could be slowed, electron transfer should compete effectively in all nanocrystal sizes. Indeed, for EDT-treated quantum dots, wherein the overall electron relaxation is expected to be slower due to effective surface passivation, we always observe the dominance of the positive SHG response from hot electron transfer (Figure 7.4B). The fluctuations in the magnitude of the pump-induced SHG signal intensity shown in Figure 7.4 are representative of sample-to-sample variability in our data. We observe that these magnitude fluctuations arise primarily from batch-to-batch variations in the nanocrystals themselves and are presumably related to the structure and overall quality of the nanocrystal surface, which should play an important role in interfacial electron transfer.

7.3. Coherent vibration of the $\text{TiO}_2(110)$ surface

One additional feature in our SHG data is the presence of large oscillations in the time-dependent response. For example, Figure 7.2A shows a size-independent frequency of $\sim 70 \text{ cm}^{-1}$ (2.1 THz or 8.7 meV). These oscillations have larger amplitude and slower dephasing at 80 K than at 300 K and are observed with both s- and p- polarized light.

Though they are not present prior to removal of oleic acid from the nanocrystal surface, observation of these oscillations does not require interfacial electron transfer as they occur in hydrazine- and EDT-treated PbSe films supported on SiO₂ (Figure 6.11 and Figure 6.12). Based on the frequency, its invariance with quantum dot size, the independence of substrate material, yet sensitivity to surface chemical treatment, we attribute these oscillations to a coherent surface optical phonon mode in electronically-coupled two-dimensional PbSe quantum dot assemblies. Close inspection of the EDT data (Figure 7.4B) reveals frequency beating in the oscillations, which becomes more apparent at lower temperatures (Figure 7.5A). A frequency-domain analysis of the p-polarized SHG waveform in Figure 7.5A reveals three dominant Fourier components (Figure 7.5B): the previously-identified PbSe surface optical mode at $\sim 70 \text{ cm}^{-1}$ (2.1 THz), the bulk PbSe longitudinal optical (LO) phonon at $133 \pm 5 \text{ cm}^{-1}$ (4.0 THz) (195), and a mode at $97 \pm 5 \text{ cm}^{-1}$ (2.9 THz) that dominates the p-polarized SHG signal but is much weaker for s-polarized probe light. The frequency of this last component is close to a predicted transverse optical phonon mode (104 cm^{-1}) of the rutile (110) surface of TiO₂, which involves the motion of Ti and O atoms in-and-out of the surface plane (201). Under the p-in/p-out configuration with our crystal orientation (Figure 7.1D), the SHG response of the (110) surface originates from anharmonic polarizability of the Ti-O zigzag bonds running along the [001] direction (Figure 7.5C) (111). As these bonds stretch and compress in phase, we observe a time-dependent modulation of the SHG intensity resulting from accompanying fluctuations of the bond hyperpolarizability. By symmetry, this modulation should arise if the driving electromagnetic wave contains an electric-field component along the Ti-O bond. Consequently, it is only observed with a p-polarized probe beam. For the s-polarized case, the SHG response arises mainly from the PbSe quantum dots and the coherent phonon mode at 70 cm^{-1} dominates.

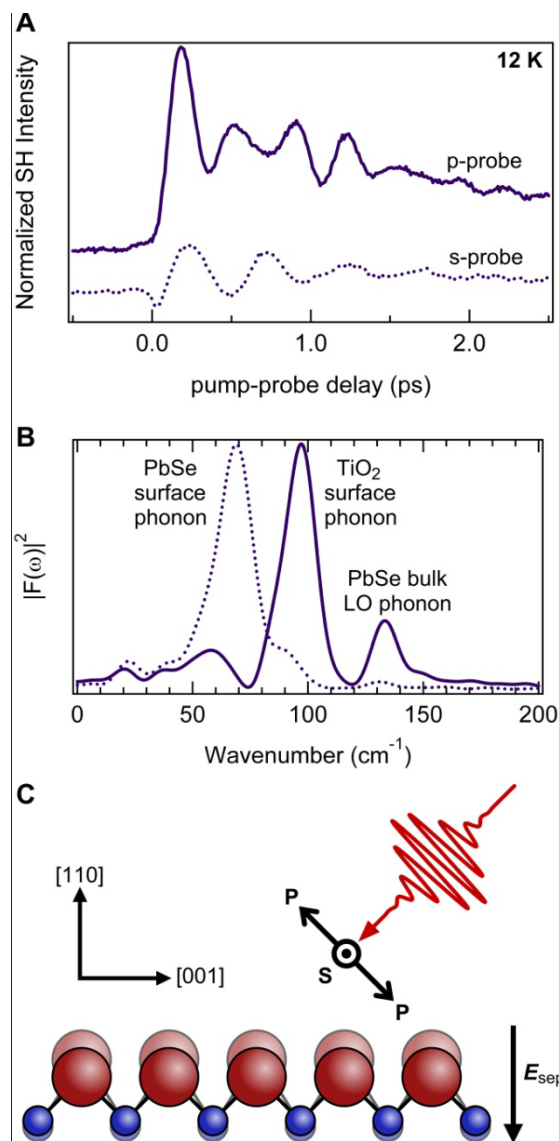


Figure 7.5 Excitation of a coherent surface phonon by ultrafast electron transfer. (A) Time-resolved response at 12 K of the TiO₂ surface coated with 1.5 monolayers of EDT-treated 6.7 nm PbSe nanocrystals probed with either p- (solid) or s- (dotted) polarized light. (B) Fourier power spectrum of the oscillatory part of the SHG response curves shown in (A). With p-polarized light, a vibrational mode at $97 \pm 5 \text{ cm}^{-1}$ attributed to a rutile (110) surface-specific coherent transverse optical phonon is observed. (C) Coherent vibration of the Ti-O zigzag bonds running along the [001] direction of the rutile (110) surface excited by ultrafast switching-on of the interfacial electric field resulting from sub-50 fs electron transfer.

We take the coherent surface phonon attributed to TiO₂ as further evidence for hot electron transfer. Such vibrations can be excited when electric fields near the surface are activated by optical pulses shorter than the vibrational period (114). Electron transfer across the PbSe-TiO₂ interface within the 50 fs width of the excitation pulse establishes

an interfacial electric field faster than the characteristic response time of the surface atoms. These atoms subsequently find themselves in a vibrationally excited state of the new electric-field-induced minimum energy surface configuration. Time-domain fitting of an appropriate model function to the data in Figure 7.5A reveals that the initial phase of this vibration is a cosine, consistent with a displacive excitation mechanism (see Section 7.8). The phase coherence of these collective motions is then lost over time due to elastic and inelastic scattering with bulk phonons.

7.4. Implications and future outlook

These results indicate hot electron transfer from semiconductor nanocrystals to a technologically relevant electron acceptor is possible. This effect is expected to be of general significance to other semiconductor nanocrystals and electron/hole conductors, provided the hot electrons and holes possess sufficiently long lifetimes and the interfaces are properly controlled to enable ultrafast charge transfer. Moreover, if hot electron (hole) transfer can be controlled to occur in very narrow energy windows to also minimize loss in the electron (hole) conductor, the highly efficient hot carrier solar cell may be realized.

7.5. Sample preparation and characterization

Colloidal PbSe nanocrystals were synthesized based on methods developed by Murphy *et al.* (178) and Luther *et al.* (177). In a typical synthesis, PbO (2.5 g), oleic acid (OA, 9 mL), and 1-octadecene (35 mL) were placed in a three-neck round-bottom flask. The reaction flask was then degassed to <40 mTorr while stirring vigorously and purged with dry nitrogen gas. The degassing process was repeated three times. The reaction vessel was heated to 180 °C under nitrogen and was maintained at that temperature for approximately 1 hr while the precursor solution turned optically clear. Meanwhile, a solution of Se dissolved in trioctylphosphine (TOPSe; 1.0 M, 21 mL total volume) was prepared and loaded into syringes inside a nitrogen glovebox. 15 mL of cold (0°C) anhydrous toluene was loaded into separate syringes. The TOPSe precursor was removed

from the nitrogen glovebox and immediately injected into the reaction vessel. The temperature of the reaction solution was maintained at 150 °C during nanocrystal growth. UV/visible/near-infrared absorption measurements (Cary 5E) were used to monitor nanocrystal growth. Once the desired nanocrystal size was obtained (growth time varied from 30 s to 10 min), the heat source was removed from the reaction vessel and 15 mL of anhydrous toluene was swiftly injected into the vessel. The reaction vessel was rapidly cooled to room temperature using an ice bath. The reaction product was cannulated from the reaction vessel into a Schlenk flask and transferred into the nitrogen glovebox. All post-synthesis methods necessary to prepare clean nanocrystal dispersions were carried out in the nitrogen glovebox. The PbSe nanocrystals were precipitated out of the growth solution using a mixture of anhydrous methanol, butanol, and 200 proof ethanol (1:1:2, respectively) and isolated after centrifuging. The supernatant was discarded and the nanocrystals were re-dispersed in dry hexane. Precipitation with 200 proof ethanol followed by re-dispersion in dry hexane was repeated three times. The final product was a solution (variable concentration) of oleic acid-capped PbSe nanocrystals (OA-PbSe) in hexane.

Nanocrystal size was determined by the energy of the first peak in the optical absorption spectrum as calibrated by Dai *et al.* (179). The first exciton absorption energies for the OA-capped nanocrystals used in this study were 0.62 eV (2010 nm), 0.67 eV (1860 nm), 0.70 eV (1770 nm), 0.71 eV (1740 nm), 0.80 eV (1540 nm), 0.84 eV (1470 nm), 0.90 eV (1380 nm), 0.97 eV (1270 nm), 1.12 eV (1110 nm), and 1.14 eV (1080 nm) corresponding to nanocrystal diameters of 6.7 nm, 6.1 nm, 5.8 nm, 5.7 nm, 5.0 nm, 4.7 nm, 4.4 nm, 4.0 nm, 3.4 nm, and 3.3 nm, respectively. The same peak positions sized according to the work of Moreels *et al.* (180) would yield nanocrystal diameters of 7.6 nm, 6.7 nm, 6.2 nm, 6.1 nm, 5.0 nm, 4.7 nm, 4.2 nm, 3.6 nm, 2.9 nm, and 2.8 nm, respectively.

Single crystal rutile TiO₂ was purchased from MTI Corporation (Richmond, CA). The <110> oriented crystals were 10 mm x 10 mm square, 1 mm thick, and mechanically polished on both sides. In-plane crystallographic orientation was determined by optical birefringence at 532 nm. Atomically flat surfaces were obtained by successive rinsing with 0.2 M NaOH then deionized water, followed by immersion in 1 M HCl under UV

irradiation (254 nm) for 30 min and finally rinsing with deionized water and acetone in air (181).

Laser quality fused silica flats were purchased from CVI Melles Griot (Albuquerque, NM). The 15 mm diameter x 1 mm thick circular substrates were cleaned by sonication in acetone followed by immersion in 1 M HCl then rinsing with deionized water in air.

All PbSe nanocrystal films were prepared in a controlled atmosphere argon glovebox to prevent PbSe oxidation. Clean substrates were rinsed with distilled hexane before partial submersion in the OA-PbSe/hexane solution followed by withdrawal at a constant velocity of 1 cm/s. Desired coverage of the TiO₂ substrate was achieved by varying the concentration of the OA-PbSe/hexane solution (typically ~5 mg/mL) and verified by atomic force microscopy (AFM). The dip-coating process yielded samples that were optically uniform over a large area in the center of the substrate with drying lines visible at the top of the sample and along the edges.

Dried OA-PbSe films were submerged in a solution of 1 M hydrazine (HYD) in acetonitrile for 20 min at room temperature then dried under argon. The HYD concentration was chosen following the work of Law *et al.*, who showed removal of oleic acid without change in nanocrystal size or chemical reduction of PbSe (176). The reaction time was chosen based on the continuous red shift of the first absorption peak during the first 10-15 min of HYD treatment followed by saturation of the red-shifted peak position with increasing duration of HYD treatment.

HYD treatment results in nearly complete removal of the oleic acid surface ligands as verified by the disappearance of C-H stretch intensity at ~2920 cm⁻¹ in FTIR spectra (66). Further, we find no evidence from either FTIR or XPS of nitrogen remaining in the film following HYD treatment (in agreement with Law *et al.* (176)), suggesting that HYD has stripped the nanocrystal surface of OA but has not replaced it.

We have used AFM to look for morphological changes in monolayer PbSe films following HYD treatment (66). As deposited, sub-monolayers of OA-capped PbSe will self-assemble into large single-layer islands of 2D hexagonal close-packed nanocrystals. After HYD treatment, the inter-nanocrystal spacing decreases and individual nanocrystals can no longer be spatially resolved, but optical absorption and height histogram analyses

reveal that individual nanocrystals remain distinct (i.e., no ripening has taken place), in agreement with the findings of Law *et al.* (176).

Following the work of Luther *et al.* (177), dried OA-PbSe films were submerged in a solution of 0.1 M 1,2-ethanedithiol (EDT) in acetonitrile for 30 s at room temperature then dried under argon. XPS reveals the presence of sulfur within the EDT-treated PbSe film, supporting the conclusions of Luther *et al.* that EDT quantitatively replaces OA.

For laser experiments, each sample was clamped to a cold finger inside a Janis ST-300 liquid helium cryostat. To prevent exposure of the sample to ambient atmosphere, the cryostat was loaded and sealed inside the argon glovebox. The cryostat was evacuated to less than 1 mTorr base pressure for at least one hour using a liquid nitrogen-cooled cryopump before making measurements.

Atomic force microscopy imaging (AFM) was carried out in a humidity-controlled ($\leq 5\%$ RH) Agilent 5500 scanning probe microscope with a silicon tip (< 10 nm radius of curvature) and rectangular cantilever (3 N/m nominal spring constant). Operation under low humidity and in AC mode with the oscillator in the net attractive regime was necessary to prevent transfer of nanocrystals to the silicon tip or otherwise disturb the PbSe film. See Ref. (66) for further information.

X-ray photoelectron spectroscopy (XPS) was used for compositional analysis of treated samples and to check for Pb oxidation following laser irradiation. Spectra were collected at room temperature in an ultrahigh vacuum spectrometer equipped with a hemispherical electron energy analyzer (Phi 5400). A Mg K_{α} ($h\nu = 1253.6$ eV) anode operated at 200 W was used as the X-ray source. The X-ray incident angle was 5° from surface normal and photoelectrons were collected at 55° from surface normal. A sealed transfer vessel was used for transporting samples from the glovebox to the XPS loading chamber air-free. Due to the high resistivity of the TiO_2 substrates, some modest sample charging was observed (less than 2 eV). To correct for this effect, energy scales were referenced to the Ti 2p binding energy of 458.6 eV (182).

Ultraviolet photoelectron spectroscopy (UPS) was used to determine interfacial alignment of occupied energy levels (see next section). All UPS spectra were collected at room temperature on the same instrument used for XPS. He-I radiation ($h\nu = 21.2$ eV)

was used as the UV light source, and the lamp power was set at 25 W. Incident light was 50° from the surface normal, and photoelectrons were collected along the sample surface normal direction with an analyzer pass energy of 4.45 eV and a sample bias of -8.0 V.

We use Fourier transform infrared (FTIR) and near-infrared (FT-NIR) spectroscopy in multiple total internal reflection geometry for spectroscopic characterization of PbSe nanocrystal films on TiO_2 . Large rutile single crystals oriented $\langle 110 \rangle$ and mechanically polished on both sides were purchased from Princeton Scientific Corporation (Princeton, NJ). These 1 mm thick crystals were cut to 32 mm x 10 mm with a polished 45° bevel on both ends to be used as ATR-FTIR waveguides. PbSe nanocrystal films were prepared on the exposed (110) surface as described. Measurements were carried out inside a nitrogen glovebox using a Nicolet 6700 FTIR-NIR spectrometer with either an InGaAs (FT-NIR) or liquid nitrogen-cooled mercury-cadmium-telluride (FTIR) detector. Periodic interference fringes in the absorption spectrum due to strong TiO_2 birefringence were removed by narrowband Fourier filtering.

7.6. Determining energy alignment using UPS and FT-NIR

While published values of the electron affinity or work function of a material can be a useful starting point for estimating the band alignment between two different semiconductors, these estimates will never reflect the inevitable charge redistribution and interfacial dipole formation that occurs when two materials are brought into close electronic interaction. Consequently, meaningful conclusions about interfacial energy alignment can only be drawn from measurements made on the as-prepared composite interface. To make these measurements, we use ultraviolet photoelectron spectroscopy (UPS), wherein the energies of near-surface occupied (valence) electronic energy levels are determined relative to the substrate Fermi level. Using UPS, the highest occupied electronic energy level of PbSe ($1S_h$) can be placed relative to the TiO_2 valence band edge and Fermi level as a function of nanocrystal size and surface chemical treatment. The position of the PbSe lowest unoccupied energy level ($1S_e$) is inferred from optical absorption measurements made in attenuated total internal reflection geometry on

identical PbSe monolayer films supported on TiO₂ rutile (110) single crystal waveguides as described. Our measurements (summarized in Figure 7.1C and Table 7.1) are in close agreement with the predictions of Hyun *et al.* (79) who determined, based on corrected $\mathbf{k}\cdot\mathbf{P}$ calculations and the cyclic voltammetry measurements of Jiang *et al.* (202), that electron transfer from the lowest excited state of PbSe to TiO₂ is energetically unfavorable for all PbSe nanocrystal sizes that can be reasonably prepared with available colloidal methods.

The photoemission spectrum of clean TiO₂ (110) in the vicinity of the valence band maximum (VBM) is shown in Fig. S1 on both linear (panel **A**) and logarithmic (panel **B**) scales. Spectra are plotted on a binding energy (BE) scale, where $BE = E - E_{\text{Fermi}}$. As is standard for semiconductor VBM determination via UPS, the position of the VBM is obtained by extrapolation from the linear data or, more accurately, by the kink in the logarithmic representation marking the transition from occupied “true” valence band states to the continuum of defect-induced surface states extending to the Fermi level. We place the TiO₂ VBM 2.7 ± 0.1 eV below the Fermi level. Rutile TiO₂ has an indirect band gap of 3.00-3.05 eV over a temperature range of 1.6 K to 300 K (203), placing the TiO₂ conduction band minimum (CBM) 0.3 eV above the Fermi level.

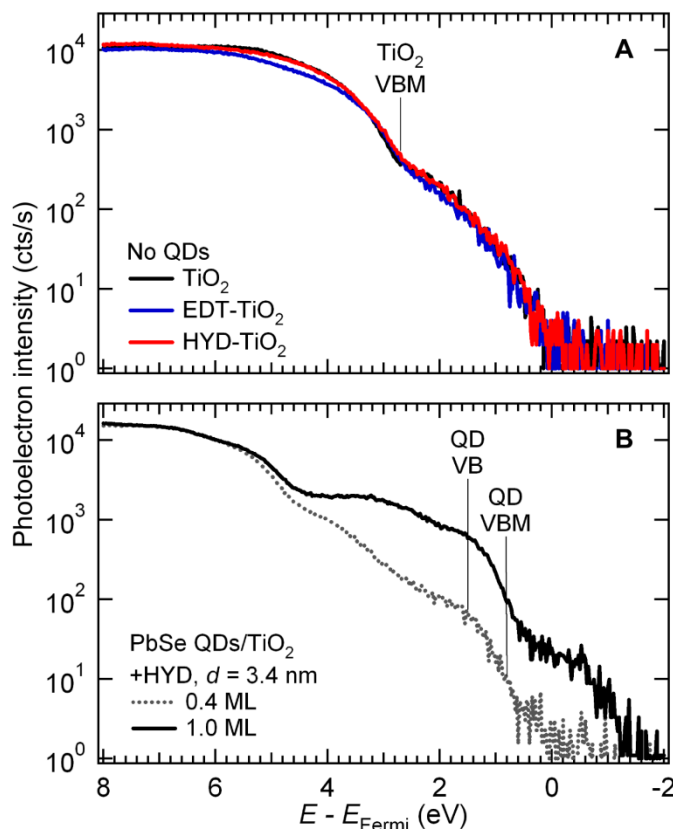


Figure 7.6 (A) UPS spectra of the bare TiO_2 (110) surface treated for 10 min with HYD or 30 s with EDT but without any PbSe nanocrystals. The UPS spectrum is unchanged by chemical treatment over this energy range. (B) UPS spectra of the TiO_2 (110) surface covered with 0.4 monolayers (ML) or 1.0 ML of 3.4 nm PbSe nanocrystals treated with HYD. PbSe valence band (VB) features are evident within the band gap of TiO_2 . The highest occupied nanocrystal energy level, or valence band maximum (VBM), is determined by the inflection point in the photoemission spectrum.

The near-surface valence band structure of clean TiO_2 (110) is largely unchanged after treatment with either HYD or EDT (Figure 7.6A). However, when the surface is covered with chemically treated PbSe nanocrystals (Figure 7.6B), the TiO_2 features are attenuated and we see an increase in photoemission intensity within the energetic region of the TiO_2 band gap. These band gap features increase in intensity with increasing nanocrystal coverage, demonstrating that these features belong to PbSe occupied states. When the surface is covered with untreated OA-capped PbSe nanocrystals, we see only the attenuated TiO_2 VB; the VB features of the nanocrystal are not visible because of the thick shell of insulating ligands surrounding the nanocrystals. Since the density of electronic states within a semiconductor nanocrystal does not follow the same $E^{1/2}$

dependence of bulk semiconductors, extrapolation of the photoemission intensity is not appropriate for nanocrystal HOMO level determination. The HOMO level or VBM is determined by the inflection point in the log-scale representation of the data at the low-binding energy edge of nanocrystal valence emission intensity. This position is most accurately obtained from the second derivative of a smoothed spectrum, i.e. where $d^2 \ln I / dE^2 = 0$.

We use two different PbSe nanocrystal sizes for the UPS experiments: $d = 3.4$ nm and $d = 6.7$ nm. Absorption spectroscopy of these nanocrystals with OA shows the first exciton peaks at 1110 nm ($d = 3.4$ nm) and 2010 nm ($d = 6.7$ nm), corresponding to optical gaps of 1.12 eV and 0.62 eV, respectively. Removal of the OA ligands by HYD leads to a red shift of the first exciton peak by 0.15 eV and 0.07 eV for $d = 3.4$ and 6.7 nm, respectively. Thus, the optical gap of nanocrystals within the treated films is $E_G = 0.97$ eV for $d = 3.4$ nm and $E_G = 0.55$ eV for $d = 6.7$ nm. With EDT treatment, the red-shift of the first exciton transition energy is much smaller, in the range of 0.02-0.04 eV across all sizes (Figure 6.6), and below the energy resolution of the UPS measurement. We take the optical gaps of the EDT-treated 2D nanocrystal assemblies to be $E_G = 1.1$ eV for $d = 3.4$ nm and $E_G = 0.6$ eV for $d = 6.7$ nm. The optical gap is smaller than the transport gap by the exciton binding energy, which generally depends on particle size but is expected to be on the order of a few tens of meV for PbSe due to the large dielectric constant (184). This exciton binding energy is negligible within our experimental energy resolution, so we take the optical gap as equal to the transport gap.

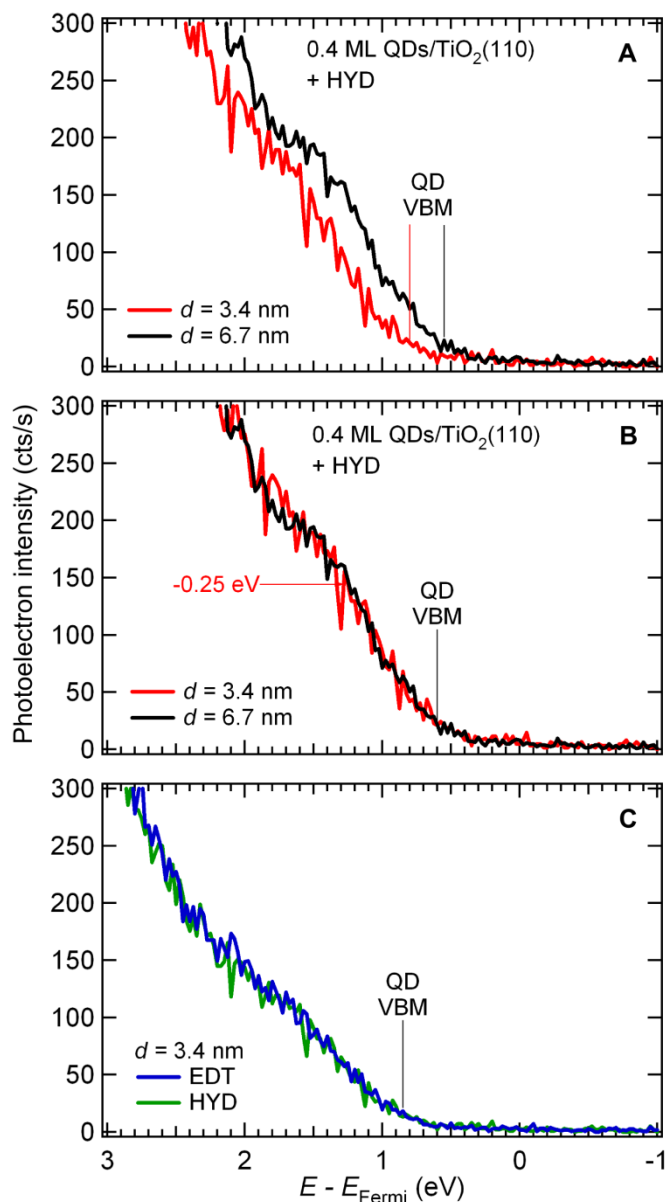


Figure 7.7 Dependence of interfacial energy alignment on nanocrystal size and chemical treatment. (A) UPS spectra of HYD-treated PbSe nanocrystal films for two different size nanocrystals, $d = 3.4$ nm and $d = 6.7$ nm. The locations of the valence band maximum (VBM – determined from log scale inflection points) are indicated by color-coded vertical lines. The intensity of the $d = 3.4$ nm data has been scaled to match the intensity at $d = 6.7$ nm. (B) The same data shown in (A), but the $d = 3.4$ nm trace has been shifted horizontally toward lower binding energy by 0.25 eV to demonstrate the energy alignment difference between the two sizes. (C) UPS spectra of 0.4 ML $d = 3.4$ nm PbSe nanocrystals after HYD or EDT treatment. The energetic alignment is the same for both treatments. Similar results are obtained at $d = 6.7$ nm.

The size dependence of the nanocrystal VBM is summarized in Figure 7.7. As the nanocrystal size is decreased from $d = 6.7$ nm to $d = 3.4$ nm, the VBM shifts further

away from the Femi level, from $BE = 0.55 \pm 0.1$ eV to 0.7-0.9 eV. To more accurately determine the energetic shift, we have normalized the intensities of the two spectra in the nanocrystal VB region and shifted the $d = 3.4$ nm spectrum horizontally to match the spectrum for $d = 6.7$ nm. We find that a binding energy shift of -0.25 ± 0.05 eV provides a nearly perfect match, as shown in Fig. S4B. Given the optical gaps of 0.55 and 0.97 eV for the HYD-treated films of $d = 6.7$ nm and 3.4 nm, respectively, the difference in the nanocrystal LUMO levels is 0.17 ± 0.05 eV. Thus, with decreasing nanocrystal size, the HOMO and LUMO levels shift away from the Fermi level nearly symmetrically. We find that the two different chemical treatments give similar interfacial VB alignment for both 3.4 nm (Figure 7.7C) and 6.7 nm nanocrystals (not shown). Our findings are summarized in Figure 7.1C and Table 7.1.

Table 7.1 Summary of interfacial energy levels (eV) referenced to the Fermi level ($E_F = 0.0$ eV) as determined by UPS and FT-NIR. These are the values plotted in Figure 7.1c. All values have an estimated uncertainty of ± 0.1 eV.

	Substrate Bands		PbSe nanocrystals + hydrazine				PbSe nanocrystals + EDT			
			$d = 6.7$ nm		$d = 3.4$ nm		$d = 6.7$ nm		$d = 3.4$ nm	
	VBM	CBM	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
TiO ₂	-2.7	0.3	-0.55	0.00	-0.80	0.17	-0.55	0.05	-0.80	0.30

7.7. TR-SHG details and control experiments

A home-built 78 MHz Ti:sapphire oscillator (830 nm, 30 fs, 50 nm bandwidth at FWHM, 200 mW) with peak-to-peak stability better than 0.01% seeds a regenerative amplifier operated at 250 kHz (Coherent RegA 9050). The output of the amplifier is compressed (810 nm, 50 fs, 30 nm bandwidth at FWHM, $\pm 0.1\%$ peak-to-peak), attenuated, and then split into two equal intensity beams. One beam (the pump) passes through a variable-length delay line before recombining with the other beam (the probe) on the sample surface. The polarization state of each beam is independently controlled with quartz waveplates and long-wave pass filters are placed immediately in front of the cryostat (in which the sample is mounted) to remove any residual 405 nm light generated in the waveplates or other optical components. The uncoated 1.5 mm thick cryostat

windows are made from Suprasil II, a high-quality amorphous silica glass transparent at 405 nm and exhibiting negligible second order nonlinear susceptibility at normal incidence. The pump and probe beams are softly focused non-collinearly at a mutual angle of $\sim 3^\circ$ onto the sample surface. The projection of the beam on the sample at 45° incidence is a $260\text{ }\mu\text{m} \times 360\text{ }\mu\text{m}$ ellipse, as measured by the knife-edge technique. The laser power is kept sufficiently low to maintain a spatially averaged fluence of less than 1 mJ/cm^2 for both pump and probe pulses. The entire laser system is housed within a light-tight enclosure.

For the two-color measurements (variable wavelength pump, 810 nm probe), a portion of the amplifier output is sent to a double-pass optical parametric amplifier (Coherent OPA 9850) for conversion to longer wavelengths in the near- or mid-infrared. The remaining 810 nm light is used for the probe beam, as above.

By conservation of momentum, second harmonic (SH) light generated from the sample surface is collinear with each reflected beam. When pump and probe pulses are overlapped on the sample in space and time, a third nonlinear signal at the sum of the two frequencies (sum-frequency, SF) is generated at a wave vector in between the two reflected SH signals. This SF signal is equivalent to the cross-correlation of the pump and probe laser pulses and provides a convenient mechanism for optimizing spatial overlap, minimizing pulse width, and calibrating “time zero” at the sample surface.

For all samples at all temperatures, the time-resolved second harmonic (TR-SH) response is observed to be independent of pump beam polarization. Unless otherwise indicated, all TR-SH data shown in this report were collected with orthogonally polarized pump and probe beams to minimize coherent artifacts near $t = 0$ (particularly scattered SF light).

For the laser power and focusing conditions used in this study, the reflected fundamental light is $\sim 10^{10}$ times more intense than the SH light propagating collinearly with it. We use a combination of dichroic mirrors (Layertec), color glass filters (CVI Melles Griot), dispersion gratings (Oriel Cornerstone 130 monochromator), and a large-work function photomultiplier tube (Hamamatsu R4220P) to achieve the desired spectral filtering. A polarizing prism is used to select only the p-polarized component of the reflected SH light. The signal from the PMT is amplified and fed to a lock-in amplifier

(Stanford Research SR850), which is phase-locked with a 500 Hz optical chopper placed in the probe beam path (to distinguish the SH light associated with the probe beam from ambient 405 nm light or scattered SH light associated with the pump). A desktop computer records data from the lock-in amplifier and controls the motorized linear delay stage (Newport – 0.1 μm per step/0.67 fs time resolution).

Because of the excellent stability of the laser system ($\pm 0.1\%$ peak-to-peak rms as measured on an oscilloscope), shot-to-shot normalization was not necessary. The primary noise source in these measurements is Poisson noise arising from the natural sampling statistics of counting discrete photons. The signal-to-noise ratio (SNR) improves as $\sqrt{N}$, where N is the total number of photons collected. Consequently, a typical TR-SH waveform takes about one hour to collect and is the result of averaging ~ 20 scans at 300 time points per scan. High-resolution data such as that presented in Figure 7.2A & Figure 7.5A represents the average of ~ 80 scans collected over the course of five hours. We choose to collect and average many scans instead of dwelling at each time point for an extended period of time so that we can detect (and ensure that we have avoided) changes to the TR-SH waveform over the course of the experiment.

Due to the quadratic dependence of the EFISH signal on incident laser power, $\Delta I^{(2\omega)} \approx \eta \left(I^{(\omega)} \right)^2 E^{\text{sep}}$, it is desirable to use high laser fluences in order to obtain large SNRs. However, high laser power can damage the PbSe nanocrystals and the TR-SH response under high intensity light may not reflect the dynamics of electron transfer under the low excitation conditions characteristic of solar radiation. To assess the effects of prolonged laser irradiation, we continuously monitor the TR-SH waveform during data collection. For the chemically-treated PbSe films investigated here, the only variations in the TR-SH waveform we observe over the course of hours are small changes in the magnitude of the signal due to drifting laser power. However, we do observe qualitative changes in the TR-SH response after a few minutes of laser exposure for PbSe films thicker than ~ 3 ML. This observation is further evidence that hot electron transfer to TiO_2 is an efficient mechanism for energy dissipation within the photoexcited nanocrystal film.

A pump laser fluence of 1 mJ/cm^2 corresponds to an average photoexcitation of one electron-hole pair per nanocrystal for the smallest PbSe nanocrystals used. We have investigated the power dependence of the SH response to laser fluences as low as 0.03

mJ/cm^2 . Only the magnitude of the SH response changes; the dynamics and overall shape of the TR-SH response function are unchanged. We also routinely check the TR-SH response at multiple locations on the sample surface. Again, the magnitude of the response varies due to spatial variation in PbSe surface concentration, but the dynamics are unchanged. Dynamics are also invariant with storage of the sample within the cryostat for days at a time or transferring the sample back to the glovebox for later re-evaluation.

The oxidation of PbSe nanocrystals in air is well documented (177). When the PbSe surface becomes oxidized, peaks in the XPS spectrum due to core level photoemission from oxygen-bound Pb will appear 1.0 eV higher in binding energy than the selenium-bound Pb (183). To be sure that laser irradiation does not lead to photo-oxidation of the PbSe surface under the residual atmosphere within the cryostat (base pressure < 1 mTorr), we measured the XPS spectrum of a 1 ML HYD-treated film after one day's worth of laser experiments (Figure 6.2). The sample was transferred to a sealed vessel inside the glovebox for air-free transfer to the XPS vacuum chamber. The Pb 4f peaks are gaussian in shape without detectable asymmetry toward higher binding energies, indicating that the PbSe surface is free from oxidation.

The 250 kHz repetition rate of the laser system is ideal for femtosecond nonlinear optics at the surface of centrosymmetric media. The small second-order nonlinear susceptibility of these materials and the quadratic dependence of SH signal intensity on laser pulse fluence means that, at conservative laser intensities, only a few SH photons are collected per laser pulse. The high repetition rate of the 250 kHz system (as compared to the typical 1 kHz rate of a standard regenerative amplifier) means that adequate SNRs can be obtained over shorter lengths of data collection time. To be sure that the $(250 \text{ kHz})^{-1} = 4 \text{ } \mu\text{s}$ period between laser pulses is sufficiently long for the system to relax to the ground state, we verify that at negative time-delays (probe arriving before pump) the SH intensity reflected from the sample surface is unchanged when the pump beam is blocked.

The TR-SHG response of bare TiO_2 (110) and bare SiO_2 (amorphous fused silica) is shown in Figure 7.8. The TR-SHG waveform is featureless for both substrates at 300 K and 80 K as well as after treatment with HYD or EDT. The Fermi level of our TiO_2 samples is 0.3 eV below the CBM, so electronic transitions from occupied defect states

within the TiO_2 band gap to the conduction band should be possible with our 1.5 eV photon energy. However, the density of these defect states in our single crystal samples is too small to produce a detectable change in SHG intensity within our signal-to-noise capabilities ($\pm 0.5\%$ of the background level).

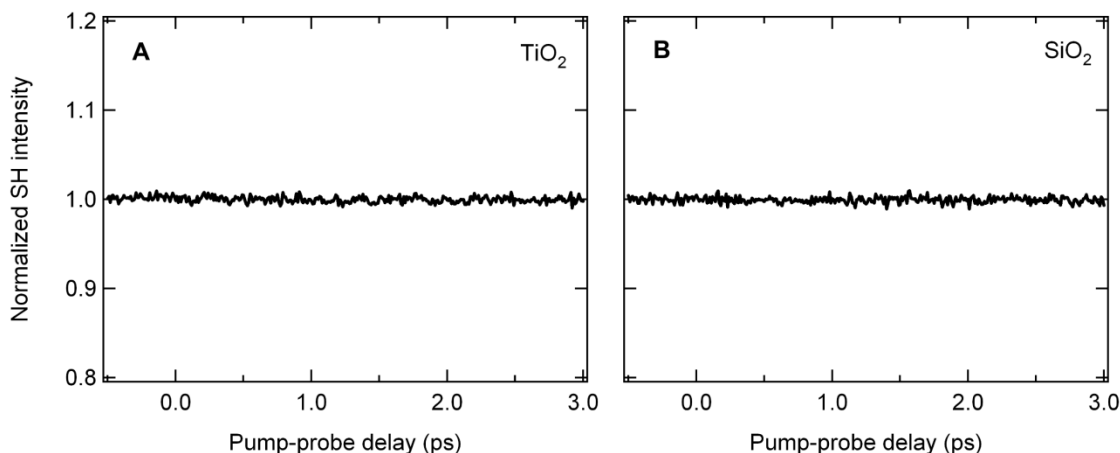


Figure 7.8 TR-SHG response at 80 K of (A) the bare TiO_2 (110) surface and (B) the bare SiO_2 (amorphous fused silica) surface. The TR-SHG response is featureless for HYD- or EDT-treated substrates (without nanocrystals) as well.

The TR-SHG response of OA-capped PbSe nanocrystals on TiO_2 is shown in Figure 7.9. Oleic acid (OA) is a carboxylic acid with an 18-carbon straight-chain aliphatic tail. The OA shell surrounding the nanocrystal electronically insulates the PbSe core from the TiO_2 substrate. Consequently, hot electron transfer from OA-capped PbSe nanocrystals to TiO_2 is not observed. The TR-SHG response of OA-capped PbSe nanocrystal films is featureless (within our signal-to-noise capabilities) for all sizes, temperatures, and substrate materials investigated here.

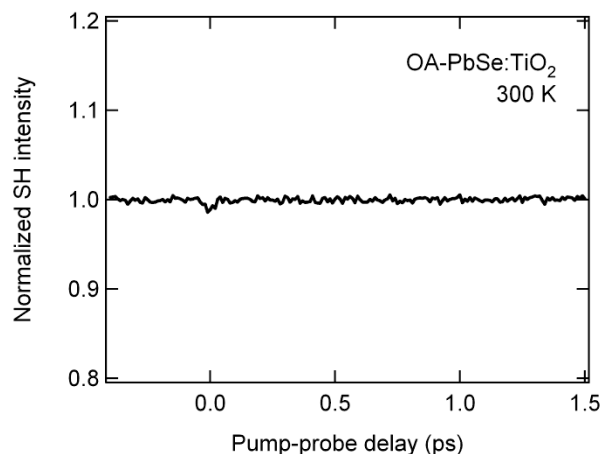


Figure 7.9 TR-SHG response at 300K of oleic acid (OA)-capped PbSe nanocrystals ($d = 6.1$ nm) on TiO_2 . The 18-carbon aliphatic straight-chain ligand insulates the PbSe core from strong electronic interaction with the substrate, preventing hot electron transfer. The small dip at $t = 0$ is a coherent artifact arising from temporal overlap of the pump and probe beams with parallel polarization. TR-SHG waveforms are featureless (within our signal-to-noise capabilities) for all OA-capped PbSe nanocrystals, regardless of nanocrystal size, temperature, or substrate material.

As a negative control, we decreased the pump photon energy to below the threshold necessary to reach the conduction band minimum of TiO_2 (Figure 7.3). The data show a clear rise in SHG intensity following photoexcitation with 810 nm (1.5 eV) light, whereas no discernible change in intensity is observed when the sample is pumped at 1180 nm (1.0 eV). In order to make a fair comparison, it is necessary to maintain the same average excitation across all wavelengths. The average excitation, η , is the average number of photons absorbed (or electron-hole pairs created) per nanocrystal, and is calculated as $\eta = J \cdot \sigma$, where J is the number of photons per laser pulse per unit area and σ is the absorption cross section of a nanocrystal at the pump wavelength (204). As σ varies with photon energy, the photon fluence J must be adjusted so that η is conserved. For the data shown in Figure 7.3, J was chosen to maintain $\eta = 1.0$ electron-hole pairs per nanocrystal.

7.8. Time-domain fitting of the TR-SHG response function

It is evident from inspection of the TR-SH response in Figs. 2A & 4A that interfacial electron transfer occurs within the first 100 fs following photoexcitation of the PbSe nanocrystals. However, the presence of large-amplitude coherent phonon oscillations obscures the underlying dynamics of electron transfer. Additionally, insight into the mechanism of coherent phonon excitation can be acquired through knowledge of the initial phase of the oscillator (191). To uncover these underlying electron transfer dynamics and elucidate the initial phase of each vibrational mode, we fit the entire time-resolved SHG waveform to a phenomenological model for the EFISH response based on first-order kinetics, taking into account the finite width of the laser pulse. While this simplistic model fails to account for quantum dynamic processes such as electronic dephasing that are important on these timescales, it nonetheless reproduces most of the features of the time-resolved SHG waveform and provides an estimate of the electron transfer time constant.

The total time-dependent SH signal, $S(t)$, can be expressed as the sum of the constant background SH intensity, the time-dependent EFISH intensity, and up to three sinusoidal coherent phonon contributions (as indicated by the Fourier transforms shown in Figure 7.5B),

$$S(t) = S_0 + \Delta S_{\text{EFISH}}(t) + \Delta S_{\text{T}}(t) + \Delta S_{\text{p}}(t) + \Delta S_{\text{LO}}(t). \quad (7.2)$$

The last three terms in Eq. (7.2) with subscripts T, p, and LO refer to the TiO_2 surface phonon, the PbSe surface phonon, and the PbSe bulk LO phonon, respectively. The EFISH contribution is proportional to the total number of electrons, $N_e(t)$, that have transferred to TiO_2 ,

$$\Delta S_{\text{EFISH}}(t) = \alpha N_e(t), \quad (7.3)$$

where α is a proportionality constant. $N_e(t)$ is found by solving a system of linear ordinary differential equations,

$$\begin{aligned}\frac{dN_{\text{nc}}^*}{dt} &= R \cdot I_{\text{pump}}(t) - \frac{N_{\text{nc}}^*}{\tau_{\text{ET}}}, \\ \frac{dN_{\text{e}}}{dt} &= \frac{N_{\text{nc}}^*}{\tau_{\text{ET}}} - \xi N_{\text{e}}\end{aligned}\quad (7.4)$$

where N_{nc}^* is the population of photoexcited nanocrystals, τ_{ET} is the electron transfer time constant, ξ is the electron transport/recombination rate, and R is a constant that depends on the laser fluence and absorption cross-section of the nanocrystals. $I_{\text{pump}}(t)$ is the Gaussian pump pulse intensity envelope,

$$I_{\text{pump}}(t) = \exp\left(-\frac{(t-t_0)^2}{\left(\text{width}/\sqrt{2\ln 2}\right)^2}\right), \quad (7.5)$$

where width is the FWHM of the pump-probe cross correlation. The number of TiO_2 surface phonons generated per unit time is proportional to the instantaneous rate of electron transfer, $K_{\text{ET}}(t)$, which is equal to,

$$K_{\text{ET}}(t) = \frac{N_{\text{nc}}^*}{\tau_{\text{ET}}}. \quad (7.6)$$

The total time-dependent modulation of the SHG intensity by the TiO_2 surface phonon population is found by convolving an exponentially decaying sine wave with $K_{\text{ET}}(t)$,

$$\Delta S_{\text{T}}(t) = A_{\text{T}} \left[K_{\text{ET}}(t) * \sin(\omega_{\text{T}}t + \varphi_{\text{T}}) \exp(-\Gamma_{\text{T}}t) \right], \quad (7.7)$$

where the symbol $*$ denotes a convolution. A_{T} , ω_{T} , φ_{T} , and Γ_{T} are the phonon amplitude, frequency, phase, and dephasing rate, respectively. The time-dependent modulation of the SH intensity by the PbSe surface optical and bulk LO phonon modes is found similarly,

$$\begin{aligned}\Delta S_{\text{p}}(t) &= A_{\text{p}} \left[I_{\text{pump}}(t) * \sin(\omega_{\text{p}}t + \varphi_{\text{p}}) \exp(-\Gamma_{\text{p}}t) \right] \\ \Delta S_{\text{LO}}(t) &= A_{\text{LO}} \left[I_{\text{pump}}(t) * \sin(\omega_{\text{LO}}t + \varphi_{\text{LO}}) \exp(-\Gamma_{\text{LO}}t) \right],\end{aligned}\quad (7.8)$$

with each contribution convolved with the pump pulse intensity envelope because these modes are directly generated by the laser pulse.

To perform the fit, we employ a parallel genetic optimization algorithm. The best-fit curve to the data in Figure 7.5A is shown in Figure 7.10A. The non-oscillatory

component of the TR-SH signal, $S_{\text{non-osc}}(t) = SH_0 + \Delta S_{\text{EFISH}}(t)$, is shown in Figure 7.10B. We extract an electron transfer time constant of $\tau_{\text{ET}} = 31 \pm 5$ fs (assigned uncertainty is the standard deviation of the fit parameter). The three sine components included in the fitting function have best-fit frequencies of $\omega_p = 66.8 \text{ cm}^{-1}$, $\omega_T = 95.3 \text{ cm}^{-1}$, and $\omega_{\text{LO}} = 131.0 \text{ cm}^{-1}$; phase $\phi_p = 3\pi/2$ rad (cosine-like/displacive), $\phi_T = 3\pi/2$ rad (cosine-like/displacive), and $\phi_{\text{LO}} = \pi$ rad (sine-like/impulsive); and dephasing times $\Gamma_p^{-1} = 520$ fs, $\Gamma_T^{-1} = 1100$ fs, and $\Gamma_{\text{LO}}^{-1} = 950$ fs.

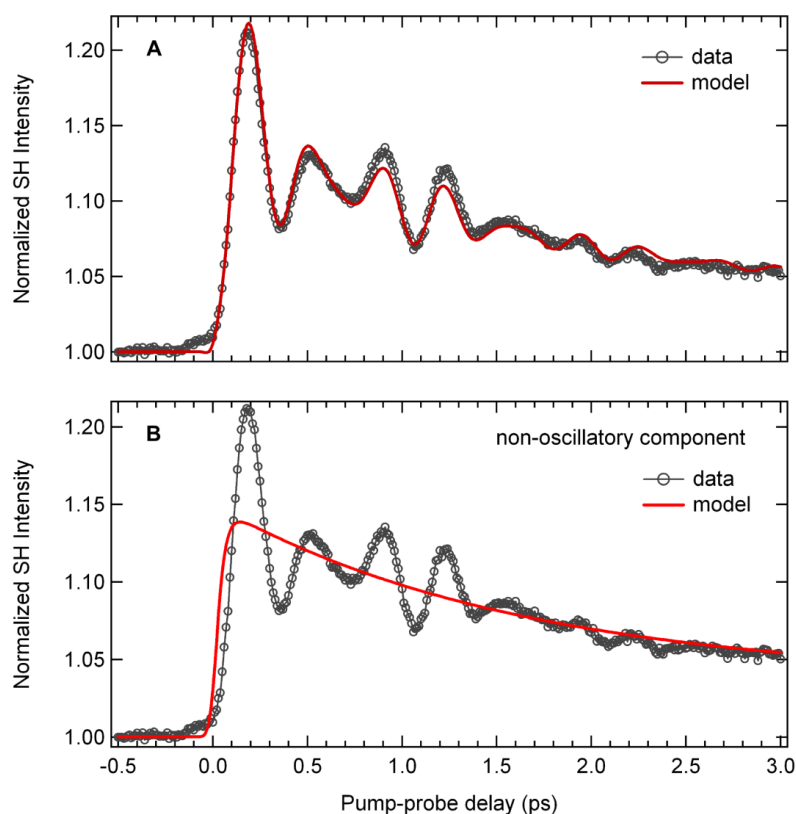


Figure 7.10 Results of TR-SHG curve-fitting to the data shown in Figure 7.5A, based on a phenomenological model for the EFISH response. We extract an electron transfer time constant of 31 ± 5 fs. Three sine components are included in the fitting function, with best-fit frequencies 66.8 cm^{-1} , 95.3 cm^{-1} , and 131.0 cm^{-1} ; phase $3\pi/2$, $3\pi/2$, and π ; and dephasing times 520 fs, 1100 fs, and 950 fs, respectively. (A) The entire best-fit TR-SH waveform. (B) The non-oscillatory part of the TR-SH signal, revealing the underlying electron transfer dynamics.

7.9. The electric field strength and the temperature dependence of SHG signal recovery

Because the distance over which electrons and holes are separated (10-20 nm, see below) is much smaller than the diameter of the laser spot on the sample (hundreds of microns), the charge-separated interface can be modeled as an infinite parallel plate capacitor. The electric field at the interface (denoted in this section by the symbol $\mathbf{E}$ to avoid confusion with the symbol for energy, E) is given by,

$$\mathbf{E} = \frac{1}{\varepsilon_r \varepsilon_0} \frac{2Q^{\text{sep}}}{A}, \quad (7.9)$$

where $2Q^{\text{sep}}$ is the total amount of separated charge (each “plate” has charge Q^{sep}), A is the irradiated area, ε_r is the dielectric constant at the interface, and ε_0 is the permittivity of free space. The surface concentration of nanocrystals is determined by the packing of OA-capped nanocrystals within the monolayer as formed during the dip-coating process. High-resolution AFM imaging of individual nanocrystals within the film reveals a hexagonally close-packed 2D array (66). For 80% efficient electron transfer from a complete monolayer with 10 nm lattice constant, $Q^{\text{sep}} / A = 1.5 \times 10^{-3} \text{ C m}^{-2}$. The dielectric constant of rutile TiO_2 perpendicular to the optical axis maintains its “low frequency” value of $\varepsilon_r = 86$ to frequencies as high as 0.3 THz (205). The corresponding dielectric constant of PbSe is $\varepsilon_r = 210$ (206). A composite value of $\varepsilon_r \approx 100$ corresponds to an electric field strength of $3 \times 10^4 \text{ V cm}^{-1}$. Thus, the electric field at the interface is on the order $\mathbf{E} \approx 10^4\text{-}10^5 \text{ V cm}^{-1}$, which is comparable to the field strengths required for observation of large EFISH signals at Si-SiO₂ interfaces in field-effect transistors (84).

After a fast rise in SH intensity due to ultrafast electron transfer, the EFISH signal decays over the course of picoseconds due to electron transport back to the TiO_2 surface and subsequent back-electron transfer to the ionized nanocrystal. The overall process involves ballistic electron injection followed by hot electron relaxation to form band-edge polarons then Drude-like transport back to the surface under the action of the interfacial electric field. Hot electron relaxation in ionic semiconductors such as TiO_2 is dominated by the emission of polar optical (LO) phonons (157), which varies weakly over the

temperature range considered here due to the very high frequency of these modes in TiO₂ (200 cm⁻¹/24 THz/100 meV) (207). The ballistic mean free path, λ_b , of an electron travelling in rutile perpendicular to the optical axis and having excess energy E^{ex} is given by,

$$\begin{aligned}\lambda_b &= \langle \tau_b \rangle \cdot v_b \\ &= \langle \tau_b \rangle \cdot \left(\frac{2E^{\text{ex}}}{m_{\perp}^*} \right)^{1/2},\end{aligned}\tag{7.10}$$

where $\langle \tau_b \rangle$ is the mean scattering time, v_b is the velocity of the ballistic electron, and $m_{\perp}^* = 1.2m_e$ is the electron band mass (208). A discrete flux of electrons crossing the surface will establish an energetically relaxed band-edge electron (polaron) density distribution of the form $n = n_0 \exp(-z / \lambda_b)$, where n is the local number concentration of electrons (polarons) and z is the coordinate in the surface normal direction, with $z=0$ at the surface and positive values of z increasing within the bulk of the crystal. The electron (polaron) population will drift back toward the interface under the action of the interfacial electric field where electron transfer back to the nanocrystal film reduces the total amount of separated charge, given by,

$$Q^{\text{sep}} = Ae \int_{z=0}^{z=\infty} n(z,t) dz .\tag{7.11}$$

Upon integration, we find that the total amount of separated charge decreases over time according to,

$$Q^{\text{sep}}(t) = Q_0 \exp\left(-\frac{v_p t}{\lambda_b}\right),\tag{7.12}$$

where $v_p = \mu E$ is the polaron drift velocity and μ is the polaron mobility. Since the change in SH intensity is proportional to the total amount of separated charge, $\Delta I^{(2\omega)}(t) \propto Q^{\text{sep}}(t)$, we may fit the SH signal to the form,

$$I^{(2\omega)}(t) = I_0^{(2\omega)} + \Delta I_0^{(2\omega)} \exp(-\xi t),\tag{7.13}$$

with the pump-induced SH signal decay rate, ξ , given by the expression $\xi = \mu \mathbf{E} / \lambda_b$. Since λ_b varies only weakly with temperature, we may (to first approximation) conclude that the temperature dependence of the SH signal recovery rate is contained in the temperature dependence of the polaron mobility,

$$\xi(T) \propto \mu(T), \quad (7.14)$$

as demonstrated by the correlation shown in Figure 7.2D.

A typical polar optical scattering time of $\langle \tau_b \rangle = 50$ fs and hot electron excess energy of $E^{\text{ex}} = 0.2$ eV lead to a ballistic mean free path of $\lambda_b = 12$ nm. For an electric field strength of 3×10^4 V cm⁻¹ and a polaron mobility at 80 K of 20 cm² V⁻¹ s⁻¹, we arrive at an expected SH signal recovery time constant of ~ 2 ps, or $\xi = 0.5 \times 10^{12}$ s⁻¹, which is close to the value at 80 K shown in Figure 7.2D.

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