Deconstructing the Room-Temperature Emission Spectra of Nanocrystals Using Photon-Correlation Fourier Spectroscopy

by

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Abstract

The photoluminescence spectrum of an ensemble of emitters is the result of the homogeneous “natural” spectra of single emitters subjected to interparticle inhomogeneities and perturbations from the environment. For semiconductor nanocrystals (NCs), efforts to tune ensemble linewidths for optical applications have focused primarily on eliminating sample inhomogeneities because conventional single-molecule methods cannot reliably build accurate ensemble-level statistics for single-particle linewidths. Photon-correlation Fourier spectroscopy in solution (S-PCFS) offers a unique approach for investigating single-nanocrystal spectra with large sample statistics, without user selection bias, with high signal-to-noise ratios, and at fast timescales.

With S-PCFS, we directly and quantitatively deconstruct the ensemble spectra of nanocrystals into contributions from the average single-NC homogeneous linewidth, spectral dynamics, and sample inhomogeneity. First, we discovered that single NCs at room temperature, in contrast to cryogenic temperatures, do not exhibit spectral dynamics on sub-millisecond timescales. Second, the linewidths of these homogeneous spectra were found to vary significantly from batch to batch and subject to synthetic control. Our findings crystallize our understanding of the synthetic challenges facing underdeveloped nanomaterials such as InP and InAs nanocrystals and introduce new avenues for the synthetic optimization of fluorescent nanoparticles.

Finally, we have made strides toward understanding the underlying physical processes responsible for the homogeneous spectra of single nanocrystals at room temperature. Through careful synthetic control over the nanocrystal structure and composition, we have been able to understand changes in the homogeneous spectral linewidth in terms of exciton-phonon coupling. Combined with a simple spectral lineshape model, we have worked towards quantitatively understanding exciton-phonon coupling with respect to specific nanocrystal structural and composition parameters.

Thesis Supervisor: Mouni G. Bawendi
Title: Lester Wolfe Professor of Chemistry
To my Mother and Father
Acknowledgments

I’ve heard it said
That people come into our lives for a reason
Bringing something we must learn
And we are led
To those who help us most to grow
If we let them
And we help them in return
Well, I don’t know if I believe that’s true
But I know I’m who I am today because I knew you . . .

Who can say if I’ve been changed for the better?
But because I knew you
I have been changed for good.
—Wicked, The Musical

In many ways, this PhD thesis represents the culmination of a lifetime of education. For such an occasion, the least I can do is take this space to deeply thank all of the people who have been instrumental in my education and in my development as a person. Even if they will never know how much they have meant to me.

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School instructors can only teach you so much. It took me a long time to realize how significantly I am affected by each and every one of my friends. Timothy Amyot and Romulo Cabeza were my first close friends in elementary school. I was particularly
close to Timothy, who had a very mature outlook on life that was completely foreign to me at the time. From him, I first learned the value of having trustworthy friends who have your back. Thomas Chae, Michael Pan, Sarah Hahn, Sarah Lewis, and Kate Thompson played significant roles in my development as a young adult. I have included their names here despite losing virtually all contact with them after middle school. It was in high school that I made some of my most memorable friendships. Alex Berg, David Bochner, and Brandon Ferguson have been some of my most loyal and dependable friends since high school. I hope that they consider me one of theirs as well.

Attending Stanford University was an extraordinary experience. As I continue to be reminded, it is always the people who make being at any place worthwhile. Some of the people I met there on my very first day remain some of my closest friends now. I particularly want to thank Kellen Schefter, Alex Berg, and Michael Ramm for their support over the years – the kind only a special kinship can cultivate. Anthony Scodary, Nico Benitez, Josh Stark, and Alex Williamson round out the remainder of the draw group and have been an endless source of wit, humor, introspection, and adventure. I also want to note how much I value my friendship with Kara Johnson, whose seemingly endless enthusiasm and energy is an inspiration in itself.

I met, worked with, and learned from incredible scientists during my time at Stanford. Ben Spry was my first TA at Stanford and became an excellent and supportive mentor during my entire time there. So Yeon Kim, my research mentor in the Moerner lab, had an endless well of patience for a clumsy undergrad. I also learned a great deal working with Whitney Duim, Erik Miller, Adam Cohen, Sam Lord, Julie Biteen, and Hsiao-lu Lee. Finally, Professor W. E. Moerner was an excellent undergraduate advisor: patient, understanding, and supportive. To this day, I am shocked at how much time and attention he afforded to working with me and he deserves a tremendous amount of my gratitude.

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There is a well-known saying that “familiarity breeds contempt”. That is, the more you get to know somebody, the less you like or respect that person. However, Moungi Bawendi is one of the rare individuals for whom this is not the case. I came to graduate school to learn to be a scientist and with each passing year, my personal growth actually coincided with holding Moungi in higher esteem. With a laid-back but professional demeanor, Moungi encouraged a freedom to explore and disagree, while maintaining sage guidance when necessary. All this with an unwavering commitment to doing science rigorously and honestly, and a grounded understanding that grad students are real people with lives that can sometimes be challenging. Thank you Moungi for all that you have done for me. It has been a tremendous honor and a unique privilege. As the Roman writer Apuleius originally wrote, “familiarity breeds contempt, but rarity wins admiration”.

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Chapter 1

Introduction

1.1 Optical Measurements of Photoluminescence

At the root of nearly all the physical sciences is the study of the properties of microscopic systems. A particularly fruitful avenue for these types of investigations has been optical measurements, which take advantage of light-matter interactions. Physical processes at the molecular scale can be investigated by monitoring the fate of a photoexcited electron. For instance, photovoltaic devices can be studied by measuring the separation and transport of optically-excited carriers.\(^1\) Also, vision in animals can be understood by studying the conformational changes of receptor proteins that occur upon absorption of light by chromophores.\(^2\) Finally, the complexities of photosynthesis can be unraveled by monitoring the transfer of energy between photosystems that eventually results in the biosynthesis of ATP.

Luminescent materials belong to a intriguing class of optically-active materials that is attractive for many applications such as bio-imaging, LEDs, and displays. Photoluminescence, the phenomenon of absorbing and subsequently emitting light, offers a particularly practical window to the microscopic world because the emitted light acts as a reporter of the emitter with minimal background. Moreover, the symmetry between the absorption and emission processes offers a neat framework for understanding the photoluminescence signal.
1.2 Single-Molecule Microscopy and Spectroscopy

Systems comprised of microscopic constituents often exhibit both significant heterogeneity between individual members as well as time-dependence in their properties. These complexities can render the results of ensemble-averaged measurements ambiguous, leaving the intrinsic physics obscured. Single-molecule microscopy and spectroscopy have revolutionized the study of microscopic systems because of their ability to unambiguously disentangle the effects of inhomogeneity and dynamical fluctuations.

Conventional single-molecule fluorescence techniques rely on removing ensemble averaging by spatially isolating single emitters on a surface and measuring their fluorescence. As shown in Figure 1-1, this is typically performed by using a laser for an excitation source and a high numerical aperture objective in an epifluorescence microscopy geometry. In this arrangement, the excitation and collection are performed using the same pathway. Scatter from the excitation laser is removed using a filter and the fluorescence from the single emitter is detected. Throughout this thesis, we reflect on variations of the schematic shown Figure 1-1 that provide access to different types of information at the single-emitter level.

While the study of biochemical and cellular systems has prominently benefited from single-molecule investigations, these techniques have also been essential for our understanding of semiconductor nanomaterials. Prior to the advent of single-
molecule fluorescence spectroscopy, many of the fundamental optical properties of colloidal semiconductor nanocrystal quantum dots were obscured by ensemble averaging over their inherent inhomogeneities. Single quantum dot spectroscopy has become a leading technique for the unambiguous determination of the governing excitonic physics of these nanoscale systems.

1.3 Semiconductor Nanocrystal Quantum Dots

The defining feature of semiconductor nanomaterials is that their electronic energy levels are determined not only by their material composition but also by their structure. This is because the energies of these states are perturbed by quantum confinement when a spatial dimension of a nanostructure becomes comparable to the effective size of the electronic wavefunction. This effect is maximized in the case of quantum dots (QDs), where confinement occurs in all three dimensions. Here, photoexcitation results in an electron-hole pair, often called an “exciton”, that is bound primarily by the dimensions of the particle rather than the carriers' mutual Coulombic interaction. The energy of these excitons, and thus the optical properties of QDs, can be directly tuned by changing the particle size. Quantum dots can be self-assembled through molecular beam epitaxy or chemically synthesized in solution. This thesis focuses on the latter, which are often referred to as “nanocrystals” (NCs), because they are colloidal suspensions of crystalline material.

Semiconductor nanocrystals are synthesized, modified, and processed in solution. They generally consist of a core, an inorganic shell, and a passivating ligand layer. The size, composition, and geometry of the core, shell, and ligands can be tuned to produce particles with high brightness and photostability from the visible to the mid-wavelength infrared. Compared to their molecular dye counterparts, they have larger absorption cross sections, broader absorption spectra, and narrower emission linewidths. Moreover, with modifications to the ligand layer on the surface of the nanocrystal, these particles can be made amenable to different environments. These versatile and unique properties have been harnessed in many
applications such as biological imaging, \textsuperscript{21} displays, \textsuperscript{24} photodetectors, \textsuperscript{25} solar cells, \textsuperscript{26} solid-state lighting, \textsuperscript{27} and more. \textsuperscript{1,28}

The growing use of nanocrystals in optical applications has relied on the interplay between advancements in synthetic methodologies and advancements in our understanding of their fundamental physical properties. However, the chemical synthesis of these materials tends to produce a structurally polydisperse sample with a distribution of optical properties. Therefore, ensemble-level investigations of nanocrystals are invariably complicated by inhomogeneous spectral broadening and averaging of any dynamical properties. \textsuperscript{7} With the advent of single-molecule fluorescence spectroscopy, nanocrystals can be investigated one at a time, bypassing ensemble averaging and revealing unforeseen phenomena. \textsuperscript{4} The signatures of these nanoscale processes are encoded within the stream of photons emitted from a single nanoparticle (Fig 1-2).

### 1.4 Overview of Thesis

In this thesis, we begin with a discussion on the application of single-molecule fluorescence techniques to single nanocrystals. In Chapters 2 and 3, we review how our understanding of nanoscale phenomena in colloidal quantum dots has developed alongside our ability to characterize the photon stream from individual particles. From
relatively simple integrative "binning" techniques to more advanced single-photon counting methods, measurements of the timing and energies of photons emitted from single nanoparticles have helped reveal complex and dynamical phenomena. Additionally, we reflect on how the inherent complexity and disorder of nanocrystals has necessitated the assembly of a diverse toolbox of single-molecule techniques. In this way, single-molecule studies of colloidal quantum dots represent an archetype for the elucidation of optical physics at the nanoscale.

However, conventional single-molecule spectroscopy suffers from a fundamental tradeoff between spectral resolution, temporal resolution, and signal-to-noise ratio. In Chapter 4, we discuss photon-correlation Fourier spectroscopy (PCFS), an advanced spectroscopic technique that monitors spectral information through a different paradigm that in the past. In essence, PCFS measures spectral information by monitoring the energy differences between photon pairs. We provide theoretical background and a summary of experimental implementations of PCFS on single nanocrystals.

Despite the power of PCFS and the new types of spectral information that it can access, this technique still relies on investigating isolated emitters one at a time. As a result, it is non-trivial to extrapolate any findings from a single particle to the sample batch as a whole. For nanocrystals, these concerns have hindered the unambiguous characterization of the links between synthetic methodologies and single-nanocrystal spectral properties. For the remainder of this thesis, we discuss an extension of PCFS that takes the principles of PCFS, but applies them to study single-nanocrystal spectral properties with ensemble-level statistics.

As a foundation for understanding this extension of PCFS, we provide in Chapter 5 an introduction to fluorescence correlation spectroscopy (FCS), which is a technique for monitoring the temporal distribution of photons from emitters in solution diffusing through a laser focus. Rather than spatially separating emitters on a surface and monitoring the emission from each emitter one at a time, FCS serves to separate the emission from emitters temporally by monitoring the relative arrival times of photons as emitters diffuse into and out of the focal volume. With this analysis, photon pairs
In this thesis, we deconstruct the ensemble spectra of nanocrystals at room temperature and determine the contributions due to inhomogeneous broadening, spectral diffusion, coupling to the bath that broadens the “natural” spectrum. Can be determined to have arrived from the same emitter or from different emitters.

Chapter 6 and the remaining chapters span a larger effort to deconstruct the room-temperature emission spectra of nanocrystals. As shown in Figure 1-3, the emission spectrum of an ensemble of emitters consists of the spectra of single emitters (the homogeneous component) convoluted with the heterogeneities in the system (the inhomogeneous component). The single-emitter spectrum originates from broadening of the lifetime-limited natural emission spectrum by intrinsic and extrinsic interactions with the environment. Typically, these interactions are a combination of photoinduced spectral diffusion (extrinsic) and excitonic coupling to the bath (intrinsic).

FCS monitors whether photon pairs originated from the same emitter of different emitters. PCFS monitors the spectral coherence between photon pairs. In Chapter 6, we discuss the marriage of FCS and PCFS, which gives us PCFS in solution, or S-PCFS. With S-PCFS, spectral information can be distinguished from photon pairs that came from the same emitter and photon pairs that came from different emitters thereby providing direct access to both single-emitter spectral information.
with ensemble-level statistics and spectral information of the entire ensemble. We first provide a theoretical treatment and then provide a proof-of-principle experiment that demonstrates the successful experimental implementation of S-PCFS.

In Chapter 7, we discuss the implementation of PCFS to study spectral diffusion. We discuss a study of spectral diffusion in nanocrystals on timescales much more rapid than conventional single-molecule techniques can access. In Chapter 8, we study the intrinsic single-nanocrystal spectral linewidth averaged over a sample batch. We observe significant variations in single-NC emission linewidths that appear to be directly linked to the structure and composition of the particles and therefore provide a new avenue for the rational design of nanocrystals for optical applications. We discuss the origins of these spectral linewidth changes in Chapter 9 and end with some concluding remarks in Chapter 10.
Chapter 2

Photoluminescence Intensity From Single Nanocrystals

The fluorescence quantum yield of luminescent materials is of paramount importance for practical applications. However, unlike the best organic dyes, which had been established to have near-unity quantum yields, early CdSe nanocrystals exhibited quantum yields that were far from unity. It was unclear whether the low ensemble quantum yield resulted from poor emission efficiency of individual particles, from subpopulations of emissive and non-emissive particles, or from temporal dynamics in the emission. In this chapter, we discuss how single-molecule techniques found an immediate niche addressing this quandary. By removing ensemble averaging, they revealed complexity in single-nanocrystal emission that could not have been inferred from ensemble measurements. All of the work discussed in this chapter was performed by other researchers, many of whom were also in the Bawendi lab. Much of this chapter appeared in a review paper written with Andrew Beyler, Thomas Bischof and Mark Wilson (Ref. 32).

2.1 Intensity Binning

Fluorescence measurements of individual nanocrystals are generally performed by dispersing them on a substrate, exciting them with a laser in an epifluorescence
Figure 2-1: a) The photon stream emitted by a single emitter can be analyzed in terms of the number of photons per integration bin of duration T. b) An intensity trace collected from a single InAs nanocrystal shows fluorescence intermittency or “blinking”. c) The probability density of on-times (red) and off-times (open) from the intensity trace of a single CdTe nanocrystal follows a power-law. The on-time distribution possesses a truncation at longer durations (Adapted from Ref. 36 with permission. Copyright 2001 by the American Physical Society). d) An ensemble of CdSe/CdS core/shell particles exhibits intrinsic photodarkening under cw excitation due to truncation in the on-time power law distribution (blue) while an ensemble of next-generation CdSe/CdS particles with suppressed blinking shows no photodarkening.15

microscope, and then detecting the photon stream emitted by each particle.5,7 The most straightforward analysis of this stream, intensity binning, quantifies the number of photons detected during a series of integration times, T, and monitors how the emission intensity changes as a function of time (Fig. 2-1a). As discussed in a number of reviews, intensity binning has been used to study the photon emission rate, the photostability of the emitter, and the timing of fluctuations in the intensity of single nanocrystals.33–35 Here, we highlight several key findings and their implications.

Single QDs exhibit far greater overall photostability than many of their molecular dye counterparts. Under ambient conditions, many single molecules emit no more than \( \sim 10^6 \) photons before they “photobleach” irreversibly.37 However, during early investigations, individual CdSe QDs were found to be much more photostable, emitting upwards of \( 10^9 \) photons before irreversibly bleaching.38
Despite their photostability, the emission from a single QD was found to exhibit nearly binary quenching and revival of intensity (Fig. 2-1b). A similar “blinking” phenomenon had been previously observed in single dye molecules. In these molecules, “on” events and “off” events could be distinguished by applying an appropriate threshold to the binned intensity traces. This analysis showed that the probability densities for the distribution of on- and off-event durations followed exponential or biexponential decays, reflecting the characteristic timescales for the intermittency process. For dyes, blinking has been understood in terms of intersystem crossing between the singlet excited state and a manifold of non-emissive triplet states.

In contrast, the on- and off-times of single nanocrystals were distributed across many orders of magnitude in time, giving rise to probability densities that were best described by a power law: \( P(\tau_{\text{on/off}}) \propto \tau_{\text{on/off}}^{-\alpha} \). The on- and off-time distributions followed the same power-law exponent, though depending on experimental conditions such as excitation intensity or temperature, the on-time power law could show a truncation, or cut-off, at longer times (Fig. 2-1c). Taken together, these observations implied that blinking in nanocrystals cannot be described by simple transition rates and that the underlying mechanism of blinking must be more complicated than intersystem crossing to a dark state. Blinking was initially believed to result from the non-radiative Auger-like interaction between the photogenerated electron-hole pair and a spectator charge within the core states. However, recent studies have challenged this hypothesis and have suggested that blinking arises from the interplay between the exciton and additional charges in the system (photogenerated or not), carrier trap states, and other non-radiative pathways.

The power-law statistics of single QD blinking have far-reaching implications for QD applications. Because individual QDs often exhibit on-time distributions with a truncation timescale much shorter than their off-time distributions, an ensemble of QDs will undergo photodarkening under cw illumination (Fig. 2-1d, blue). In other words, the emission intensity of an ensemble of QDs will decrease to an equilibrium value because, for any given nanocrystal, long off-times occur more frequently than long on-times. This effect, also referred to as statistical aging, is an intrinsic
and purely statistical photodarkening process and is therefore reversible (Fig. 2-1d, blue).\textsuperscript{50,51} This result illustrates the intimate connection between single-molecule properties and ensemble photodynamics.

There have been considerable synthetic efforts toward mitigating the effects of blinking. In the past five years, advancements in the synthesis of CdSe core/shell particles have led to particles with strongly suppressed blinking.\textsuperscript{15,52–54} Characterized by short off-time durations and long on-time durations, these particles were found to possess high on-time fractions, unusual exponents in their on- and off-time power-law distributions, and a lack of intrinsic photodarkening (Fig. 2-1d, red).\textsuperscript{15} This blinking suppression was initially believed to be largely due to the thickness of the CdS shell, however recent studies suggest that the structure at the core/shell interface may play a greater role.\textsuperscript{15,52,55} Despite these tremendous strides in nanocrystal synthesis, the physical origin of blinking and the mechanism of its suppression remain open questions.\textsuperscript{56}

### 2.1.1 Limitations of Intensity Binning

Intensity binning methods are excellent for many investigations because they can access timescales ranging from milliseconds to thousands of seconds and probe signals over a large dynamic range. However, this method alone is insufficient for fully understanding the physical mechanisms underlying QD emission. First, analysis of on- and off-times requires the use of thresholds, which can introduce artifacts.\textsuperscript{57} Moreover, all binning methods suffer from the same fundamental drawback: they cannot resolve individual photon detection events. An intensity trace can show, for example, that in a given 50 ms interval, 200 photons were emitted by the particle. However, it cannot report on the timing between individual excitation and emission events nor can it show how these photons were temporally dispersed inside that integration time. To address this fundamental limitation of integrated binning techniques, we turn to time-resolved photoluminescence and photon-correlation techniques, which analyze the precise arrival times of emitted photons.
Figure 2-2: a) The photoluminescence (PL) decay is the histogram of photon arrival times relative to an excitation pulse. The shape and rate of the decay provides insight into the radiative and non-radiative processes of the single emitter. b) The PL decay of most organic dyes is monoexponential, reflecting time-invariant first-order recombination kinetics (Adapted from Ref.62 with permission. Copyright 2005 MIT).

### 2.2 Photoluminescence Decay

Unlike intensity binning, which reveals dynamics that span many fluorescence cycles, time-resolved photoluminescence (PL) decay measurements examine the processes that affect individual emission events. The PL decay kinetics of single molecules are typically measured using time-correlated single-photon counting (TCSPC), which determines the elapsed time between an excitation pulse and the subsequent detection of a single photon emitted by the sample (Fig. 2-2a). The PL decay trace is a histogram that is built up over many excitation pulses, with each one contributing at most one stochastically-determined arrival time. In practice, TCSPC allows for the measurement of picosecond-to-microsecond-scale temporal dynamics regarding the emission process.\(^{58,59}\)

Processes that affect radiative and non-radiative relaxation manifest themselves in the rate and functional form of the PL decay.\(^{60,61}\) Figure 2-2b shows the PL decay for the organic dye Rhodamine 640 in solution.\(^{62}\) In this case, the PL decay is monoexponential, indicating time-independent first-order relaxation kinetics with a time constant given by the lifetime of the excited state.\(^{31}\) In contrast, PL decay measurements of single nanocrystals have revealed complexities often unseen in the world of molecular dyes. We summarize below two single-QD PL decay studies: the first explores the more complex decay dynamics of multiexcitons and the second demonstrates how the excitonic fine structure results in multiple radiative pathways.
Figure 2-3: Upon increased excitation, the PL decay of a single nanocrystal develops a rapid
decay on sub-nanosecond timescales. This is a signature of emission from multiexcitons. Here, \( n \) is the average number of excitons per nanocrystal (Adapted from Ref. 62 with
permission. Copyright 2005 by The American Physical Society).

2.2.1 Multiexciton Emission

In a departure from the typical photophysics of organic dyes, single semiconductor
nanocrystals are capable of supporting multiple excitations concurrently.\(^63\) In this
way, nanocrystals are akin to bulk semiconductors, where free excitons can interact
to give rise to bound multiple-excitonic states, or multiexcitons.\(^64\) Multiexcitons
have decay pathways unavailable to single excitons, including non-radiative Auger-
like channels.\(^65\) As a result, multiexcitonic recombination dynamics can be distinct
from those of single excitons and, if they are sufficiently emissive, their photophysics
can be extracted from the PL decay of single nanocrystals.

Figure 2-3 shows the change in the PL decay of a single nanocrystal at room tem-
perature upon increased excitation intensity.\(^66,67\) At higher excitation intensities, the
PL decay develops a distinct component at much faster timescales. The intensity de-
pendence of the fast component is reversible, eliminating the possibility that it arises
from photodegradation. Instead, this feature arises from multiexcitons, which are
more prevalent at higher excitation intensities due to the increased probability of se-
quential absorption. The rapid decay of the multiexcitonic emission is consistent with
previous demonstrations of enhanced Auger decay in quantum-confined systems.\(^65\)
Figure 2-4: The PL decay curves for a single QD measured at 2.7, 10, 12, 15, 18, and 28 K show that the lifetime decreases with increasing temperature, an indication of thermal mixing between a low-energy dark excitonic state and a higher-energy bright state (Adapted from Ref. 68 with permission. Copyright 2003 by the American Physical Society).

2.2.2 Excitonic Fine Structure

The PL decay lifetime of an ensemble of CdSe nanocrystals at cryogenic temperatures was measured to be hundreds of nanoseconds, much longer than bulk CdSe. This observation clashed with conventional thinking: the radiative rate was expected to increase upon confinement of the electron-hole pair. Moreover, the lifetime of the PL decay increases by over an order of magnitude as the temperature is lowered from 26 K to 2 K, a phenomenon not commonly seen to such an extent in organic dyes. Measurements of single nanocrystals have confirmed that the lengthening of the PL lifetime is an intrinsic property, not a diffusion effect (Fig. 2-4). Though initially believed to be due to surface effects, this result has been explained by the electronic fine structure of CdSe nanocrystals.

The lowest-energy exciton, or ground-state exciton, of CdSe is eight-fold degenerate. Calculations predict a lifting of this degeneracy to five states due to the effects of the nanocrystal crystal field, the particle shape anisotropy, and the electron-hole exchange interaction. Notably, these calculations show that within the fine structure, the lowest-energy state is optically inactive or “dark” and the second-lowest energy state is optically active or “bright”. Thus, the temperature dependence of the PL
decay lifetime can be attributed to thermal relaxation to the lowest-energy optically-
inactive state, which has a slow radiative recombination time because the transition is
spin-forbidden. This process is reminiscent of low-temperature phosphorescence
in some organic molecules. Using temperature- and magnetic-field dependent mea-
surements, single-nanocrystal investigations have robustly corroborated the theory of
excitonic fine structure in CdSe particles.

2.3 Combining Intensity Binning and PL Decay

Thus far, our discussion of PL decay measurements has focused solely on time-
averaged measurements. That is, the PL decay trace contains all of the photons
emitted from the single nanocrystal. However, single-photon detection events can
also be monitored in absolute time, which captures both their timing with respect
to the excitation pulse that created it and its relative position in the photon stream.
This technique allows sub-histograms to be constructed from selected portions of the
photon stream, making it possible to determine whether decay dynamics are corre-
lated with other observables, such as integrated intensity or time. We summarize
below several key results that highlight the additional complex physics that can be
probed through the application of this technique to single nanocrystals.

2.3.1 Fluctuating Non-Radiative Rates and Single-Nanocrystal
Quantum Efficiency

Ensembles of nanocrystals typically exhibit complex, multiexponential PL decays.
However, it was unclear whether this was due to heterogeneity between nanocrystals,
multiple emission processes within individual particles, or complex temporal dynamics
in single nanocrystals. As such, measurements on single nanocrystals have been
necessary to distinguish between these possibilities.

Studies of single CdSe/ZnS core/shell particles showed that although PL decay
dynamics fluctuated over slow timescales (seconds), they approached monoexpo-
Figure 2-5: a) The PL decay of single NCs is found to vary with the emission intensity. Although decay dynamics are nearly monoexponential over short time windows, b) they are multiexponential when averaged over long times at all but the highest emission intensities. This suggests slow fluctuations in the non-radiative rate, while the consistent monoexponential decay at peak emission intensities reflects purely radiative decay (Adapted from Ref. 62 with permission. Copyright 2004).

 exponential behavior during sufficiently short integration times (Fig. 2-5a). At the same time, PL decays generated from all photons emitted at moderate intensities were multiexponential (Fig. 2-5b),\textsuperscript{80} indicating that the effective non-radiative rate was time-varying. Intimately tied to the blinking process, these variations were attributed to interactions of the exciton with its environment.\textsuperscript{80,83}

Notably, PL decay traces constructed selectively from photons detected when the integrated intensity was >90% of the peak intensity were not only reliably monoexponential, but yielded a consistent decay time constant – even between particles from different synthetic batches or sizes (Fig. 2-5b).\textsuperscript{80} This led to the assertion that the decay dynamics observed when a single CdSe/ZnS dot is brightest reflects the intrinsic radiative decay.\textsuperscript{80}

The consequence of this observation, as later confirmed directly in measurements of single nanocrystals exposed to changing dielectric environments, is that the quantum efficiency of emission when CdSe/ZnS particles are at their brightest is nearly unity.\textsuperscript{84,85} In fact, the low ensemble quantum yields of nanocrystals in solution have been explained by the existence of subpopulations of non-emissive particles.\textsuperscript{86} As
such, the synthesis of nanocrystal batches possessing near-unity solution quantum yield was predicted to be possible, and indeed, has been achieved.\textsuperscript{14,15}

### 2.3.2 Trion Emission

Although the general mechanism of blinking is still under debate, single-nanocrystal studies have identified a subclass of intensity fluctuations with a distinct physical origin. As shown in Figure 2-6, the emission trace of single CdSe/CdS nanocrystals can exhibit a “grey” state, with a well-defined intensity between those of the “on”- and “off”-states.\textsuperscript{87} Additionally, the PL decay of the grey state has a shorter lifetime than the on-state. These grey states have been attributed to emission from the trion – an exciton in the presence of a spectator charge in the core states of the nanocrystal.\textsuperscript{54,87–89} Therefore the shortened PL decay lifetime results from the additional electron-hole recombination channels.

Trions and other charged nanocrystal species can be controllably generated in
electrochemical cells.\textsuperscript{90} In a recent study, it was found that PL decay lifetimes in single CdSe/CdS with very thick shells (16–19 monolayers) could vary significantly without having a discernible effect on the emission intensity.\textsuperscript{82} Here, the thick shell was proposed to suppress the non-radiative Auger decay mechanism in the negative trion, making it as emissive as the neutral exciton. Thus, the intensity remains constant while the PL decay lifetime shortens upon trion formation. This result shows that trions need not necessarily be “grey”.

Trion formation was once believed to be the primary mechanism responsible for blinking.\textsuperscript{45} However, Figure 2-6 shows that additional mechanisms are involved.\textsuperscript{87} While the “grey” state has been convincingly explained by trion formation, these and other investigations have concluded that trions cannot be responsible for the “off” state.\textsuperscript{46,47,91,92}

### 2.3.3 Type A and Type B Intensity Fluctuations

An additional way in which PL decay measurements can be combined with intensity binning is using a “fluorescence lifetime-intensity distribution” (FLID) diagram. As shown in Figure 2-7, it is a two-dimensional histogram showing the correlation between intensity and PL decay lifetimes.\textsuperscript{93} This analysis was recently applied to single-nanocrystal electrochemical studies. Upon application of different potentials, two types of fluorescence intensity dynamics were observed in single CdSe/CdS nanocrystals with thick shells (7–9 monolayers).\textsuperscript{81}

The first type of intensity fluctuation, called “Type A”, occurred when changes in the PL decay lifetime tracked that of the emission intensity (Fig. 2-7a).\textsuperscript{81} These dynamics were attributed to negative trion formation. In contrast, the second type of fluctuation, called “Type B”, occurred when the PL decay lifetime was independent of changes in intensity (Fig. 2-7b). It was argued that these dynamics occurred when a rapid, non-radiative channel captured “hot” photoexcited electrons before they could relax. In this scenario, photons are only detected when excitons decay normally, leaving the lifetime unaffected. This hot electron trapping process was offered as a possible mechanism responsible for the “off”-state in blinking.
Figure 2-7: a) For “Type A” fluctuations, the PL decay lifetime changes in parallel with the emission intensity. b) For “Type B” fluctuations, the PL decay lifetime is unchanged with changes in the emission intensity (Adapted from Ref. 81 with permission from Macmillan Publishers Ltd: Nature, 2011).

However, a recent report has challenged this mechanism and suggested a different surface-dependent non-radiative process.92 These authors provide corroborating evidence that photoinduced charging, involving the reversible trapping of the “hot” hole by surface states, does indeed lead to “grey” states. However, they suggest that the “off”-state results from occasional, reversible chemical oxidation of a surface species by the photogenerated hole. Additional mechanisms have been proposed for the “off”-state in single nanocrystals48 and further investigations are necessary to resolve the physical processes responsible for all intensity fluctuations in nanocrystals.

PL decay measurements, which resolve the temporal relationship between an absorption event and the subsequent emitted photon, probe the nature of the emissive state. This methodology becomes even more powerful when combined with other analytical tools such as intensity binning. As nanocrystals further evolve synthetically and our ability to manipulate them in environments such as electrochemical cells becomes more sophisticated, these techniques will continue to unearth new photophysics.
2.4 Photon Correlation

In PL decay measurements, the arrival times of photons are compared to their corresponding photoexcitation event. When PL decay is combined with intensity binning, the short-time dynamics of exciton recombination can be related to long-time dynamics affecting the nanocrystal. However, this broad range of dynamical information can also be accessed by analyzing the relative arrival times of photons within the stream itself. This is the essence of photon correlation, a means for analyzing emission dynamics over the complete range of relevant timescales without the use of binning or thresholds.

Photon correlation analyzes the photon stream in terms of the time spacing between pairs of photons. This is typically done by calculating the normalized correlation function:

\[ g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} \]  

for an intensity signal \( I(t) \) and temporal delay \( \tau \). Depending on whether \( I(t) \) is treated as a continuous or discrete signal, \( g^{(2)}(\tau) \) can be interpreted in two different ways.

If \( I(t) \) is treated as a continuous, analog signal, \( g^{(2)}(\tau) \) reflects the tendency for \( I(t) \) to have changed after some delay \( \tau \). The correlation operation is related to the convolution operation in that the product of two signals is compared as a function of their relative delay. Therefore, it is useful to think of \( g^{(2)}(\tau) \) as mapping the timescale at which \( I(t) \) no longer resembles itself. This concept will be useful for interpreting the spectral correlation function discussed later in the context of photon-correlation Fourier spectroscopy.

If \( I(t) \) is treated as a discrete, digital signal, \( g^{(2)}(\tau) \) reflects the tendency for photons to be detected after some relative delay \( \tau \). In photon correlation, \( g^{(2)}(\tau) \) is proportional to the histogram of photon pairs with time \( \tau \) between them. Therefore, an appropriate way of thinking about \( g^{(2)}(\tau) \) is as the conditional probability: given that a photon has been detected, what is the probability of detecting another photon
Figure 2-8: a) In photon correlation, the temporal separations between pairs of photons in the photon stream are analyzed. b) The unnormalized intensity autocorrelation function for a single PbS/CdS nanocrystal under CW excitation shows the “antibunching dip”, where the probability of detecting two photons simultaneously is reduced. Here, the intensity correlation function at \( \tau \to 0 \) does not reach zero because of the presence of background and because this NC is an imperfect two-level quantum mechanical emitter (Adapted from Ref. 94 with permission. Copyright 2012 American Chemical Society).

We note that this is not to be confused with the so-called “waiting time distribution”, which is the probability density that the next photon is detected at time \( \tau \) later.\(^95,96\)

Physical phenomena can be revealed by the structure of \( g^{(2)}(\tau) \). If intensity fluctuations have no characteristic timescale, or if photon arrivals are independent from one another (\textit{i.e.} they follow Poisson statistics), then \( g^{(2)}(\tau) = 1 \). In the intensity-correlation picture, this either means that the signal is unchanging or that fluctuations are no different across all timescales. In the photon correlation picture, the probability of detecting a second photon is the same for all \( \tau \) after the first detection event.\(^95,96\)

Therefore, deviations from unity in \( g^{(2)}(\tau) \) indicate that photons within the stream are not independent from one another, but are related by some physical mechanism.

2.4.1 Broad Timescale Dynamics: Blinking

Intensity-correlation analysis has long been applied to the blinking of single dye molecules. In these studies, the decay of \( g^{(2)}(\tau) \) can be modeled with a summation of exponentials because intersystem crossing into non-emissive triplet states occurs on
well-defined timescales. However, this technique is less applicable to nanocrystal blinking because the power-law blinking statistics span such a large range of timescales. As such, individual $g^{(2)}(\tau)$ measurements tend to be highly irreproducible and distinct decay timescales are difficult to resolve. Moreover, because a single correlation function is used to compare all photons in the stream, it cannot be used to study the distributions of “on”- and “off”-times.

### 2.4.2 Antibunching of Emission from Single Emitters

While intensity correlation and photon correlation are nearly identical in mathematical usage and interpretation, there is one situation where the distinction is paramount: the limit of $\tau \to 0$. In this limit, the quantum mechanical nature of fluorescent emitters renders the intensity-correlation interpretation inaccurate.

If the emission from a single emitter were a classical electromagnetic field,

$$\lim_{\tau \to 0} g^{(2)}(\tau) = \frac{\langle I(t)^2 \rangle}{\langle I(t) \rangle^2} = C$$

where $C$ is a non-zero constant. However, for a two-level quantum mechanical emitter,

$$\lim_{\tau \to 0} g^{(2)}(\tau) = 0$$

That is, the probability of detecting two photons simultaneously from a single quantum mechanical emitter is identically zero.

The Hanbury Brown and Twiss dual-detector setup (Fig. 2-9) is used to characterize such a photon stream and can illustrate this antibunching effect. Here, an emitted photon can be detected either by detector 0 or detector 1, but not by both at the same time. Therefore, under continuous-wave (CW) excitation, antibunching reveals itself as a dip in the cross-correlation of the two detectors as $\tau \to 0$ as in Figure 2-8b.

Antibunching can also be observed in photon-correlation measurements using pulsed excitation. These pulsed correlation measurements have the advantage of
Figure 2-9: The Hanbury Brown and Twiss correlation setup is used in many photon-correlation studies. An emitted photon can be detected either by APD0 or APD1, but not by both at the same time. While any single-photon detector may be used, avalanche photodiodes (APDs) were used in all measurements in this thesis.

associating photon detection events to particular excitation events.\cite{105,106} Here, the timing between detected photons indicates whether they were emitted from the same excitation pulse or different excitation pulses. As such, $g^{(2)}(\tau)$ appears as a series of peaks for each successive excitation (Fig. 2-10). The side peaks at integer multiples of the repetition time are the result of single-photon events, where two distinct excitation pulses have produced two emission photons. The absence of a center peak at $\tau \rightarrow 0$ demonstrates that the emitter cannot emit two photons after a single excitation pulse.

2.4.3 The Antibunching Signal of Single Nanocrystals Reflects Multiexciton Recombination

Antibunching has often been used as a litmus test for the presence of a single quantum mechanical emitter because classical signals cannot produce an initial rise in their $g^{(2)}(\tau)$.\cite{101} Incomplete antibunching can be an indication of multiple radiative processes in a single emitter, or the presence of multiple emitters. Many organic dyes have sufficiently simple photophysics that the degree of antibunching directly reflects the number of emitters present.\cite{107,108} However, the existence of multiexciton emission in single nanocrystals necessitates an extension of this interpretation.

As discussed in Section 2.2.1, nanocrystals can support multiexcitons, which can be created via sequential absorption events. Consequently, a single nanocrystal can be
understood as a collection of interacting two-level systems, which may emit multiple photons after a single excitation pulse. As such, the extent of antibunching in the emission from a single nanocrystal is controlled by the radiative quantum efficiency of the multiexcitons.\textsuperscript{106}

We consider a pulsed photon-correlation measurement in the limit of low excitation intensity, where triexcitons and higher-order excitons are unlikely to be created. Here, the ratio of the integrated areas of the center and side peaks of $g^{(2)}(\tau)$, which we define as $g_0^{(2)}$, is quantitatively related to the ratio of biexciton and exciton quantum yields:\textsuperscript{109}

$$g_0^{(2)} = \frac{n(n-1)}{\langle n \rangle^2} \approx \frac{\eta_{BX}}{\eta_X} \quad \text{(2.4)}$$

where $n$ is the number of photons emitted by the nanocrystal.

This result shows that the use of antibunching as a litmus test for the presence of a single nanocrystal is unwarranted.\textsuperscript{109} Moreover, it shows that photon correlation can be used as a direct window into the recombination dynamics of biexcitons in nanocrystals – a species that is difficult to spectrally resolve from the single exciton\textsuperscript{110} and temporally resolve from higher-order excitons. Until this recent result, biexcitons had remained relatively unstudied at the single-nanocrystal level.

### 2.4.4 Variability of Biexciton Quantum Yields

In the initial report of this pulsed photon-correlation technique applied to single core/shell nanocrystals, the authors observed significant heterogeneity in the biexciton quantum yield between particles within a synthetic batch (Figure 2-11).\textsuperscript{109} They attributed the variations to slight differences in structure between individual particles that affected Auger recombination, the non-radiative mechanism believed to be responsible for quenching biexciton emission. We discuss below two reports that corroborate this finding and further investigate the mechanisms of biexciton recombination.

Combining the pulsed photon-correlation method and single-nanocrystal PL spectroscopy, the first study reported instances of near-unity biexciton quantum yields in
Figure 2-10: This cartoon illustrates the shape of $g^{(2)}(\tau)$ for a single nanocrystal under pulsed excitation. Here, the side peaks ($\tau = \pm t_{\text{rep}}$) correspond to photon pairs from separate excitation pulses, while the center peak ($\tau = 0$) corresponds to photon pairs from a single excitation pulse. The presence of a peak at $\tau = 0$ indicates emission from multiexcitons. In the limit of low excitation intensity, the ratio of the areas under the center and side peaks is equal to the ratio of biexciton and exciton quantum yields (Adapted with permission from Ref. 109. Copyright 2011 American Chemical Society).

single CdSe/CdS particles.\textsuperscript{111} Extremely large dot-to-dot variations were observed for the biexciton quantum yield, even though all particles displayed strongly suppressed blinking. Reasoning that Auger recombination was the mechanism quenching biexciton emission, the authors suggested that blinking suppression of the exciton must originate from a different mechanism, possibly reduced rates of carrier trapping or migration.

The second study combined photon correlation with intensity binning to probe the relationship between blinking and biexciton quantum yields.\textsuperscript{112} A strong correlation between biexciton quantum yields and blinking was expected if the same process, Auger recombination, were responsible for both. However, only a weak correlation between biexciton quantum yield and on-time fraction was found for single CdSe/CdS particles. This further supported the hypothesis that biexciton quenching and blinking do not share the same mechanism. These authors proposed a mechanism where biexciton recombination occurs through a combination of Auger- and trap-assisted pathways.
Figure 2-11: The biexciton quantum yield can vary substantially over multiple nanocrystals within the same synthetic batch. The biexciton quantum yield scales with the biexciton lifetime (Adapted from Ref. 109 with permission. Copyright 2011 American Chemical Society).

### 2.4.5 New Directions for Photon-Correlation Studies of Multiexcitons in Single Nanocrystals

As we have discussed, photon-correlation techniques provide unique insight into biexciton recombination dynamics at the single-nanocrystal level. These methods will continue to make important contributions towards our understanding of fundamental nanocrystal physics and more complicated nanoscale systems. For example, a topic that has been of interest for several years is the interaction between single nanocrystals and metallic surfaces.\(^\text{113}\) Several recent investigations have reported changes in the photon statistics of single core/shell particles in proximity to gold or silver nanostructures or films.\(^\text{114–117}\) Each study reported modifications of both the radiative and non-radiative rates for the exciton and biexciton, with the outcome being an enhancement in the ratio between the center and side peaks. One study has even reported strong photon bunching, where photons are more likely to be emitted in groups than individually – a radical change in the photon statistics.\(^\text{114}\)

Moreover, advances in photon-counting technologies are allowing for even more sophisticated analyses of the photon stream. Rather than merely looking at the coincidences of photons from a given excitation pulse, a few recent investigations have explored the precise timing of all photons relative to their excitation pulse.\(^\text{116}\) This
allows one, for instance, to determine if simultaneously detected photons originated from biexcitonic recombination in a single nanocrystal or from a cluster of particles. These types of approaches offer a window into the recombination dynamics of biexcitons separate from that of the exciton and will likely continue to be explored.

Through increasingly sophisticated methods of determining the quantity and timing of photons, we have learned a tremendous amount about the unique emission properties of single nanocrystals. However, we have yet to discuss an orthogonal axis in the analysis of the photon stream that provides even more information: the energy axis. Our understanding of the photoluminescence spectra of colloidal quantum dots has benefited tremendously since the application of single-molecule techniques to their study.
Chapter 3

Single-Nanocrystal Spectroscopy

Early spectroscopic investigations of ensembles of nanocrystals were difficult to interpret due to inhomogeneous broadening as individual nanocrystals could each emit at different peak energies. Upon isolation of individual particles, investigations of the spectral landscape and temporal dynamics were freed of this concern. In this chapter, we discuss methods for accessing the spectral dimension of the photon stream. These methods have followed a similar developmental trajectory as the intensity-only methods discussed in Chapter 2, from binning to photon correlation. Deconstructing the photon stream in terms of both photon timing and photon energy provides a multifaceted approach toward understanding these materials. As with the previous chapter, the work presented here was performed by other researchers both in and outside of the Bawendi lab. Also, much of this chapter appeared in a review paper written with Andrew Beyler, Thomas Bischof and Mark Wilson (Ref. 32).

3.1 CCD-based Spectroscopy

Single-molecule spectroscopic measurements are conventionally performed by dispersing the fluorescence from a single emitter with a spectrometer and detecting with a CCD camera (Fig. 3-1a). The signal on each element of the detector is integrated until enough photons have been detected to resolve the shape of the spectrum. This method is directly analogous to intensity binning (Chapter 2) but with a projection
Figure 3-1: a) The spectrometer disperses the photon stream spatially into bins based on the energy of the photons. The number of photons per bin are detected using a multi-pixel detector such as a CCD. b) At low temperature, the single-nanocrystal spectrum is narrow and highly dynamic (Adapted from Ref. 119 with permission. Copyright 2011 MIT). c) At low temperature, features in the single-nanocrystal spectrum are markers of exciton-phonon coupling (Adapted from Ref. 120 with permission. Copyright 2013 by the American Physical Society).

into the spectral domain.

3.1.1 Spectral Diffusion at Low Temperature

The emission spectra of single nanocrystals have primarily been studied at cryogenic temperatures (∼10 K) because the narrowing of spectral linewidths at low temperatures reveals a complex menagerie of physical phenomena.\textsuperscript{121,122} For example, early investigations of single nanocrystals at low temperature showed that the emission spectrum was highly dynamic in both amplitude and time (Fig. 3-1b).\textsuperscript{7,30,123} These spectra exhibited large, infrequent jumps over tens of meV as well as rapid jitter that appeared to define the measured time-integrated linewidth on sub-second timescales.

As in the case of blinking, these observations were reminiscent of spectral diffusion
observed in single dye molecules. However, in organic dyes, these spectral dynamics were often understood in terms of fluctuations in the local environment that distorted the conformation of the molecule.\textsuperscript{124,125} In nanocrystals, particularly those that possess shells that isolate the exciton from the exterior environment, such distortions of the lattice are both unlikely to occur or produce these effects.

The low-temperature spectral dynamics of single nanocrystals have been artificially replicated upon application of an external electric field. This suggests that they are caused by quantum-confined Stark interactions between the core states of the NC and charges in the local environment.\textsuperscript{126} Therefore, the large spectral jumps are believed to be caused by carrier trapping events themselves and the spectral jitter by the photo-induced migration of trapped carriers amongst the numerous and heterogeneous trap sites. The role of trap states in spectral dynamics was further supported by the observation that large spectral jumps are correlated with blinking events, which are believed to rely on carrier trapping events.\textsuperscript{127} The characterization of the identity of these trap states and the local dynamics of trapped charges continues to be a subject of investigation.\textsuperscript{128,129}

### 3.1.2 Spectral Features at Low Temperature

Advances in detection technology and nanocrystal synthesis have revealed features in the low-temperature single-nanocrystal spectrum that were previously hidden by spectral diffusion. For example, side peaks of the purely electronic zero-phonon line (ZPL) report on different types of excitonic coupling to local vibrations (Fig. 3-1c). Fröhlich-like interactions between the exciton and longitudinal optical phonons result in distinct, well-separated side peaks.\textsuperscript{122,126} Meanwhile, several studies have reported a progression of side-peaks on the shoulder of the ZPL, which are attributed to piezoelectric and deformation potential coupling between the exciton and acoustic phonons.\textsuperscript{89,130,131} The discrete nature of these side-peaks suggests either stringent vibrational selection rules or discrete, confined phonon modes. We note that the nature of exciton-phonon coupling in nanocrystals has been a topic of controversy, particularly with regards to nanocrystal charging in single-nanocrystal experiments.\textsuperscript{132–134}
The spectroscopic fingerprints of other nanocrystal phenomena can also be resolved at cryogenic temperatures. Several investigations have identified the spectral markers of the exciton fine structure in single nanocrystals using polarization-dependent, temperature-dependent, and magnetic field-dependent studies. A redshifted peak that resembles a second zero-phonon line has been attributed to biexciton emission. Lastly, several studies have reported that charging of the NC core results in spectrally-distinct emission from positive and negative trions, each with rapid PL decay lifetimes and characteristic susceptibility to magnetic fields. These studies demonstrate how conventional single-molecule spectroscopy is being used to understand the physics underlying all forms of nanocrystal emission.

3.1.3 Limitations of CCD-based Spectroscopy

In the case of some single molecules, the emission spectrum can be measured with lifetime-limited “natural” linewidths. That is, the spectral breadth is not broadened by interactions with the environment, but only by the natural decoherence of the excited state. While this measurement is possible with single dye molecules that do not undergo significant spectral dynamics, the linewidth of the zero-phonon line of single nanocrystals has always been measured to be significantly broader than the natural linewidth. To determine whether this is due solely to rapid spectral diffusion, as was initially presumed, it is necessary to rigorously characterize both the homogeneous spectrum and its full temporal dynamics.

However, conventional CCD-based spectroscopy has been unable to resolve these dynamics. As with the binning techniques described for analyzing emission intensity, this method is limited in temporal resolution because it requires, at minimum, tens of milliseconds to collect enough photons for sufficient signal-to-noise. Furthermore, diffraction-based techniques suffer from low signal throughput as photons are lost in diffraction modes that do not contribute to the measurement.
3.2 Adding Spectral Resolution to Time-Resolved Measurements

In Chapter 2, we showed how measuring the timing of individual photons can provide insight into excitonic processes that are inaccessible through intensity binning. For the remainder of this chapter, we discuss how the incorporation of spectral resolution into single-photon counting methods gives access to a new domain of nanocrystal physics. We highlight several studies that extend established time-resolved PL decay and photon-correlation methods to include spectral discrimination. These methods, based on spectral splitting of the photon stream from a single nanostructure, have been used to study dual-color emitting nanostructures, multiexcitons, and rapid spectral diffusion.

3.2.1 Measuring Distinct Emission Processes in a Single Nanostructure

Some semiconductor heterostructures, such as seeded rods or tetrapods, are comprised of multiple emissive components. Provided that their respective spectral peaks are sufficiently distinct in energy, the emission from each substructure can be directed to different detectors and studied simultaneously. For example, a report on “dot-in-bulk” CdSe-CdS nanostructures has shown that while fluorescence from the core of the NC exhibits antibunching, fluorescence from the bulk-like shell exhibits classical Poisson emission.\(^\text{141}\) In a study on complex seeded-rod structures, individual particles were found to emit two distinct colors, each with very different recombination dynamics.\(^\text{140}\) Nevertheless, the two signals maintained antibunching with respect to one another, supporting a model where a single exciton possesses two radiative recombination pathways (Fig. 3-2a).

Spectrally-resolved studies have also been performed to monitor multiexciton recombination dynamics. Triexciton emission can arise from the recombination of higher-energy 1P-1P electron-hole states, rather than 1S-1S states of the exciton and
Figure 3-2: a) Spectrally-resolved PL decay and $g^{(2)}(\tau)$ measurements reveal distinct and independent processes within dual-color emitting single nanocrystal (Reprinted with permission from Ref. 140. Copyright 2012 American Chemical Society). b) Two-color cross-correlation measurements show an asymmetry in the center peak. This shows that triexciton emission occurs before emission of the biexciton or exciton (Adapted from Ref. 67 with permission. Copyright 2005 by the American Physical Society).

Therefore, unlike the biexciton, triexciton emission can be spectrally resolved from exciton emission, even at room temperature. This distinction allows for pulsed cross-correlation experiments between the 1P-1P and 1S-1S emission channels. An asymmetry in the $\tau \to 0$ feature of $g^{(2)}(\tau)$ indicates that photons in the 1P-1P channel are emitted before photons in the 1S-1S channel (Fig. 3-2b). This observation, evidenced in single nanocrystals, definitively shows the time-ordered emission of multiexcitons in these materials.

### 3.2.2 Spectral Diffusion Under Two Detection Channels

The research area that has seen the most innovation in spectrally-resolved time-resolved experiments on single emitters has been the study of fast spectral diffusion processes. Conventional CCD-based single-molecule spectroscopy has only allowed us
to indirectly deduce the nature of fast-timescale spectral dynamics in single nanocrystals. For example, a statistical analysis of time-integrated spectra suggested that the spectral jitter is actually comprised of small, discrete spectral jumps.\textsuperscript{143} Further, the spectral trajectories of this rapid jitter were consistent with a sub-diffusive process.\textsuperscript{144}

High temporal resolution single-photon analysis enables a more direct look into these processes.

One method that has been used to measure rapid spectral in single epitaxial quantum dots employs two monochromators to direct the blue and red sides of the integrated spectrum to different detectors (Fig. 3-3(a,d)).\textsuperscript{142,145,146} In this configuration, a bunching feature arises at short timescales in the autocorrelation of the

Figure 3-3: The emission from an epitaxial quantum dot is split using two monochromators. The autocorrelation function for the signal from one side contains a bunching feature that indicates the timescale on which the spectrum jumps from one side of the spectrum to the other. Assuming a spectral lineshape, the underlying homogeneous linewidth can be inferred (Reprinted with permission from Ref. 142. Copyright 2012 by the American Physical Society).
signal from one side of the integrated spectrum. The decay of the bunching feature
denotes the timescale over which the underlying spectrum diffuses to the other side
of the integrated spectrum. If a model for the spectral lineshape and its dynamics
is presupposed, both the parameters of diffusion and the underlying homogeneous
linewidth can be extracted.\textsuperscript{142}

This method can resolve spectral dynamics on timescales faster than nanoseconds,
and is straightforward to interpret, but it has several drawbacks that limit its appli-
cation to systems such as colloidal quantum dots. First, the monochromators must
be precisely tuned to separate the different portions of the time-integrated spectrum.
However, the spectra of single nanocrystals at low temperature can undergo shifts of
tens of meV, leading to events where the spectrum falls outside of the set spectral win-
dows.\textsuperscript{144} More significantly, this measurement cannot be used to directly measure the
shape of the spectrum or the manner of its diffusion. A different technique is required
for a model-independent look into the intrinsic spectra of individual nanocrystals and
their complex spectral dynamics.
Chapter 4

Photon-Correlation Fourier Spectroscopy (PCFS)

Photon-correlation Fourier spectroscopy (PCFS) combines the high photon throughput and spectral resolution of interferometry with the fast temporal resolution of photon correlation for an in-depth look into the spectra of single emitters. In this chapter, we flesh out the theoretical framework for PCFS and explain how its results are interpreted. These considerations are crucial for understanding the liquid-phase variant of PCFS, Solution PCFS, that is the focus of this thesis. Then, we highlight recent experimental progress on the implementation of PCFS for the study of single nanocrystals at cryogenic temperatures. The derivations presented in this chapter were either adapted from the literature or derived with input from Andrew Beyler and Xavier Brokmann. The experimental results were obtained by other researchers both in and outside of the Bawendi lab.

4.1 Description of PCFS

The dual-monochromator photon-correlation technique discussed in the previous chapter provides a way to bypass the temporal resolution limitations of conventional CCD-based spectroscopy. Rather than building up spectra and monitoring peak shifts, it determines whether pairs of photons with temporal spacing $\tau$ have energies that are
dramatically different. The goal of PCFS is to move beyond this binary measurement to determine these energy differences $\zeta$ quantitatively (Fig. 4-1a).\textsuperscript{147}

This goal is achieved experimentally using the scheme shown in Figure 4-1b. Rather than splitting the emission from a single emitter to two detectors as in the Hanbury Brown and Twiss setup, the two beams are sent along two paths and recombined as in an interferometer. In this scenario, the total signal is preferentially directed to one of two detectors based on the optical path-length difference due to the effects of interference. The degree of anticorrelation between the two output signals reflects the spectral coherence of the emission at the given path-length difference. Thus, by monitoring the cross-correlation of the two outputs of the interferometer, the spectral coherence between photon pairs can be determined. Rather than measuring a single, spectrally-resolved correlation function, PCFS combines the measurement of many correlation functions over a range of optical path-length differences to extract quantitative information about the single-emitter spectrum and its evolution in time.
Just as Fourier transform spectroscopy reveals the spectrum by monitoring the intensities of the interferometer outputs as a function of path-length difference, PCFS monitors the intensity correlation as a function of path-length difference to give the spectral correlation,

\[ p(\zeta, \tau) = \langle \int_{-\infty}^{\infty} s(\omega, t) s(\omega + \zeta, t + \tau) d\omega \rangle_t \]  \hspace{1cm} (4.1)

where \( s(\omega, t) \) is the single-emitter spectrum at time \( t \) and \( \langle \cdots \rangle_t \) represents a time average. The spectral correlation is a two-dimensional function that is equivalent to the histogram of energy differences \( \zeta \) between photon pairs as a function of their temporal spacing \( \tau \).

Though absolute photon energies are no longer preserved, the spectral correlation function contains a wealth of information about the spectrum and its dynamics. Figure 4-1c shows the results of a simulation where two types of spectra are compared: a static doublet and a dynamic doublet. In the case of a static doublet, the spectrum always consists of emission from two frequencies separated by \( \Omega \). In the dynamic doublet, a singlet peak jumps between the same two emission frequencies. When photons are closely spaced in time, (i.e. as \( \tau \to 0 \)), \( p(\zeta, \tau) \) represents the spectral autocorrelation of the underlying homogeneous spectrum because both photons are drawn from the same quasi-static spectrum (i.e. \( s(\omega, t) \approx s(\omega, t + \tau) \)). Then, as \( \tau \) increases, \( p(\zeta, \tau) \) broadens, as the autocorrelation of the homogeneous spectrum is convolved with the probability density function of spectral diffusion.

### 4.2 Interferometry, Coherence, and Spectra

In this section, we show how the outputs of an interferometer are related to the first-order correlation function and the spectrum of the source. Many derivations in optics first assume that the electric field is a monochromatic plane wave. While this is very illustrative and mathematically easier, it is rather unphysical. Here, we discuss a more physical situation by including the effects of coherence. This will give us a more
realistic handle of interferometry before discussing PCFS. We will do this based on the knowledge presented in the book “The Quantum Theory of Light” by Rodney Loudon.\textsuperscript{149}

### 4.2.1 Derivation of the Interferometer Output Intensity

We consider the Mach-Zehnder interferometer (Fig. 4-2), which is essentially identical to the Michelson interferometer setup that we use in PCFS. Using the notation seen in Loudon, we have an incoming field $E(t)$ that is split by a beam-splitter along two paths, $z_1$ and $z_2$. The two beams then recombine with two outputs $E_a(t)$ and $E_b(t)$. Let us consider the output $E_a(t)$:

$$E_a(t) = \mathcal{R}\mathcal{T}E(t_1) + \mathcal{T}\mathcal{R}E(t_2) \quad (4.2)$$

where $\mathcal{R}$ and $\mathcal{T}$ are the reflection and transmission coefficients for each beamsplitter and $t_1 = t - z_1/c$ and $t_2 = t - z_2/c$. Again, $c$ here is the speed of light. We have defined these electric fields such that the pseudo-instantaneous intensity takes the form:

$$I_a(t) = \frac{1}{2}\epsilon_0c|E_a(t)|^2 \quad (4.3)$$
Given that $E_a(t)$ is a complex function, we must multiply complex conjugates to obtain:

\[
I_a(t) = \frac{1}{2} \epsilon_0 c \left[ R^* T^* E^*(t_1) + T^* R^* E^*(t_2) \right] [R T E(t_1) + T R E(t_2)]
\]

\[
= \frac{1}{2} \epsilon_0 c |R|^2 |T|^2 \left\{ |E(t_1)|^2 + |E(t_2)|^2 + 2 \text{Re} \left[ E^*(t_1) E(t_2) \right] \right\}
\]

(4.4)

where * indicates complex conjugate. For the last term, we used the identity $2 \text{Re}[z] = z + z^*$. If we take the time average of the intensity, we obtain:

\[
\langle I_a(t) \rangle = \epsilon_0 c |R|^2 |T|^2 \left\{ \langle |E(t)|^2 \rangle + \text{Re} \langle E^*(t_1) E(t_2) \rangle \right\}
\]

(4.5)

\[
= \epsilon_0 c |R|^2 |T|^2 \left\{ 1 + \frac{\text{Re} \langle E^*(t_1) E(t_2) \rangle}{\langle |E(t)|^2 \rangle} \right\}
\]

(4.6)

(4.7)

where the angled brackets $\langle \ldots \rangle$ represent a time average or statistical ensemble average. It is important to note that the types of light, and therefore fields, being studied must be stationary. That is, the fluctuations of a stationary field occur on timescales much faster than the integration time $T$ and the processes governing the fluctuations do not change with time. In other words, the system is ergodic because the time average over long time $T$ is equivalent to the statistical ensemble average over all values of the electric field. Thus, the electric field can be analyzed for time separations $\tau$ and do not depend on the absolute time $t$.

Here, time averaging over a stationary field gives us $\langle |E(t_1)|^2 \rangle = \langle |E(t_2)|^2 \rangle$. Moreover, this also gives us:

\[
\frac{\text{Re} \langle E^*(t_1) E(t_2) \rangle}{\langle |E(t)|^2 \rangle} = \text{Re} \left[ \frac{\langle E^*(t) E(t + \tau_\delta) \rangle}{\langle E^*(t) E(t) \rangle} \right]
\]

(4.8)

where the time average in the equation above can be more explicitly written as:

\[
\langle E^*(t) E(t + \tau_\delta) \rangle = \frac{1}{T} \int_{t}^{t+T} E^*(t) E(t + \tau_\delta) \, dt
\]

(4.9)

The second term is the definition of the first-order correlation function $g^{(1)}(\tau_\delta)$ which
is defined as:

\[ g^{(1)}(\tau_\delta) = \frac{\langle E^*(t)E(t+\tau_\delta) \rangle}{\langle E^*(t)E(t) \rangle} \]  

(4.10)

where \( \tau_\delta = (z_1 - z_2)/c \) and indicates the delay due to the path-length difference \( \delta = z_1 - z_2 \).

By the Wiener-Khintchine theorem, \( g^{(1)}(\tau_\delta) \) is related to the spectrum of the underlying field by Fourier transform.

\[ s(\omega) = \int_{-\infty}^{\infty} g^{(1)}(\tau_\delta)e^{-i2\pi\omega\tau_\delta} d\tau_\delta \]  

(4.11)

This makes intuitive sense because the autocorrelation function reflects fluctuations in a signal and in the context of an electric field, those temporal fluctuations are related to frequencies in Fourier space. Using the form \( \langle I(t) \rangle = \frac{1}{2} \epsilon_0 c \langle |E(t)|^2 \rangle \) and assuming a perfect 50:50 beamsplitter (\( |R|^2 = |T|^2 = \frac{1}{2} \)), we finally obtain the key result of this derivation:

\[
\langle I_0(t) \rangle = \frac{1}{2} \langle I(t) \rangle \left\{ 1 + \text{Re} \left[ g^{(1)}(\tau_\delta) \right] \right\} \\
= \frac{1}{2} \langle I(t) \rangle \left( 1 + \text{Re} \left\{ \text{FT} [s(\omega)] \right\} \right)
\]

(4.12)

(4.13)

This result shows that the intensity at the output of the interferometer is modulated by the real portion of the first-order correlation function \( g^{(1)}(\tau_\delta) \), which is the Fourier transform of the spectrum \( s(\omega) \). Therefore, by measuring the intensity as a function of the path-length difference between the two arms of the interferometer, the spectrum can be determined.
Figure 4-3: We show here the interferogram of a spectrum with an emission peak at 650 nm (1.907 eV) and a Gaussian lineshape with FWHM of 50 meV. At path-length differences much larger than the coherence length $l_c = 16.5 \, \mu m$, there are no more oscillations because interference effects no longer occur.

### 4.2.2 Interferogram of a Gaussian Spectrum

In the previous section, we showed that the output intensity from an interferometer oscillates as a function of optical path-length difference as:

$$
\langle I_a(t) \rangle = \frac{1}{2} \langle I(t) \rangle \left\{ 1 + \text{Re} \left[ g^{(1)}(\tau_0) \right] \right\} 
$$

$$
= \frac{1}{2} \langle I(t) \rangle \left( 1 + \text{Re} \{ \text{FT} [s(\omega)] \} \right) 
$$

Let us consider the case where the spectrum is a normalized Gaussian:

$$
s(\omega) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(\omega-\omega_0)^2/(2\sigma^2)} 
$$
The Fourier transform of this is:

\[ \text{FT} [s(\omega)] = \text{FT} \left[ \frac{1}{\sqrt{2\pi\sigma}} e^{(\omega - \omega_0)^2 / 2\sigma^2} \right] \] (4.17)

\[ = \text{FT} \left[ \frac{1}{\sqrt{2\pi\sigma}} e^{(\omega)^2 / 2\sigma^2} * \delta(\omega - \omega_0) \right] \] (4.18)

\[ = \text{FT} \left[ \frac{1}{\sqrt{2\pi\sigma}} e^{(\omega)^2 / 2\sigma^2} \right] \text{FT} \left[ \delta(\omega - \omega_0) \right] \] (4.19)

\[ = e^{-2\pi^2\sigma^2\delta^2} e^{-i2\pi\omega_0\delta} \] (4.20)

where \(*\) indicates a convolution and the bold-font \(\delta\) is the Dirac delta. This was essentially calculated by taking the Fourier transform of the Gaussian function when \(\omega_0 = 0\) and then applying the shift theorem. Taking the real part, we have:

\[ \text{Re} \left\{ \text{FT} [s(\omega)] \right\} = e^{-2\pi^2\sigma^2\delta^2} \cos (2\pi\omega_0\delta) \] (4.21)

Therefore, the intensity modulation observed as a function of path-length difference is:

\[ 2 \frac{\langle I_a(t) \rangle}{\langle I(t) \rangle} - 1 = e^{-2\pi^2\sigma^2\delta^2} \cos (2\pi\omega_0\delta) \] (4.22)

This is the “interferogram”, the Fourier transform of which gives the spectrum. We can clearly see that the envelope of the interferogram is dictated by the envelope of the spectrum and there is an oscillation dependent on the mean frequency of the spectrum.

Loudon defines the coherence time as:

\[ \tau_c = \int_{-\infty}^{\infty} |g^{(1)}(\tau)|^2 \, d\tau \] (4.23)

The coherence time thereby determines the coherence length:

\[ l_c = c\tau_c \] (4.24)

where the value \(c\) is the speed of light and the subscript \(c\) refers to coherence. In the
case of the Gaussian spectrum,

\[
l_c = \int_{-\infty}^{\infty} \left| \text{FT} [s(\omega)] \right|^2 d\tau \\
= \int_{-\infty}^{\infty} e^{-4\pi^2 \sigma^2 \delta^2} d\delta \\
= \frac{1}{2\sqrt{\pi}\sigma}
\]

(4.25)

(4.26)

(4.27)

This shows that the distance over which the source is coherent, that is, the path-length distances where interference occurs, is dictated by the inverse of the width of the spectrum.

In Figure 4-3, we show an example interferogram. Here, the spectrum of an emitter is a Gaussian centered at 650 nm with a full-width at half-maximum (FWHM) of 50 meV or 403 cm\(^{-1}\). These are reasonable values for single NC spectra. We can determine \(\sigma\) in the Gaussian using the relation: FWHM = \(2\sqrt{2\ln 2}\sigma\). Here, \(\sigma = 171.4\) cm\(^{-1}\). The interferogram oscillates with periodicity \(1/\omega_0\) and has a Gaussian envelope whose width is determined by the inverse of the spectral width. Finally, at path-length differences much larger than the coherence length \(l_c = 16.5\) \(\mu\)m, there are no more oscillations because interference effects no longer occur.

### 4.3 Derivation of PCFS Using Coherence

PCFS analyzes the intensity cross-correlation function of the two outputs of an interferometer to measure the spectral correlation function (Fig. 4-1). We present here a derivation of the governing equation for PCFS on a single emitter. While based on the first PCFS derivation found in Ref. 147, the main difference is that rather than monitoring all pairs of photons with instantaneous energies, this derivation takes coherence, and therefore a spectrum, into account.

From the derivation of the Mach-Zehnder interferometer, we have the intensity of one of the outputs of the interferometer. From power conservation, we also know the
intensity at the other output. Thus, we have:

\[ I_a(t) = \frac{1}{2} I_0(t) \left[ 1 + \text{Re} \{ \text{FT} [s(\omega, t)] \} \right] \] (4.28)

\[ I_b(t) = \frac{1}{2} I_0(t) \left[ 1 - \text{Re} \{ \text{FT} [s(\omega, t)] \} \right] \] (4.29)

Here, \( I_0(t) \) is the input intensity into the interferometer and \( s(\omega, t) \) is the time-dependent spectrum of the source.

For the time-dependent spectrum \( s(\omega, t) \), we assume the following model. Let us assume that the spectrum consists of a static envelope function \( \Phi(\omega) \) with a time-averaged frequency denoted by \( \omega_0 \). At times shorter than the integration time, the peak frequency can change, but the envelope stays intact. Therefore,

\[ s(\omega, t) = \Phi(\omega) \ast \delta(\omega - \omega_0 - \Delta \omega(t)) \] (4.30)

where \( \ast \) indicates a convolution and the bold-font \( \delta \) is the Dirac delta. \( \Delta \omega(t) \) describes the time-dependent changes in the spectral frequency.

Using this, we calculate the normalized intensity cross-correlation function:

\[ g^\times(\tau) = \frac{\langle I_a(t)^* I_b(t + \tau) \rangle}{\langle I_a(t) \rangle \langle I_b(t + \tau) \rangle} \] (4.31)

where \( ^* \) indicates complex conjugate and \( \tau \) is the delay time for the time correlation between the two signals. This is important because the interferometer introduces a different delay time regarding the optical path-length difference \( \delta \).

### 4.3.1 Denominator

We begin with the first term in the denominator of the intensity cross-correlation function:

\[ \langle I_a(t) \rangle = \left\langle \frac{1}{2} I_0(t) \left[ 1 + \text{Re} \{ \text{FT} [s(\omega, t)] \} \right] \right\rangle \] (4.32)

For the purposes of this derivation, we assume that fluctuations in the total intensity are uncorrelated with the spectrum or its time dependence. We note that while
this is not necessarily the case in nanocrystals, this correlation can be taken into account simply by changing the normalization of the spectral correlation function. Nevertheless, making this assumption, the expression becomes:

\[ \langle I_a(t) \rangle = \frac{1}{2} \langle I_0(t) \rangle \left[ 1 + \langle \text{Re} \{ \text{FT} [s(\omega, t)] \} \rangle \right] \quad (4.33) \]

We focus now on the last term. Using the definition of the spectrum (Eq. 4.30), we can calculate the Fourier transform of the spectrum:

\[
\text{FT} [s(\omega, t)] = \text{FT} [\Phi(\omega) \ast \delta (\omega - \omega_0 - \Delta \omega(t))] \\
= \text{FT} [\Phi(\omega)] e^{-2\pi i \delta(\omega_0 + \Delta \omega(t))} \quad (4.35)
\]

where the bold-font \( \delta \) is the Dirac delta, and \( \delta \) is the variable of unit \( \frac{1}{\text{Energy}} \) and corresponds to the path-length difference in the interferometer. Taking the real component gives us:

\[
\text{Re} \{ \text{FT} [s(\omega, t)] \} = \text{Re} \{ \text{FT} [\Phi(\omega)] \} \cos \{ 2\pi \delta [\omega_0 + \Delta \omega(t)] \} \quad (4.36)
\]

Note that the negative sign inside the cosine was removed because cosine is an even function.

At this point, the implementation of PCFS must be considered in order to reduce this equation. First, we reflect on the form of \( I_a(t) \). In the absence of spectral dynamics, \( \Delta \omega(t) = 0 \). Thus,

\[
I_a(t) = \frac{1}{2} I_0(t) \left[ 1 + \text{Re} \{ \text{FT} [\Phi(\omega)] \} \cos(2\pi \delta \omega_0) \right] \quad (4.37)
\]

This is the interferogram discussed in the previous section, where the intensity “fringes” oscillate over path-length differences \( \delta \) according to the mean frequency \( \omega_0 \) of the spectrum with an envelope determined by the envelope of the spectrum \( \Phi(\omega) \).

In PCFS, the interferometer is scanning during the integration time. That is, the path-length difference changes as a function of time. More specifically, \( \delta(t) = \delta_i + 2Vt \), where \( V \) is the scanning speed given initial path-length difference \( \delta_i \). The scanning
speed is set such that, for any $\tau$ of interest, the change in the optical path length difference due to scanning, $2V\tau$, is much smaller than the coherence length of the emitter. Additionally, provided that the scanning distance during the integration time is sufficiently larger than one period of the fringe oscillation of the interferogram, all cosine and sine terms that contain $\omega_0$ will effectively average to 0. As a result,

$$\int_0^T \cos \{2\pi \delta [\omega_0 + \Delta \omega(t)]\} \, dt \approx 0 \quad (4.38)$$

We note that this also makes the assumption that $\Delta \omega(t) \ll \omega_0$, which is physically very reasonable for single nanocrystals in the visible. Therefore, we can conclude:

$$\langle I_a(t) \rangle = \frac{1}{2} I_0(t) \left[ 1 + \text{Re} \{\text{FT} \Phi(\omega)\} \right] \langle \cos \{2\pi \delta [\omega_0 + \Delta \omega(t)]\} \rangle \quad (4.39)$$

$$= \frac{1}{2} \langle I_0(t) \rangle \quad (4.40)$$

Through similar arguments, we can also determine that

$$\langle I_b(t + \tau) \rangle = \frac{1}{2} \langle I_0(t + \tau) \rangle \quad (4.41)$$

Finally, we have the denominator for the cross-correlation function:

$$\langle I_a(t) \rangle \langle I_b(t) \rangle = \frac{1}{4} \langle I_0(t) \rangle \langle I_0(t + \tau) \rangle \quad (4.42)$$

### 4.3.2 Numerator

We now take a look at the numerator with the same approach. Inputting the expression for the output intensities into $\langle I_a(t)^* I_b(t + \tau) \rangle$, we obtain:

$$\left\langle \left[ \frac{1}{4} I_0(t) I_0(t + \tau) \right] \left[ 1 + \text{Re} \{\text{FT} \left[ s(\omega, t) \right]\} \right] \left[ 1 - \text{Re} \{\text{FT} \left[ s(\omega, t + \tau) \right]\} \right] \right\rangle \quad (4.43)$$

Assuming the total intensity is not correlated with the spectrum, we have:

$$\left\langle \left[ \frac{1}{4} I_0(t) I_0(t + \tau) \right] \left[ 1 + \text{Re} \{\text{FT} \left[ s(\omega, t) \right]\} \right] \left[ 1 - \text{Re} \{\text{FT} \left[ s(\omega, t + \tau) \right]\} \right] \right\rangle \quad (4.44)$$
We will focus on the product of the two binomials. Expanding, we obtain:

\[
1 - \text{Re} \{ \text{FT} \{ s(\omega, t + \tau) \} \} + \text{Re} \{ \text{FT} \{ s(\omega, t) \} \}^* - \text{Re} \{ \text{FT} \{ s(\omega, t) \} \}^* \text{Re} \{ \text{FT} \{ s(\omega, t + \tau) \} \}
\]  

As discussed for the denominator, the two middle terms go to zero due to the effects of scanning:

\[
\langle \text{Re} \{ \text{FT} \{ s(\omega, t + \tau) \} \} \rangle \approx 0 \quad (4.46)
\]

\[
\langle \text{Re} \{ \text{FT} \{ s(\omega, t) \} \}^* \rangle \approx 0 \quad (4.47)
\]

We calculate the last term explicitly using the model for the spectrum: \( s(\omega, t) = \Phi(\omega) \ast \delta (\omega - \omega_0 - \Delta \omega(t)) \). This gives us:

\[
\text{Re} \left\{ \text{FT} \left[ \Phi(\omega) \right] e^{-2\pi i \delta (\omega_0 + \Delta \omega(t))} \right\}^* \text{Re} \left\{ \text{FT} \left[ \Phi(\omega) \right] e^{-2\pi i \delta (\omega_0 + \Delta \omega(t + \tau))} \right\}
\]

Taking the real part and the complex conjugate, we obtain:

\[
|\text{FT} \left[ \Phi(\omega) \right]|^2 \cos \left\{ 2\pi \delta \left[ (\omega_0 + \Delta \omega(t)) \right] \right\} \cos \left\{ 2\pi \delta \left[ (\omega_0 + \Delta \omega(t + \tau)) \right] \right\}
\]

Again, we have removed the negative signs within the cosines because \( \cos \) is even.

We are able to expand the product of two cosines using the trigonometric identity \( \cos(\theta) \cos(\phi) = \frac{1}{2} [\cos(\theta - \phi) \cos(\theta + \phi)] \) to obtain:

\[
|\text{FT} \left[ \Phi(\omega) \right]|^2 \frac{1}{2} \left( \cos \left\{ 2\pi \delta \left[ \Delta \omega(t) - \Delta \omega(t + \tau) \right] \right\} + \cos \left\{ 2\pi \delta \left[ 2\omega_0 + \Delta \omega(t) + \Delta \omega(t + \tau) \right] \right\} \right)
\]

Again, as discussed in the previous section, the term containing \( \omega_0 \) disappears because of scanning over the interference fringes. The numerator now looks like:

\[
\left\langle \frac{1}{4} I_0(t) I_0(t + \tau) \right\rangle \left\langle 1 - \frac{1}{2} |\text{FT} \left[ \Phi(\omega) \right]|^2 \cos \left\{ 2\pi \delta \left[ \Delta \omega(t) - \Delta \omega(t + \tau) \right] \right\} \right\rangle
\]
4.3.3 Combining Numerator and Denominator

We are now in a position to combine the numerator and denominator to calculate the full intensity cross-correlation function. We begin with the first term that can be simplified to give $g^{(2)}(\tau)$, the normalized intensity autocorrelation of the input intensity $I_0(t)$.

$$g^x(\tau) = \frac{\langle I_a(t)I_b(t+\tau) \rangle}{\langle I_a(t) \rangle \langle I_b(t+\tau) \rangle}$$

(4.52)

$$= \frac{1}{4} \left\{ \langle I_0(t)I_0(t+\tau) \rangle \right\} \langle \cdots \rangle$$

(4.53)

$$= g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT}[\Phi(\omega)]|^2 \cos \{2\pi\delta[\Delta\omega(t) - \Delta\omega(t+\tau)]\} \right)$$

(4.54)

$$= g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT}[\Phi(\omega)]|^2 \langle \cos \{2\pi\delta[\Delta\omega(t) - \Delta\omega(t+\tau)]\} \rangle \right)$$

(4.55)

We now focus on the time average of the cosine term, which contains all the information on spectral dynamics. Before doing that, we introduce the following notation for a term that describes the time-dependent spectral dynamics:

$$\epsilon(t, \tau) = \Delta\omega(t+\tau) - \Delta\omega(t)$$

(4.56)

This gives us:

$$g^x(\delta, \tau) = g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT}[\Phi(\omega)]|^2 \langle \cos \{-2\pi\delta\epsilon(t, \tau)\} \rangle \right)$$

(4.57)

At this point, we use a trick from the first PCFS derivation. From statistical mechanics, we know that the time average of spectral fluctuations can be replaced by the ensemble average of all possible spectral changes $\epsilon$ over some distribution $p(\epsilon, \tau)$ for each $\tau$. Therefore, we can write:

$$\langle \cos \{-2\pi\delta\epsilon(t, \tau)\} \rangle = \frac{1}{T} \int_{-\infty}^{\infty} \cos \{-2\pi\delta\epsilon(t, \tau)\} \, dt$$

(4.58)

$$= \int_{-\infty}^{\infty} \cos(-2\pi\delta\epsilon)p(\epsilon, \tau)$$

(4.59)
We recognize this to be the Fourier cosine transform, or taking the real part of the Fourier transform. Therefore, we write:

\[
\int_{-\infty}^{\infty} \cos(-2\pi \delta \epsilon) p(\epsilon, \tau) \, d\epsilon = \text{Re} \left\{ \int_{-\infty}^{\infty} e^{-i2\pi \delta \epsilon} p(\epsilon, \tau) \, d\epsilon \right\} \tag{4.60}
\]

\[
= \text{Re} \left\{ \text{FT} \left[ p(\epsilon, \tau) \right]_{\epsilon \rightarrow \delta} \right\} \tag{4.61}
\]

Finally, we obtain the governing equation of single-emitter PCFS:

\[
g^{\times}(\delta, \tau) = g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT} \left[ \Phi(\omega) \right]|^2 \text{Re} \left\{ \text{FT} \left[ p(\epsilon, \tau) \right]_{\epsilon \rightarrow \delta} \right\} \right) \tag{4.62}
\]

This equation shows that by measuring the cross-correlation of the intensities of the two outputs of an interferometer along with the autocorrelation of the total signal, one can obtain a function that describes the spectral envelope and its temporal dynamics.

### 4.3.4 Relationship to the First PCFS Derivation

The equation derived in the previous section is similar to, but not precisely the same as, the equation introduced in Ref. 147. We compare the two results below.

\[
g^{\times}(\delta, \tau) = g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT} \left[ \Phi(\omega) \right]|^2 \text{Re} \left\{ \text{FT} \left[ p(\epsilon, \tau) \right]_{\epsilon \rightarrow \delta} \right\} \right) \tag{4.63}
\]

\[
g^{\times}(\delta, \tau) = 1 - \frac{1}{2} \text{FT} \left[ p(\zeta, \tau) \right]_{\zeta \rightarrow \delta} \tag{4.64}
\]

The first equation is the result obtained through our derivation and the second is the result from Ref. 147.

The first difference is the inclusion of \( g^{(2)}(\tau) \). The reason it was not included in Ref. 147 is because fluctuations in the total intensity were not considered. Practically, taking this term into account allows for PCFS to be performed even in the presence of blinking.

The second is the difference between \( p(\zeta, \tau) \) and \( p(\epsilon, \tau) \). \( p(\zeta, \tau) \) describes energy differences between all pairs of photons. \( p(\epsilon, \tau) \) describes the time-dependent energy shifts of the spectrum, whose envelope remains static in shape. We can show that

71
the two equations are equivalent when we consider the effect of the envelope:

\[ |\text{FT} [\Phi(\omega)]|^2 \text{Re}\{\text{FT} [p(\epsilon, \tau)]\} = \text{FT} [\Phi(\omega)]^* \text{FT} [\Phi(\omega)] \text{FT} [p(\epsilon, \tau)] \tag{4.65} \]
\[ = \text{FT} [\Phi(\omega) \ast \Phi(\omega) \ast p(\epsilon, \tau)] \tag{4.66} \]
\[ = \text{FT} [p(\zeta, \tau)] \tag{4.67} \]

where \( \ast \) indicates the cross-correlation operation. By the cross-correlation theorem, we see that what we measure is the Fourier transform of the autocorrelation of the spectral envelope that is further correlated with the distribution of energy shifts due to spectral dynamics. The spectral autocorrelation tells us about the energy differences between photon pairs of the homogeneous linewidth, which we can further monitor over the course of spectral dynamics. This is precisely equivalent to the entire distribution of energy differences between photon pairs, \( p(\zeta, \tau) \).

Another way to consider the distribution of photon energies is to take the limit where the spectral envelope is simply a delta function. That is, each photon contributes a single frequency. Then, because the Fourier transform of the Dirac delta is 1, we have

\[ g^\times(\delta, \tau) = g^{(2)}(\tau) \left( 1 - \frac{1}{2} |\text{FT} [\Phi(\omega)]|^2 \text{Re}\{\text{FT} [p(\epsilon, \tau)]_{\epsilon \to \delta}\} \right) \tag{4.68} \]
\[ = g^{(2)}(\tau) \left( 1 - \frac{1}{2} \text{Re}\{\text{FT} [p(\zeta, \tau)]_{\zeta \to \delta}\} \right) \tag{4.69} \]

and we see that the two equations are equivalent.

4.4 PCFS on Single Nanocrystals at Low Temperature

Experimental implementations of PCFS have only just begun to unlock the full analytical potential of this technique. The first experimental implementation of low temperature PCFS on single nanocrystals tracked the width of the spectral correlation.
on timescales ranging from hundreds of milliseconds to tens of microseconds.\textsuperscript{150,151} These timescales are much faster than the temporal resolution of conventional single-molecule spectroscopy. In these studies, the previously observed power-law spectral diffusion was found to continue down to the millisecond regime, whereupon the linewidth reduction saturated at \( \sim 10\,\mu\text{eV} \). This findings have been corroborated by spectral hole burning and ultrafast measurements.\textsuperscript{152–154}

We also note that several studies have observed integrated linewidths as narrow as \( \sim 10\,\mu\text{eV} \), setting an upper limit on the single-NC intrinsic linewidth.\textsuperscript{137,155} However, these measurements were performed using resonant photoluminescent excitation spectroscopy and Fabry-Perot interferometry, which rely on the selection of particles with minimal spectral diffusion. Moreover, neither of these methods have the temporal resolution to effectively characterize sub-second spectral diffusion processes in nanocrystals.

These first studies realized the utility of PCFS in probing spectral dynamics on timescales faster than hundreds of milliseconds and in identifying the intrinsic linewidth of a single nanocrystal. However, they did not delve into the mechanistic details of spectral diffusion embedded in the evolving shape of the spectral correlation. With improved signal-to-noise from high-quality samples, it has become possible to analyze both the width and shape of the spectral correlation function.

Recent work with PCFS on single nanocrystals at low temperature has demonstrated that the shape of the spectral correlation can directly reveal mechanistic details of spectral diffusion.\textsuperscript{120} Discrete and continuous spectral diffusion processes each have their own qualitative footprint in the spectral correlation measured by PCFS (Fig. 4-4). The spectral correlation \( p(\zeta,\tau) \) of a continuous diffusion process features a single, smoothly broadening distribution that represents its probability distribution function (Fig. 4-4a). In contrast, \( p(\zeta,\tau) \) of a discrete diffusion process features two distinct distributions: a narrow distribution with fixed width, which represents photon pairs without a diffusion event between them, and a broadening distribution representing photon pairs with at least one diffusion event between them (Fig. 4-4b). Our measurements on single nanocrystals at low temperature show that
the rapid spectral jitter is indeed the result of a $\sim 10 \mu$eV FWHM intrinsic spectrum undergoing discrete diffusion events (Fig. 4-4c).\textsuperscript{120}

### 4.5 Beyond Probing Single Emitters

While the study of individual nanoparticles one at a time can provide a tremendous amount of information, it is non-trivial to extrapolate these findings to the sample as a whole. This is not only because efforts to characterize the entire sample at the single-particle level can be time-consuming, but also because effects such as user selection bias, photodegradation, and unwanted interactions between the sample and its environment must be carefully addressed. For nanocrystals, these concerns have hindered the unambiguous characterization of the links between synthetic methodologies and single-nanocrystal spectral properties.

For the remainder of this thesis, we discuss an extension of PCFS that takes the principles of PCFS but applies them to study single-nanocrystal spectral properties in solution with ensemble-level statistics. However, before providing a detailed description of Solution PCFS (S-PCFS), we believe it is useful to first consider a related technique: fluorescence correlation spectroscopy (FCS).
Chapter 5

Fluorescence Correlation Spectroscopy (FCS)

In Chapter 2, we discussed how broad-timescale intensity correlation analysis applied to single nanocrystals has not been particularly successful because of the power-law nature of blinking. An instance where broad-timescale intensity correlation has been successfully applied to nanocrystals is fluorescence correlation spectroscopy (FCS), the analogue of dynamic light scattering for fluorescent species.\textsuperscript{156,157} FCS uses the intensity correlation function of a dilute solution of emitters diffusing through a laser focus to extract single-emitter properties such as particle size.\textsuperscript{158}

In this chapter, we provide some theoretical background for FCS and show how it can be used to study nanoparticles. This chapter serves as the bridge between PCFS and its solution analogue, S-PCFS. Here, derivations were taken from the literature or derived with input from Andrew Beyler. FCS measurements were performed on samples synthesized by Ou Chen and Cliff Wong.

5.1 FCS Theory

The goal of this section is to provide some theoretical intuition into why FCS works the way that it does. In particular, the intensity correlation function \( g^{(2)}(\tau) \) measured in FCS can be recast in terms of the sum of photon pairs from the same emitter and
photon pairs from different emitters. This distinction provides the foundation for Solution PCFS discussed in the following chapter.

5.1.1 Photon Pairs from an Ensemble of Emitters

Before considering the implementation of FCS, we consider the intensity correlation function $g^{(2)}(\tau)$ for any collection of $N$ emitters. Rather than using a continuous signal interpretation, we consider the photon-correlation paradigm where $g^{(2)}(\tau)$ reflects the probability of detecting photon pairs of given temporal spacing.

In Ref. 95, they define $G(t + \tau | t)$ as the “conditional probability density to find any other photon at time $t + \tau$ if one was observed at time $t.” Furthermore, they define the intensity correlation function:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (5.1)$$

They then assert that $G(\tau) = G(t + \tau | t)$ is related to $g^{2}(\tau)$ by:

$$g^{(2)}(\tau) = \frac{G(\tau)}{\langle I(t) \rangle} \quad (5.2)$$

Using this, we derive a simple equation describing the photon pairs emitted from the same emitter and from different emitters from this relationship from probability and counting.

From the $N$ particles in our ensemble, Photon $A$ is detected at time $t$ and then a subsequent Photon $B$ is detected at time $\tau$ later. Let us consider the scenario where Photon $A$ is detected and it was emitted by particle $j$. We then consider the detection of subsequent Photon $B$:

$$G(\tau) = \frac{\sum_{i=1}^{N} P(B = i | A = j)}{\sum_{i=1}^{N} P(B = i)} \quad (5.3)$$

The numerator is simply the definition of the conditional probability of detecting
Photon $B$ given a detection of Photon $A$. The denominator is the probability of detecting a photon from any particle summed over all particles, which would give the average total intensity.

If we split the numerator into the sum of photons from the same emitter or different emitters, we obtain:

$$G(\tau) \frac{\langle I(t) \rangle}{\langle I(t) \rangle} = \frac{(N - 1) \langle I_i(t) \rangle + P (B = j \mid A = j) \langle I_j(t) \rangle}{N \langle I_i(t) \rangle}$$

(5.4)

Here, because we have $N$ particles, there is some probability that both photons came from the same particle and that is weighted by the average intensity $\langle I_i(t) \rangle$ of that particle. Similarly, we can determine that the probability of detecting pairs from different particles is $N - 1$ scaled by the average intensity of each of those particles. Assuming that all particles emit with the same average intensity, the equation reduces to:

$$g_r^{(2)}(\tau) = G(\tau) \frac{\langle I(t) \rangle}{\langle I(t) \rangle} = \frac{N - 1}{N} + \frac{1}{N} P (B = j \mid A = j)$$

(5.5)

(5.6)

The first term, corresponding to photon pairs from different emitters, manifests itself as an amplitude of $\sim 1$ for all $\tau$. The second term, corresponding to photon pairs from the same particle, has a vanishing probability of observing photon pairs from the same particle with larger $N$. Any $\tau$ dependence is in the $P (B = j \mid A = j)$ term, with its particular form depending on the nature of detection.

The key to making this result of practical use was the advent of confocal microscopy applied to dilute solutions of particles. In modern FCS (Fig. 5-1), a small focal volume is constructed and a small number of particles $N$ is in the focal volume at any given time. With this, a larger fraction of the total number of photon pairs comes from the same particle. Because this scales with the average number of emitters in the focal volume $\langle N \rangle$, the single-particle component can be more easily distinguished from the ensemble contribution. With a carefully characterized focal
volume, properties such as the sample-averaged diffusion coefficient of the emitters can be determined from the single-emitter $P(B = j \mid A = j)$ term.

In Figure 5-1b, the decay of $g^{(2)}(\tau)$ at $\sim 200\mu$s gives the characteristic timescale for the diffusion of emitters into and out of the focal volume. Because the solution is dilute, the emission signal $I(t)$ is characterized by short bursts of intensity as each particle passes through the focal volume. In the intensity-correlation interpretation, the self-similarity of $I(t)$ decays at the average dwell time of the particle. In the photon-correlation interpretation, pairs of photons are more likely to be detected during the time the particle is within the focal volume. At longer $\tau$, photon pairs originate from different emitters and are uncorrelated because they depend on the random Poisson statistics of diffusion of particles into the focus.\textsuperscript{31}

With this concept in mind, we spend the remainder of this chapter considering the practical implementation of FCS and the analysis of its data.
5.1.2 Derivation of Two Forms for the Intensity Correlation Function

In the FCS literature, a slightly different intensity autocorrelation function than the one previously considered is typically used. Moreover, many hardware correlators, such as the ALV-7004FAST used in this work, will output this value. This is the autocorrelation of intensity fluctuations, which we call $g_{\text{fluc}}^{(2)}(\tau)$, as opposed to the autocorrelation of the intensity $g^{(2)}(\tau)$. We provide below a simple derivation showing how the autocorrelation of an intensity is related to the autocorrelation of intensity fluctuations.

The definition of the intensity autocorrelation function is:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}$$

where the angled brackets indicate a time average. For the purposes of this derivation, we are interested in the time-dependent fluctuation terms. What we mean by that is the deviation of the intensity from the mean intensity during the course of the experiment. So, we define:

$$I(t) = \langle I(t) \rangle - \delta I(t)$$

Inputting this into the definition of the intensity correlation function, we have:

$$g^{(2)}(\tau) = \frac{\left\langle \left[ (I(t)) - \delta I(t) \right]\left[ (I(t+\tau)) - \delta I(t+\tau) \right] \right\rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}$$

$$= \frac{\left\langle (I(t)) \langle I(t+\tau) \rangle - \langle I(t) \rangle \delta I(t+\tau) - \langle I(t+\tau) \rangle \delta I(t) + \delta I(t)\delta I(t+\tau) \right\rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}$$

We focus now on the middle two terms. To simplify, we again use the definitions for intensity fluctuations:

$$\delta I(t) = \langle I(t) \rangle - I(t)$$

$$\delta I(t+\tau) = \langle I(t+\tau) \rangle - I(t+\tau)$$
Inputting those, we have for the middle terms:

\[
\begin{align*}
\langle - \langle I(t) \rangle (\langle I(t + \tau) \rangle - I(t + \tau)) - \langle I(t) \rangle (\langle I(t) \rangle - I(t)) \rangle \\
\langle -2 \langle I(t) \rangle \langle I(t + \tau) \rangle + \langle I(t) \rangle I(t + \tau) + \langle I(t + \tau) \rangle I(t) \rangle \\
= 0
\end{align*}
\]

By taking the full time average, all of these terms cancel out. As a result, we are left with:

\[
g^{(2)}(\tau) = 1 + \frac{\langle \delta I(t) \delta I(t + \tau) \rangle}{\langle I(t) \rangle \langle I(t + \tau) \rangle} = 1 + g_{\text{fluc}}^{(2)}(\tau)
\]

While the difference of 1 may seem somewhat arbitrary, this difference lies in the fact that \( g_{\text{fluc}}^{(2)}(\tau) \) is focused only on fluctuations in the intensity signal, which occur when individual particles enter and exit the focal volume. Therefore, in practice, the difference of 1 is simply the subtraction of the ensemble component of \( g^{(2)}(\tau) \):

\[
(N - 1)/N.
\]

### 5.2 FCS in Practice

In practice, FCS can be performed on a setup very similar to the antibunching setup from Chapter 2. However, rather than measuring the emission from a single nanocrystal on a substrate, emission is collected from a dilute solution of emitters (Fig. 5-2). Most measurements presented in this thesis were taken with a 60x 1.2 NA water-immersion objective on quantum dot samples diluted in hexanes with excess cadmium oleate and decylamine held in flat capillary tubes. The cadmium oleate and decylamine are used to passivate the surface of the dots to increase their quantum yield and prevent aggregation. For measurements on nanoparticles in aqueous buffers, cover slips were treated with a casein/PBS solution before using a silicone perfusion chamber. We note that for our particular setup, we used the interferometer of PCFS,
but set the path-length difference to be much larger than the coherence length of the emitter. In this regime, there are no interference effects and the interferometer essentially acts as a beamsplitter.

5.2.1 Experimental Considerations

The beamsplitter geometry is important for FCS measurements because it allows for the measurement of the intensity cross-correlation function $g^x(\tau)$ as opposed to the intensity autocorrelation function $g^{(2)}(\tau)$. The benefit of cross-correlation measurements here is purely due to practical experimental reasons. When autocorrelation functions are calculated using a single detector, they are subject to afterpulsing. Afterpulsing is the term used to describe a general effect where fluorescence photons appear to be detected at short $\tau$ in the autocorrelation function when they are not present. This effect is often attributed to trapping and detrapping of charges that lead to detection events in avalanche photodiodes.\(^{159}\)

With cross-correlation, afterpulsing is generally eliminated, providing access to short $\tau$ information in the intensity correlation function, such as antibunching, that would normally be obscured by the afterpulsing signal. We emphasize that the cross-correlation is simply an experimental means to measure the intensity autocorrelation without the obscuring effects of antibunching and therefore, we will refer to measurements of this still as $g^{(2)}(\tau)$.
The other defining feature of the FCS setup is the confocal pinhole. The pinhole serves to reject light that is out of focus, thereby defining the detection volume. Careful alignment of the setup, particularly the pinhole, such that the detection volume overlaps with the excitation volume, is required for a well-defined focal volume. Moreover, a slightly underfilled objective helps to create a more Gaussian intensity distribution within the focal volume, which is closer to the assumptions necessary for accurate fitting. The dimensions of the focal volume can be characterized by using a series of calibration standards. With a well-characterized focal volume, the average diffusion time through the focal volume can be converted into a diffusion coefficient, which can in turn be converted into an average hydrodynamic diameter of the particle.

5.2.2 Fitting in FCS

We now review several of the equations that are relevant for practical use of FCS. A rigorous derivation of several functional forms for $g^{(2)}_{\text{fluc}}(\tau)$ in FCS experiments can be found elsewhere. We begin by modeling the excitation and collection intensity focal volume as a three-dimensional Gaussian:

$$I(r) = I_0 \exp \left[ - \frac{2(x^2 + y^2)}{\omega^2_{xy}} - \frac{2z^2}{\omega^2_z} \right]$$  \hfill (5.15)

for beam waist radius $\omega_{xyz}$ in all three dimensions, where $z$ is along the direction of beam propagation. We note that the beam waist radius $\omega_{xyz}$ is defined as twice the standard deviation $\sigma$ typically used in the Gaussian functional form. In this case, the beam waist radius is at the point where the intensity drops to $1/e^2$ of its peak value. Though the three-dimensional Gaussian is not always a good assumption for the FCS focal volume, this assumption results in a nice close-formed solution.

For an ensemble of a single emitting species undergoing free diffusion through this focal volume with no rapid intensity dynamics, it is possible to show that the intensity
fluctuation correlation function has the form:

$$g^{(2)}_{\text{fluc, 3D}}(\tau) = \frac{1}{\langle N \rangle} \frac{1}{1 + \frac{\tau}{\tau_D}} \frac{1}{\sqrt{1 + \frac{\omega_{xy}^2 \tau}{\omega_x^2 \tau_D}}}$$  \hspace{1cm} (5.16)

This is sometimes referred to as the isotropic 3D-translational diffusion model.

In modern FCS, high numerical aperture (NA) objectives are commonly used. With these optics, the beam is focused so tightly such that $\omega_{xy} \ll \omega_z$. In this case, diffusion through the focal volume occurs primarily through the x,y plane and the correlation function is well-approximated by the isotropic 2D translational diffusion model:

$$g^{(2)}_{\text{fluc, 2D}}(\tau) = \frac{1}{\langle N \rangle} \frac{1}{1 + \frac{\tau}{\tau_D}}$$  \hspace{1cm} (5.17)

This result is nice for fitting because it has only two free parameters: the amplitude, which is inversely related to the average occupancy number within the focal volume, and the characteristic diffusion time, which describes the average dwell time of the emitter within the focus. The characteristic diffusion time $\tau_D$ is easily determined as it is the value at which $g^{(2)}_{\text{fluc, 2D}}(\tau)$ decays to half its initial value.

From our understanding of Brownian motion, we also know that the characteristic diffusion time $\tau_D$ is related to the size of the focal volume beam waist by the diffusion coefficient $D$ by:

$$\omega_{xy}^2 = 4D\tau_D$$  \hspace{1cm} (5.18)

where the constant 4 comes from the fact that this is 2D diffusion. With the diffusion coefficient, we can then calculate the hydrodynamic radius of the particle using the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi \eta r}$$  \hspace{1cm} (5.19)

Thus far, our discussion of FCS has been restricted to a single diffusing species whose emission does not fluctuate. We briefly provide the results for two modifications that are relevant when studying single emitters: blinking and antibunching. As discussed in Chapter 2, many single emitters, including nanocrystals, undergo emis-
sion intensity fluctuations. For power-law blinking, as observed in many nanocrystals, the intensity autocorrelation function also goes as a power law:

\[ g_{\text{fluc}, 2D}(\tau) = A \left( 1 - B\tau^{2-m} \right) \frac{1}{1 + \frac{\tau}{\tau_D}} \] (5.20)

The power law term is multiplied to the diffusion term because it modifies intensity fluctuations for all particles.

To include antibunching, we simply subtract a rapidly decaying exponential term as photons are not observed as \( \tau \) approaches than the emission lifetime.\(^{163} \) Therefore, the final equation that can be used to describe nanocrystals in FCS is:\(^{62} \)

\[ g_{\text{fluc}, 2D}(\tau) = A \left( 1 - B\tau^{2-m} \right) \frac{1}{1 + \frac{\tau}{\tau_D}} - ke^{-\tau/n} \] (5.21)

We note that there are a large number of free variables in this equation: \( A, B, m, \tau_D, k, \) and \( n \). In practice, if we are concerned only with diffusion, we use only the 2D translational diffusion model. In cases where the full expression has been necessary, we fit only the short \( \tau \) values to the blinking and antibunching terms and longer \( \tau \) values to the diffusion term.

### 5.3 Application of FCS

FCS can be an excellent tool for characterizing nanoparticles in solution. This is particularly the case for measurements of nanoparticles in solution with many other constituents. Measurements such as dynamic light scattering (DLS) and chromatography can be useful for determining the size of particles, but they can be affected by the presence of other comparably sized particulates in solution. FCS, on the other hand, is sensitive only to fluorescence. So, as long as the other constituents in solution are non-luminescent, FCS can directly probe the species of interest. In the last section of this chapter, we describe two FCS studies performed on nanoparticles in aqueous solutions that have complimented the determination of the efficacy of these particles for their intended purpose.
5.3.1 Biocompatibility

A crucial element of using nanoparticles for biological applications is its biocompatibility. Nanoparticles must be stable in a biological environment, but moreover, they must interact in a specific manner. That is, they must not disrupt the workings of its environment except in ways that have been rationally designed. For example, quantum dots can be used to target and track specific proteins in cells. If the nanoparticles were to interact with other biomolecules, observers would not be able to study the movement of the protein of interest without false-positive readings. In the worst case scenario, the quantum dots would disrupt the cell so severely that no meaningful results could be obtained. We have used FCS as an in vitro technique to diagnose the biocompatibility of engineered nanoparticles for biological applications.

We provide here an FCS study that we performed on magneto-fluorescent particles for biological applications. These superparticles, comprised of CdSe/CdS QDs and superparamagnetic Fe$_3$O$_4$ nanoparticles, have the dual functionality of luminescence and magnetism. With high loading of both types of particles, these particles can act as fluorescent labels as well as MRI contrast agents. Additionally, their spatiotemporal location can be controlled within individual cells and tissues using micromagnetic manipulation. However, a key component of this study is determining if these particles can be rendered completely biocompatible. The surface reactivity of silica can be exploited to add polymers such as polyethylene glycol (PEG) to provide biocompatibility. A simple test of biocompatibility would then be to determine if these particles agglomerate with biomolecules.

In Figure 5-3, we show the results from two experiments. In the first, the silica-coated superparticles were incubated in phosphate-buffered saline (PBS) and in the second, they were incubated in fetal bovine serum (FBS). PBS is a commonly used aqueous buffer containing only phosphates and several other salts. FBS, a commonly-used serum for cell culture, contains a vast array of biomolecules. After incubation, the particles were diluted into PBS and their diffusion properties were measured using FCS. If the particles are biocompatible, they would show no difference in their
average diffusion time in FCS because it means that biomolecules did not adhere to the surface of the particles. We see in Figure 5-3c that there is no significant difference in diffusion times, showing that these particles are indeed biocompatible.

We also highlight two aspects of Figure 5-3. First, the fits to the isotropic 2-D translational diffusion model are a testament to the monodispersity of these particles because particles with high size inhomogeneity tend to smear out the correlation function, making the fit rather poor. The nice fit shows that these particles are highly monodisperse. Second, we note that there is no antibunching feature in either correlation function. Each superparticle contains many quantum dots and as such, no individual superparticle would be expected to produce the signature of a single quantum emitter.

### 5.3.2 Size-Changing Cancer Nanotherapeutics

A key challenge to cancer therapeutics is specific drug delivery. That is, the ideal chemotherapy drug introduced to the human body should kill only cancer cells, not benign cells. Cancer nanotherapeutics offer one approach to targeting tumors because they rely on the enhanced permeation and retention (EPR) effect, which results in ∼100 nm-diameter particles accumulating near tumors. However, nanoparticles of this size cannot easily deliver drugs to the center of the tumor where the most virulent cancer cells reside. A creative approach to delivering drugs to the center of the tumor
is size-changing nanoparticles. If a larger nanoparticle could be triggered to break down into smaller drug-carriers nearby the tumor, drugs could be delivered to the tumor interior.

As a proof of principle, gelatin nanoparticles were synthesized with quantum dots on the surface. A glutaraldehyde cross-linker was used to keep the gelatin nanoparticle intact. In the presence of MMP-2 and MMP-9, enzymes found at the edge of tumors that cleave the extracellular matrix, gelatin is cleaved and the QDs on the surface are released. QDs were used as a stand-in for the therapeutic drug carriers so that they could be imaged using microscopy. Before performing in vivo measurements, FCS was used as a characterization tool to determine whether MMP proteins could indeed cleave these particles and release quantum dots. We note that DLS could not be used to determine this because of the presence of gelatin and glutaraldehyde fragments in solution after enzymatic digestion.

As Figure 5-4 shows, the incubation of MMP-2 dramatically changes the diffusion time of the fluorescence emitters. Before cleaving, the hydrodynamic diameter measured with FCS was 81.1 ± 2.3 nm. This value was reasonably consistent with the DLS measurement of 90.9 ± 1.3 nm. After MMP-2 digestion, the hydrodynamic diameter decreased to 9.7 ± 0.3 nm. The smaller value is the size of individual QDs in solution, indicating the absence of non-specific binding of the QDs to gelatin/glutaraldehyde fragments in solution. The FCS results show a clear and definitive size change that
are also in agreement with measurements of the diffusion of these multistage particles through a collagen gel and a tumor in a mouse model.

5.4 Conclusion

Though FCS is a powerful characterization tool for the study of particles diffusing in solution, we refocus our attention to how we can take advantage of FCS for spectroscopy. FCS monitors the temporal distribution of photons from emitters in solution diffusing through a laser focus. Rather than spatially separating emitters on a surface and monitoring the emission from each emitter one at a time, FCS serves to separate the emission from emitters temporally by monitoring the relative arrival times of photons as emitters diffuse into and out of the focal volume. With this analysis, photon pairs can be determined to have arrived from the same emitter or from different emitters. This principle is critical for the projection of FCS into the spectral domain using PCFS.
Chapter 6

PCFS in Solution (S-PCFS)

Traditional spectroscopy of particles diffusing in solution only provides the spectrum of the ensemble. We have developed an extension of PCFS that allows us to extract spectral information regarding single emitters in solution while maintaining ensemble-level statistics. As discussed in Chapter 5, FCS measures photon pairs detected as emitters diffuse through a focal volume. Pairs of photons are statistically likely to have originated from the same emitter if the time separation $\tau$ between photons is shorter than the average diffusion time of the particle in the focal volume. Conversely, if $\tau$ is much longer than the average diffusion time, then photon pairs are likely to have originated from different emitters. By combining PCFS with FCS, the spectral information of each type of photon pair can be measured. In essence, the combination of FCS with PCFS serves to project the FCS correlation function into the spectral domain.$^{166}$

In this chapter, we provide the theoretical background necessary to understand how FCS is combined with PCFS to give S-PCFS. We then give an experimental proof of principle demonstration of how S-PCFS is able to extract single-emitter spectral information from a heterogeneous ensemble. The formal derivation of S-PCFS was adapted from an unpublished derivation by Xavier Brokmann. The experimental result was obtained in conjunction with Lisa Marshall with guidance from Xavier Brokmann and with samples obtained from Cliff Wong, Zoran Popović, Andrew Greytak, Brian Walker, and Numpon Insin. These results were published in Ref 148.
Figure 6-1: The S-PCFS setup combines confocal microscopy setup used in FCS with the interferometer and correlation setup of PCFS.

6.1 S-PCFS Theory: Combining FCS with PCFS

When the emission from FCS is passed through an interferometer, we can take advantage of one of the unique properties of PCFS: the measurement of the energy differences between photons rather than their absolute energies. In the solution-phase version of PCFS, or S-PCFS, the energy differences between pairs of photons emitted by the same particle reflect the single-nanocrystal spectral profile. In contrast, photon pairs emitted from different particles depend on the peak emission energies of each particle and therefore reflect the inhomogeneously-broadened ensemble spectrum. Because the detection of photons originating from the same NC is statistically enhanced at timescales shorter than the particle dwell time in the focal volume, the single-particle contribution can be disentangled from the ensemble while maintaining ensemble-level statistics. Thus, the spectral correlation function for the average single emitter, \( p_{\text{single}}(\zeta, \tau) \), as well as the spectral correlation function for the ensemble, \( p_{\text{ens}}(\zeta, \tau) \), can be simultaneously measured with S-PCFS. In this section, we provide the theoretical background for understanding how this is accomplished.
6.1.1 Intuition For Combining PCFS and FCS

As discussed in Chapter 4, PCFS measures the spectral coherence between photon pairs (i.e., the energy differences between them). The intensity correlation function describing the photon pairs emitted by the particle are modulated by a spectral term as:

\[ g^\times(\delta, \tau) = g^{(2)}(\tau) \left( 1 - \frac{1}{2} \text{Re}\left\{ \text{FT}\left[p(\zeta, \tau)\right]_{\zeta \rightarrow \delta} \right\} \right) \]  

(6.1)

In Chapter 5, we discussed how the diffusion of particles into and out of a small focal volume modulates the intensity correlation function. Moreover, FCS can measure the sample-averaged properties of single emitters by monitoring photon pairs that were emitted from the same emitter as opposed to photon pairs from different emitters. Therefore, if the intensity from FCS were analyzed through an interferometer as in PCFS, the different types of photon pairs would be modulated by a spectral component: one giving the average single-emitter spectrum and the other the ensemble spectrum. Therefore, we would expect that \( g^\times(\delta, \tau) \) would be split as in FCS:

\[ g^\times(\delta, \tau) = g^{\text{single}}(\delta, \tau) + g^{\text{ens}}(\delta, \tau) \]  

(6.2)

As described in Chapter 5, the ensemble term is constant for all \( \tau \) and goes as \( (N - 1)/N \). The single-emitter term, which scales as \( 1/N \), is described by the shape and amplitude of \( g^{(2)}(\tau) \). More specifically,

\[ g^{(2)}(\tau) = g^{(2)}_{\text{fluc}}(\tau) + \frac{N - 1}{N} \]  

(6.3)

By literally combining the equations from PCFS and FCS, we would expect:

\[ g^{\text{single}}(\delta, \tau) = g^{(2)}_{\text{fluc}}(\tau) \times \left( 1 - \frac{1}{2} \text{Re}\left\{ \text{FT}\left[p^{\text{single}}(\zeta, \tau)\right]_{\zeta \rightarrow \delta} \right\} \right) \]  

(6.4)

\[ = \left( g^{(2)}(\tau) - \frac{N - 1}{N} \right) \times \left( 1 - \frac{1}{2} \text{Re}\left\{ \text{FT}\left[p^{\text{single}}(\zeta, \tau)\right]_{\zeta \rightarrow \delta} \right\} \right) \]

\[ g^{\text{ens}}(\delta, \tau) = \frac{N - 1}{N} \times \left( 1 - \frac{1}{2} \text{Re}\left\{ \text{FT}\left[p^{\text{ens}}(\zeta)\right]_{\zeta \rightarrow \delta} \right\} \right) \]  

(6.5)
We note that if $N = 1$ and there is no diffusion of the emitter out of the focal volume, we recover the equation used for single emitter PCFS:

$$
g_{\text{single}}^\delta(\tau) = g^{(2)}(\tau) \times \left(1 - \frac{1}{2}\text{Re}\{\text{FT}[p_{\text{single}}^{\delta}(\zeta, \tau)]_{\zeta \to \delta}\}\right) \quad (6.6)$$

In the limit $N \to \infty$, we would then obtain the governing equation for Solution PCFS.

$$
g^\times(\delta, \tau) = g^{(2)}(\tau) - \frac{1}{2}\text{Re}\left\{\text{FT}[p_{\text{ens}}^{\times}(\zeta) + (g^{(2)}(\tau) - 1)p_{\text{single}}^{\delta}(\zeta, \tau)]_{\zeta \to \delta}\right\} \quad (6.7)$$

### 6.1.2 Formal Derivation of S-PCFS Governing Equation

Having given an intuitive description of how the intensity cross-correlation function of S-PCFS encodes both the average single-emitter and ensemble spectral correlations, we provide here a formal derivation. We begin with the result of our derivation of single-emitter PCFS:

$$
g_{\text{single}}^\delta(\delta, \tau) = g^{(2)}(\tau) \times \left(1 - \frac{1}{2}\text{Re}\{\text{FT}[p_{\text{single}}^{\delta}(\zeta, \tau)]_{\zeta \to \delta}\}\right) \quad (6.8)$$

We now have an ensemble of $N$ emitters with total intensity $I(t) = \sum_{i=1}^{N} I_i(t)$ for emitter $i$ at time $t$. We note that $N$ refers to all particles in solution and that $I_i(t)$ is defined at all times but is only non-zero when emitter $i$ is in the focal volume. We now recast the term inside of the Fourier transform in terms of summations over all particles:

$$
\frac{\langle I(t) I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle} p^{\delta}(\zeta, \tau) = \sum_{i,j=1}^{N} \frac{\langle I_i(t) I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{ij}(\zeta, \tau) \quad (6.10)
$$

The key procedure at this point is to separate the summation in terms of photon pairs that came from the same emitter ($i = j$) or different emitters ($i \neq j$). Therefore, the summation splits into:

$$
\frac{\sum_{i=1}^{N} \langle I_i(t) I_i(t+\tau) \rangle}{\sum_{i,j=1}^{N} \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{ii}(\zeta, \tau) + \sum_{i \neq j}^{N} \frac{\langle I_i(t) I_j(t+\tau) \rangle}{\sum_{i,j=1}^{N} \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{i\neq j}(\zeta, \tau) \quad (6.11)
$$
We now count the photon pairs from this ensemble. Photon pairs either come from the same emitter \((i = j)\) or different emitters \((i \neq j)\). It is useful to consider the following matrix where \(N\) is the total number of particles.

\[
\begin{pmatrix}
11 & 12 & 13 & 14 & \ldots \\
21 & 22 & 23 & 24 & \ldots \\
31 & 33 & \ldots \\
\vdots & \ddots & \ddots & \ddots & \ddots
\end{pmatrix}
\] (6.12)

The photon pairs that come from the same particle 11, 22, etc. correspond to the elements along the diagonal of the matrix. The total number of these photon pairs is thus \(N\). The total number of photon pairs, however, is \(N^2\). Therefore, the number of photon pairs that come from different particles is \(N^2 - N\). Including these contributions by counting over the summations, we have:

\[
\frac{N \langle I_i(t)I_i(t+\tau) \rangle}{N^2 \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{ii}(\zeta, \tau) + \frac{(N^2 - N) \langle I_i(t)I_j(t+\tau) \rangle}{N^2 \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{i\neq j}(\zeta, \tau)
\] (6.13)

\[
\frac{1}{N} \frac{\langle I_i(t)I_i(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{ii}(\zeta, \tau) + \frac{N - 1}{N} \frac{\langle I_i(t)I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{i\neq j}(\zeta, \tau)
\] (6.14)

We can simplify the second term because we know that these photon pairs came from different, independent particles. As such,

\[
\frac{\langle I_i(t)I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} = \frac{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} = 1
\] (6.15)

The first term, however, cannot so easily be simplified. In order to do this in a way that is still useful to us, we reconsider the derivation from FCS. There, we were able to decompose the total signal into contributions from the same particle and from different particles. Using this knowledge and a very similar procedure as the derivation thus far, we can recast the term above as a function of \(g^{(2)}(\tau)\), the
autocorrelation of the total signal:

\[
    g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}
\]  

(6.16)

\[
    = \sum_{i,j=1}^{N} \frac{\langle I_i(t)I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle}
\]  

(6.17)

\[
    = \frac{\sum_{i=1}^{N} \langle I_i(t)I_i(t+\tau) \rangle + \sum_{i \neq j}^{N} \langle I_i(t)I_j(t+\tau) \rangle}{\sum_{i,j=1}^{N} \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle}
\]  

(6.18)

\[
    = \frac{N \langle I_i(t)I_i(t+\tau) \rangle + (N^2 - N) \langle I_i(t)I_j(t+\tau) \rangle}{N^2 \langle I_i(t) \rangle \langle I_j(t+\tau) \rangle}
\]  

(6.19)

\[
    = \frac{1}{N} \frac{\langle I_i(t)I_i(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} + \frac{N-1}{N}
\]  

(6.20)

Therefore,

\[
    \frac{1}{N} \frac{\langle I_i(t)I_i(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} = g^{(2)}(\tau) - \frac{N-1}{N}
\]  

(6.21)

We can now plug this into the term corresponding to photon pairs from the same particle in Eq. 6.14 to obtain a simplification for Eq. 6.10:

\[
    \sum_{i,j=1}^{N} \frac{\langle I_i(t)I_j(t+\tau) \rangle}{\langle I_i(t) \rangle \langle I_j(t+\tau) \rangle} p_{ij}(\zeta,\tau) = \left( g^{(2)}(\tau) - \frac{N-1}{N} \right) p_{ii}(\zeta,\tau) + \frac{N-1}{N} p_{i \neq j}(\zeta,\tau)
\]  

(6.22)

Putting all of this back into the intensity cross-correlation function, we obtain:

\[
    g^{\times}(\delta,\tau) = g^{(2)}(\tau) - \frac{1}{2} \text{Re} \left\{ \text{FT} \left[ \left( g^{(2)}(\tau) - \frac{N-1}{N} \right) p_{ii}(\zeta,\tau) + \frac{N-1}{N} p_{i \neq j}(\zeta,\tau) \right] \right\}
\]  

(6.23)

Taking the limit of large \( N \), we have the governing equation for Solution PCFS:

\[
    g^{\times}(\delta,\tau) = g^{(2)}(\tau) - \frac{1}{2} \text{Re} \left\{ \text{FT} \left[ \left( g^{(2)}(\tau) - 1 \right) p_{\text{single}}(\zeta,\tau) + p_{\text{ens}}(\zeta,\tau) \right]_{\zeta \to \delta} \right\}
\]  

(6.24)

6.1.3 Notation

In S-PCFS, the intensities at both outputs of the interferometer are measured and the intensity cross-correlation function \( g^{\times}(\delta,\tau) \) is calculated at different interferometer path-length differences \( \delta \) for temporal spacings between photons \( \tau \). As we have shown,
the governing equation of S-PCFS relates \( g^\times(\delta, \tau) \) to the single-emitter and ensemble spectral correlation functions as:

\[
g^\times(\delta, \tau) = g^{(2)}(\tau) - \frac{1}{2} \text{Re} \left\{ \text{FT} \left[ (g^{(2)}(\tau) - 1) p^{\text{single}}(\zeta, \tau) + p^{\text{ens}}(\zeta, \tau) \right]_{\zeta \rightarrow \delta} \right\} \tag{6.25}
\]

This is equivalent to the governing equation shown in Ref. 148 where \( g^{(2)}(\tau) = g^{\text{FCS}}(\tau) \) represents the autocorrelation function of the total intensity before entering the interferometer. This correlation function describes fluctuations in the total signal and accounts for the diffusion of the particles as in fluorescence correlation spectroscopy (FCS) as well as fluctuations in the single-emitter signal (e.g. “blinking”).

Here, we introduce the notation \( \tilde{g}(\delta, \tau) \) as the Fourier transform of the spectrally-relevant component of the cross-correlation function.\(^{167} \) This is equivalent to the “\( \delta \)-dependent component” of \( g^\times(\delta, \tau) \) because \( g^{(2)}(\tau) \) arises from the sum of the detector intensities and should show no dependence on the interferometer path-length difference.

\[
\tilde{g}(\delta, \tau) = \text{Re} \left\{ \text{FT} \left[ (g^{(2)}(\tau) - 1) p^{\text{single}}(\zeta, \tau) + p^{\text{ens}}(\zeta, \tau) \right]_{\zeta \rightarrow \delta} \right\} \tag{6.26}
\]

\( \tilde{g}(\delta, \tau) \) is the “PCFS interferogram” that is equivalent to the Fourier transform of the “diffusion weighted spectral correlation” described in Ref. 148.

We have further split \( \tilde{g}(\delta, \tau) \) into its single-emitter and ensemble components. This gives us \( \tilde{g}^{\text{single}}(\delta, \tau) = \text{Re} \left\{ \text{FT} \left[ p^{\text{single}}(\zeta, \tau) \right]_{\zeta \rightarrow \delta} \right\} \) and \( \tilde{g}^{\text{ens}}(\delta) = \text{Re} \left\{ \text{FT} \left[ p^{\text{ens}}(\zeta) \right]_{\zeta \rightarrow \delta} \right\} \).

The ensemble component does not have a \( \tau \) dependence because it is determined by the statistics of different particles entering and exiting the focal volume, which is governed by Poisson statistics.

### 6.2 Advantages, Disadvantages, and Tradeoffs

PCFS offers fast temporal resolution simultaneously with high spectral resolution to study the emission spectra of single emitters. Moreover, because it relies on interferometry as opposed to diffraction gratings, its signal throughput is much higher than
conventional CCD-based single-molecule spectroscopy. In addition to these benefits of PCFS, S-PCFS overcomes several additional shortcomings of traditional single-molecule spectroscopy. Assuming a single unique emitter within the focal volume at a time, a measurement of 123 intensity correlation functions with 30 s integration times for particles with an average dwell time of 300 $\mu$s has a throughput of $\sim 10^7$ particles with no user selection bias. This ensures ensemble-level sample statistics, even when measuring single-molecule spectral correlations. Furthermore, because of short exposure times, low-intensity CW excitation, and a correction for fluctuations in the total signal, emission intermittency and bleaching are no longer experimental concerns. Finally, integration time and temporal resolution are decoupled in PCFS, which means that arbitrarily high signal-to-noise ratios can be obtained simply by increasing the integration time for each correlation function.

As with any methodology, there are tradeoffs for extracting particular pieces of information. The one most fundamental to PCFS is the sacrifice of the absolute spectrum for spectral correlations at high temporal resolution. With S-PCFS, there are additional tradeoffs. Single-molecule spectroscopy has illuminated the underlying heterogeneity in a number of systems by analyzing the probability distribution of an observable at the cost of repeated measurements of different individual molecules under identical experimental conditions. Solution PCFS sacrifices this population information in order to obtain high-resolution spectral information averaged over many different individual emitters.

We note that powerful nonlinear spectroscopic techniques such as photon echo, transient absorption, and spectral hole burning can be performed on solution samples with extremely high temporal resolution. While lacking in temporal resolution, S-PCFS does not rely on the sample having appreciable nonlinear cross-sections and, because it measures PL, it can achieve high signal-to-noise ratios in a very short amount of time.
6.3 S-PCFS on a Broad Mixture of Quantum Dots

In this section, we demonstrate the experimental execution of S-PCFS to measure the spectra of single emitters obscured by an ensemble in solution. With S-PCFS, we obtain a diffusion-weighted spectral correlation, \( p_{\text{ens}}(\zeta) + [g^{(2)}(\tau) - 1] p_{\text{single}}(\zeta, \tau) \), where \( g^{(2)}(\tau) \) is the intensity correlation measured in conventional FCS experiments and \( p_{\text{ens}}(\zeta) \) is the spectral correlation of the ensemble spectrum. The quantity \( p_{\text{single}}(\zeta, \tau) \) coincides with the single-emitter spectral correlation averaged over all observed emitters. Spectral correlations are independent of absolute energy, so heterogeneity in average emission frequency does not obscure spectral information encoded in \( p_{\text{single}}(\zeta, \tau) \).

For our demonstration, we constructed the exceptionally polydisperse ensemble shown in Fig. 6-2(inset) by mixing eight different sizes of CdSe QDs together in a solution of decane with cadmium-oleate and decylamine. Each of the single QDs in this ensemble was expected to have spectral linewidths much narrower than the ensemble’s, with vastly different center frequencies. The significant difference in linewidth for the single particle and ensemble spectra will allow for a clear distinction between \( p_{\text{single}}(\zeta, \tau) \) and \( p_{\text{ens}}(\zeta) \).

We begin by examining the emission of our artificially broadened ensemble at the outputs of the interferometer. When the path difference \( \delta \) between the arms of the interferometer is significantly longer than the coherence length of the spectrum, the intensity cross-correlation is determined by the diffusion of the QDs, as seen in FCS. The total-intensity correlation for our sample, \( g^{(2)}(\tau) \), is shown in Fig. 6-2(black).

As the optical path-length difference \( \delta \) between the arms of the interferometer approaches the coherence length of the spectrum, interference influences the intensities at the two outputs of the interferometer to an extent determined by the Fourier transform of the spectrum. These intensities can be expressed as a sum over the intensities of all the individual N particles in solution, each with their own respective spectrum and interference pattern. The intensity-cross correlation can then be...
Figure 6-2: In this proof of principle experiment, S-PCFS was performed on a mixture of nanocrystals spanning the visible spectrum. The cross-correlation function (dark blue) was measured at different interferometer path-length differences $\delta$. Correcting for the autocorrelation of the total signal (black), the Fourier transform at a given $\tau$ gives the spectral correlation function. This result shows that the ensemble spectral correlation can be measured at long $\tau$ while the single-nanocrystal spectral correlation can be measured at short $\tau$ (Adapted with permission from Ref. 148. Copyright 2010 by the American Physical Society).

written as follows:

$$g^x(\delta, \tau) = \frac{I_a(t)I_b(t + \tau)}{I_a(t)} = \frac{\sum_{i=1}^N \sum_{j=1}^N I_a^{(i)}(t)I_b^{(j)}(t + \tau)}{\sum_{i=1}^N I_a(t)I_b(t + \tau)}.$$  \hspace{1cm} (6.27)

While measuring the cross-correlation function, we dither one arm of the interferometer slightly to average the cross correlation over a small distance. Effectively, dithering removes sensitivity to absolute energies while retaining information on relative energy separations. We can separate this cross correlation into parts dependent on pairs of photons emitted from the same QD ($i = j$) and pairs of photons emitted from different QDs ($i \neq j$). Only photons from the same QD have an intensity correlation that also depends on $g^{(2)}(\tau)$ because the motion of different QDs is uncorrelated. This allows us to separate single-QD spectral correlations from the ensemble.
Because the number of QDs in our solution is very large ($N \gg 1$) and the dithering rate is slow such that the timescales of interest are not affected by the change in the path-length difference, we can simplify and obtain the following governing equation:

$$g^x(\delta, \tau) = g^{(2)}(\tau) - \frac{1}{2} \text{Re} \left\{ \text{FT} \left[ p^{\text{ens}}(\zeta, \tau) + (g^{(2)}(\tau) - 1) p^{\text{single}}(\zeta, \tau) \right]_{\delta \rightarrow \zeta} \right\} \quad (6.28)$$

where $p^{\text{single}}(\zeta, \tau)$ is the previously defined average single-particle spectral correlation and $p^{\text{ens}}(\zeta) = \langle S(\omega)S(\omega + \zeta) \rangle$ is the same for the ensemble with $S(\omega) = \langle \sum s_i(\omega, t) \rangle$.

The cross correlation now depends on the Fourier transform (in path length $\delta$) of the diffusion-weighted spectral correlation, $p^{\text{ens}}(\zeta) + [g^{(2)}(\tau) - 1] p^{\text{single}}(\zeta, \tau)$. The diffusion-weighted spectral correlation measured for our artificially broadened sample is shown in Figure 6-2 for different temporal separations $\tau$. At short $\tau$, the enhanced probability of detecting photons from the same particle leads to a large single particle component in the spectral correlation. As the amplitude of $g^{(2)}(\tau)$ decreases, the narrow $p^{\text{single}}(\zeta, \tau)$ peak also decreases in magnitude while the broader $p^{\text{ens}}(\zeta)$ remains constant. At the longest $\tau$, $g^{(2)}(\tau)$ has fully decayed and only $p^{\text{ens}}(\zeta)$ remains.

The $\tau$-independent ensemble component can be removed from the diffusion-weighted spectral correlation leaving the time-dependent spectral correlation of the average single particle. Assuming that the underlying single-emitter spectrum is Gaussian, we can extract an average single-QD spectral FWHM of 74 meV from this polydisperse ensemble. We are not aware of other experiments capable of extracting this linewidth at similar timescales and excitation conditions. We compare our results to single-QD measurements taken at longer timescales\textsuperscript{128} and nonlinear measurements taken at higher powers.\textsuperscript{169} It may be the case that the assumption of a Gaussian line shape leads to a slightly larger value for the FWHM of the average single QD than these previous measurements.

In this first experiment, the count rate was $\sim 15$ kHz on each detector. From fitting $g^{(2)}(\tau)$, we obtain the diffusion time for a QD moving through the focal volume to be $\sim 0.18$ ms and the average number of QDs in the focal volume to be 1.5; thus we are obtaining single particle spectral information with bursts averaging less than
four photons from each QD traversing the focal volume. Assuming a 5% collection efficiency and an 80% quantum yield, the QD is excited, on average, every 2 $\mu s$. This timescale is significantly longer than the temporal resolution of our technique, indicating that we may have the ability to measure an intrinsic linewidth free of photoinduced dynamics from multiple excitation events. The characterization of spectral dynamics and the intrinsic single-QD spectrum is the topic of the following chapter.
Chapter 7

Spectral Dynamics in Nanocrystals at Room Temperature

In the previous chapter, we showed how S-PCFS can isolate the average single-emitter spectral correlation function from an ensemble in solution. Referring back to Figure 1-3, we have been able to remove the inhomogeneous broadening within the ensemble spectrum due solely to different peak emission energies of different nanocrystals. However, another contributing factor to the ensemble spectrum is spectral dynamics. As discussed in Chapters 3 and 4, spectral dynamics have been observed in single nanocrystals at low temperature across a broad range of timescales. At room temperature, spectral dynamics have also been observed in single nanocrystals, but on the timescale of seconds. However, these studies used conventional CCD-based fluorescence spectroscopy and were unable to definitively determine whether rapid spectral dynamics on faster timescales contribute to the measured single-NC spectra.

In this chapter, we discuss the use of S-PCFS to address this question. We first describe the theory of how to interpret the temporal dependence of the spectral information obtained by S-PCFS. We then show some experimental results and discuss their implications. The theoretical considerations were obtained with input from Andrew Beyler. The experiments were performed in collaboration with Lisa Marshall on a quantum dot sample synthesized by Cliff Wong and Zoran Popović. These results were published in Ref. 148.
7.1 Analyzing Spectral Dynamics using PCFS

Recall the governing equation of single-emitter PCFS:

\[ g^* (\delta, \tau) = g^{(2)} (\tau) \left( 1 - \frac{1}{2} |\text{FT} [\Phi(\omega)]|^2 \text{Re} \{\text{FT} [p(\epsilon, \tau)]_{\epsilon \rightarrow \delta} \} \right) \]  

(7.1)

To consider the temporal dependence of the spectrum, it is useful to look at one of the expression derived prior to the governing equation:

\[ g^* (\delta, \tau) = g^{(2)} (\tau) \left( 1 - \frac{1}{2} |\text{FT} [\Phi(\omega)]|^2 \langle \cos \{2\pi \delta [\Delta \omega(t) - \Delta \omega(t + \tau)] \} \rangle \right) \]  

(7.2)

Recall that the time average of the cosine term eventually gives the governing equation of PCFS. We focus on the PCFS interferogram, which we can isolate for the average single-emitter in S-PCFS. We recast the PCFS interferogram as:

\[ \tilde{g}(\delta, \tau) = |\text{FT} [\Phi(\omega)]|^2 \text{Re} \{\text{FT} [p(\epsilon, \tau)]_{\epsilon \rightarrow \delta} \} \]  

(7.3)

\[ = |\text{FT} [\Phi(\omega)]|^2 \langle \cos \{2\pi \delta [\Delta \omega(t) - \Delta \omega(t + \tau)] \} \rangle \]  

(7.4)

7.1.1 Small-\(\tau\) Limit

We see that in the limit \(\tau \rightarrow 0\), the time-average reduces to 1. Then, by the cross-correlation theorem, we have:

\[ \tilde{g}(\delta, 0) = |\text{FT} [\Phi(\omega)]|^2 \langle \cos \{2\pi \delta [\Delta \omega(t) - \Delta \omega(t + \tau)] \} \rangle \]  

(7.5)

\[ = |\text{FT} [\Phi(\omega)]|^2 \]  

(7.6)

\[ = \text{FT} [\Phi(\omega)]^* \text{FT} [\Phi(\omega)] \]  

(7.7)

\[ = \text{FT} [\Phi(\omega) \star \Phi(\omega)] \]  

(7.8)

where \(\star\) indicates the cross-correlation operation. Furthermore, by taking the inverse Fourier transform of both sides, we obtain:

\[ \text{FT}^{-1} [\tilde{g}(\delta, 0)] = p(\zeta, 0) = \Phi(\omega) \star \Phi(\omega) \]  

(7.9)
This result indicates that at sufficiently short $\tau$, the spectral correlation function $p(\zeta, \tau)$ reduces to the autocorrelation of the intrinsic spectral envelope because sufficient time has not elapsed for spectral jumps to occur.

### 7.1.2 Absence of Spectral Dynamics

A second important scenario is when there are no spectral dynamics between $t$ and $t + \tau$. That is,

$$\Delta \omega(t + \tau) = \Delta \omega(t)$$

(7.10)

The expression again reduces to the same result:

$$\tilde{g}(\delta, 0) = |\text{FT}[\Phi(\omega)]|^2 \langle \cos \{2\pi \delta [\Delta \omega(t) - \Delta \omega(t + 0)]\} \rangle$$

(7.11)

$$= \text{FT}[\Phi(\omega) \ast \Phi(\omega)]$$

(7.12)

### 7.1.3 Dynamic Spectra

In cases where the spectrum is dynamic, we can use the formalism expressed thus far to characterize the extent of spectral diffusion over time. We know that:

$$\tilde{g}(\delta, \tau) = |\text{FT}[\Phi(\omega)]|^2 \text{Re}\{\text{FT}[p(\epsilon, \tau)]_{\epsilon \rightarrow \delta}\}$$

(7.13)

Above, we showed that we can access the autocorrelation of the spectral envelope at small $\tau$:

$$\tilde{g}(\delta, 0) = \text{FT}[\Phi(\omega) \ast \Phi(\omega)] = |\text{FT}[\Phi(\omega)]|^2$$

(7.14)

Therefore, we can isolate the term describing the spectral dynamics by taking by the small-$\tau$ limit of the PCFS interferogram.

$$\frac{\tilde{g}(\delta, \tau)}{\tilde{g}(\delta, 0)} = \langle \cos \{2\pi \delta [\Delta \omega(t) - \Delta \omega(t + \tau)]\} \rangle = \text{Re}\{\text{FT}[p(\epsilon, \tau)]_{\epsilon \rightarrow \delta}\}$$

(7.15)

This equation is a tad misleading because we don’t necessarily need to go to the point where $\tau = 0$, but rather, we need to be at some $\tau$ when the spectrum is no longer
Figure 7-1: a) At each optical path-length difference, a cross-correlation was measured while slowly dithering one mirror. The sinusoidal intensity correlation from dithering appears only at long ($\tau > 70$ ms). b) The autocorrelation of the sum of the two APD intensities is fit at small $\tau$ to avoid the effects of afterpulsing and dead times and used as $g^{(2)}(\tau)$. c–g) The extracted single-NC PCFS interferograms were fit to Gaussians to calculate effective spectral linewidths. Figure adapted from Ref. 148.

7.2 Absence of Spectral Dynamics in CdSe/CdZnS Particles

In order to investigate room-temperature spectral dynamics in nanocrystals, we applied S-PCFS to a batch of 620-nm emitting CdSe/CdZnS QDs illuminated with 16 $\mu W$ at 514 nm and spatially filtered through a 50 $\mu m$ pinhole. We acquired the cross-correlation function at a range of interferometer positions separated by $1 \mu m$ and dithered over $\sim 1 \mu m$ distance (Fig. 7-1a). Each cross correlation was averaged
for 40 s.

We simultaneously collected the autocorrelation of the sum of the two APD intensities, \( g^{A+B}(\tau) \), which was fit to avoid artifacts from short-timescale afterpulsing and dead times and then used as \( g^{(2)}(\tau) \) in the governing equation. The fitted values replaced the actual data only at short timescales (\( \tau \leq 6 \mu s \)). For accurate fitting, we first measured \( g^{(2)}(\tau) \) as the cross-correlation when the path length difference \( \delta \) was large. We fit this to \( A \left[ (1 - B \cdot \tau^{2-m}) / (1 + \tau/\tau_D) - k e^{-\tau/n} \right] \), which takes into account diffusion, blinking, and antibunching\(^{62,95,163} \) and adjusted only its amplitude for each individual, afterpulse-corrected, \( g^{A+B}(\tau) \). The afterpulse correction was determined from a count-rate-corrected removal of \( g^{A+B}(\tau) - g^x(\tau) \) as measured in a region where the path-length difference is much larger than the coherence length.\(^{171} \) The final intensity correlations used for \( g^{(2)}(\tau) \) are shown in Figure 7-1b.

For each \( \tau \) value between 34 ns and 10 ms, we corrected for \( g^{(2)}(\tau) \) and \( p^{ens}(\zeta) \) to extract the average single-QD linewidth assuming a Gaussian line shape. Representative plots of the single-NC PCFS interferograms with Gaussian fits are shown in Figures 7-1c–7-1g. In Figure 7-2, we plot the full-width at half-maximum of the effective spectral linewidth obtained from the Gaussian fit as a function of \( \tau \). We can see that the linewidth is nearly constant over the temporal regime examined.
Spectral dynamics in QDs are thought to be caused by interactions with phonons on fast time scales and charging or discharging of surface states on slower time scales. While interactions with phonons are much too fast to be probed with this experiment, the slower, charging-based dynamics have previously been observed in single QDs at time scales from seconds to minutes. At cryogenic temperatures, the single QD linewidth becomes narrower with spectral jumps approaching that of the broad room temperature linewidth. It was previously unknown whether these dynamics become faster at room temperature and became a significant contributor to the room-temperature spectral linewidth.

Our result demonstrates that the conventionally-measured room-temperature spectrum is not broadened by spectral dynamics at time scales between 34 ns and 10 ms and suggests that charging or discharging events, if they occur at all, must be on shorter or longer time scales. This is a surprising result given the broad range of timescales in the spectral dynamics of single nanocrystals at low temperature. It is unlikely that photoinduced spectral dynamics are occurring on faster timescales because the average excitation rate is still much longer than the lifetime. Therefore, the spectrum that we are accessing on these sub-millisecond timescales represents the sample-averaged intrinsic single-nanocrystal spectral correlation.

### 7.3 Comparing S-PCFS to Conventional Fluorescence Spectroscopy

With the absence of rapid spectral diffusion, the single-nanocrystal spectrum obtained through conventional CCD-based spectroscopy likely represents the intrinsic spectrum. In this case, S-PCFS serves to simply average over the peak frequencies of the single nanocrystals in solution. A good control experiment would be to determine whether the spectral correlations obtained from S-PCFS are consistent with the spectral correlations of the ensemble spectrum and many single-QD spectra taken by conventional CCD-based spectroscopy.
In Figure 7-3a, we compare the $p_{\text{ENS}}(\zeta)$ from S-PCFS with a conventional ensemble spectrum measured through a spectrometer and then correlated with itself. We find good agreement between the two techniques, confirming that our method is truly accessing a large enough sample size of particles that is representative of the entire ensemble.

In addition, we used confocal microscopy to measure the spectrum for 25 individual QDs on a surface and calculated the average spectral correlation using a 1 s integration time and 440 W/cm$^2$ illumination from a 514 nm argon ion laser. This direct measurement, as compared to the spectral correlation obtained from S-PCFS at $\tau=5$ µs, is shown in Fig. 7-3b. The two spectral correlations are nearly identical, implying that the single-QD spectrum is indeed the intrinsic spectrum. In addition, we have learned that the single-QD spectrum is not significantly influenced by the substrate.

These control experiments definitively show that the average single-QD spectral correlation obtained from S-PCFS is both representative of the sample and reflect the intrinsic spectrum. Perhaps more significantly, our findings have implications for the utility of S-PCFS to study spectral linewidths. In the absence of spectral dynamics, the spectral correlation function $p(\zeta, \tau)$ reduces to the energy autocorrelation of the spectrum. Thus, the breadth of the spectral correlation function reflects the breadth
of the underlying spectrum. An in-depth study of these intrinsic spectral linewidths is the topic of the following chapter.
Chapter 8

Single-Nanocrystal Spectral Linewidths

Photon-correlation Fourier spectroscopy performed on emitters diffusing in solution (S-PCFS) offers a unique approach for investigating the spectra of single nanocrystals with large sample statistics, without user selection bias, with high signal-to-noise ratios, and at timescales fast enough to avoid the spectral diffusion commonly observed in single-NC spectroscopy. In the previous chapter, we demonstrated that S-PCFS can be used to directly and quantitatively deconstruct the ensemble spectral linewidth into contributions from the average single-particle linewidth and from sample inhomogeneity.

In this chapter, we show how the single-particle spectral correlations can be analyzed and understood with respect to the overall ensemble spectrum. We find that single-particle linewidths vary significantly from batch to batch and can be synthetically controlled. These findings crystallize our understanding of the synthetic challenges facing underdeveloped nanomaterials such as InP and InAs core/shell particles and introduce new avenues for the synthetic optimization of fluorescent nanoparticles.

This work was performed with input from Andrew Beyler, Lisa Marshall, and Xavier Brokmann. Nanoparticle synthesis and TEM characterization was performed by Ou Chen, Daniel Harris and Darcy Wanger. These results were published in Ref. 167.
Figure 8-1: a) The single-nanocrystal PCFS interferogram $\tilde{g}^{\text{single}}(\delta, \tau \approx 5 \mu s)$ along with fit and fitting residual. Note the high signal-to-noise ratio at a timescale more than 3 orders of magnitude faster than conventional methods can access. b) The Fourier transform of $\tilde{g}^{\text{single}}(\delta, \tau \approx 5 \mu s)$ gives the spectral correlation $p^{\text{single}}(\zeta, \tau \approx 5 \mu s)$. The good fit is conserved through the transform. c) The effective spectral lineshape (ESL) is calculated from the initial fit to $\tilde{g}^{\text{single}}(\delta, \tau \approx 5 \mu s)$ and its full-width at half-maximum is the effective “single-nanocrystal linewidth”. Figure reprinted from Ref. 167.

8.1 Fitting

Though S-PCFS directly measures spectral correlation functions, additional analysis is necessary to gain insight into the underlying spectrum. As discussed in the previous chapter, CdSe/CdZnS core/shell nanoparticles exhibited no appreciable spectral diffusion at submillisecond timescales approaching the lifetime of the emitters under low excitation flux and ambient conditions.\textsuperscript{148} In the absence of spectral dynamics, the single-particle spectral correlation function $p^{\text{single}}(\zeta, \tau)$ simply reduces to the energy autocorrelation of the spectrum. Thus, the breadth of the spectral correlation function reflects the breadth of the underlying spectrum. For both the single-particle and ensemble components, a broader spectral correlation $p(\zeta)$ means a broader spectrum $s(\omega)$.

In order to obtain a quantitative spectral linewidth, we adopt a model to fit the data because, without assumptions, the spectrum cannot mathematically be uniquely
recovered from its autocorrelation. Knowing that the single-NC spectrum at room temperature is a singly peaked, nearly symmetric function, we model the spectral lineshape using a superposition of Gaussian functions and obtain a functional form to fit $\tilde{g}^{\text{single}}(\delta, \tau)$. An effective spectral lineshape (ESL) can be calculated from the fit and its full-width at half-maximum gives the effective “single-nanocrystal linewidth”. The ensemble component is fit similarly.

For both the single-emitter and ensemble components, we have assumed here that the true spectral lineshape $s(\omega)$ is well-approximated by an effective spectral lineshape composed of the summation of an arbitrarily large number of Gaussian functions. In practice, we find that for all samples measured here, both $\tilde{g}^{\text{single}}(\delta)$ and $\tilde{g}^{\text{ens}}(\delta)$ are well-fit by a spectrum composed of the sum of two Gaussian functions with amplitudes $A$, $B$ and widths $c$, $d$, but centered at the same frequency $\omega_0$ as follows. The inclusion of additional Gaussian functions into the model does not improve the fit.

$$s(\omega) = Ae^{-\frac{(\omega-\omega_0)^2}{2c^2}} + Be^{-\frac{(\omega-\omega_0)^2}{2d^2}}$$  (8.1)

This model gives a spectral correlation $p(\zeta)$ that is a sum of three Gaussians: one term from the first Gaussian, the second term from the second Gaussian and a cross-term. Fourier transform to $\tilde{g}(\delta)$ gives another sum of three Gaussians resulting in the fitting equation below. The absence of the center frequency $\omega_0$ in the fitting equation indicates that absolute frequencies are indeed lost, but information regarding spectral breadth is conserved.

$$\tilde{g}^{\text{single/ens}}(\delta) = 2\pi \left( A^2c^2e^{-4\pi^2c^2\delta^2} + B^2d^2e^{-4\pi^2d^2\delta^2} + 2ABcde^{-2\pi^2(c^2+d^2)\delta^2} \right)$$  (8.2)

Figure 8-1 provides an example of our data analysis. The measured $\tilde{g}^{\text{single}}(\delta, \tau \simeq 5 \mu s)$ is plotted in blue in Figure 8-1a for a batch of CdSe/CdS core/shell particles. We highlight the high signal-to-noise ratio at $\tau \simeq 5 \mu s$, which is at least 3 orders of magnitude faster in temporal resolution than conventional single-molecule spectroscopy can achieve. Plotted in red is the fit to our model. Figure 8-1b shows that the fit is well-conserved to the spectral correlation $p^{\text{single}}(\zeta, \tau \simeq 5 \mu s)$. The effec-
Figure 8-2: a) Spectral correlations for the ensemble spectrum of CdSe/CdS core/shell particles with 4.0 monolayers of CdS taken by both S-PCFS and the fluorometer agree well with each other. b) Though the effective spectral lineshape for the ensemble calculated from fitting to the PCFS interferogram cannot capture the slight asymmetry of the spectrum, the linewidths are nearly identical. Figure reprinted from Ref. 167.

tive spectral lineshape calculated from this fit is shown in Figure 8-1c. The ratio of the areas of the two Gaussians is approximately 2:1, indicating that both Gaussians contribute significantly to the fitting.

To illustrate the accuracy of S-PCFS and our fitting, we compare the ensemble component obtained through S-PCFS to the ensemble spectrum obtained through a conventional fluorometer for the same batch of particles. As also shown in the previous chapter (Fig. 7-3), $p_{\text{ens}}^s(\zeta)$ obtained from S-PCFS is remarkably consistent with the energy autocorrelation of the spectrum obtained through conventional spectroscopy (Figure 8-2a). In Figure 8-2b, we plot the effective spectral lineshape (ESL) calculated from our fit to the S-PCFS data to the actual spectrum from the spectrometer. Because our model is based on overlapping Gaussians, it cannot account for the slight asymmetry in the spectrum. However, the linewidths are nearly identical, giving credence to our method.
8.2 S-PCFS as a Direct Probe of Spectral Inhomogeneity

Having demonstrated how S-PCFS can be used to measure the spectral linewidth of the average single NC, we apply our method to explore the dependence of this linewidth on several nanocrystal parameters in core/shell particles.

First, we investigate the effect of the core composition on the single-NC linewidth. Given that different material compositions are associated with different effective masses, dielectric constants, deformation-potential coupling, and other properties that affect the materials’ response to optical excitations, changing the core composition was expected to have a significant effect on spectral linewidths. In this experiment, we compare CdSe, InP, and InAs core/shell particles. InP was chosen because it is a Cd-free alternative to CdSe and InAs was chosen for its emission tunability into the near-infrared. These materials are of great interest for applications in displays, solid-state lighting, and biological imaging.

In Figure 8-3, we overlay the single-NC and ensemble spectral correlation functions for CdSe, InP, and InAs core/shell particles. The ensemble spectral correlations
confirm what is often observed in InP and InAs nanocrystals – their ensemble spectra are much broader than those of CdSe particles. Surprisingly, however, the single-NC linewidths are nearly the same. This result emphasizes that single-nanocrystal linewidths cannot be known a priori simply from the ensemble spectrum. Moreover, it shows that differences in the properties of the core material composition do not necessarily have a dramatic effect on single-NC linewidths.

It has been speculated that the broad ensemble spectral linewidths of InP and InAs core/shell particles are due to broad single-nanocrystal linewidths. As a direct probe of spectral inhomogeneity, S-PCFS reveals that the ensemble spectral linewidths of InP and InAs core/shell particles are limited not by the intrinsic properties of these materials, but rather by the inhomogeneities among the particles in the sample batch (Fig. 8-3 and Table 8.1). Thus, there appears to be no intrinsic barrier preventing the synthesis of InP and InAs core/shell particles with ensemble spectral linewidths as narrow as CdSe.

We provide another example of how S-PCFS can be used to characterize the spectral polydispersity of samples. A new generation of CdSe/CdS core/shell nanocrystals with superior optical properties that were developed in our group was found to possess very narrow ensemble spectral linewidths. The origin of these narrow linewidths was
likely either: a) the average photoluminescence peak width of single-QDs synthesized here is narrower than that of single-QDs synthesized by other methods, resulting in a narrower ensemble photoluminescence peak or b) the narrow ensemble emission peak comes from the high sample uniformity, minimizing inhomogeneous broadening from size/morphology distributions.

The average single-QDs and ensemble spectral correlations for the new-generation QDs are shown in Figure 8-4a. After fitting, the ensemble emission FWHM is 69 meV, which is nearly identical to that obtained using a spectrometer. The average single-QD emission FWHM is 63 meV. The small difference (6 meV, ~10%) between the single-QDs and the ensemble emission line widths indicates extremely high uniformity of the sample, including uniform shape, narrow size distribution, high shell crystallinity, sufficient surface passivation, and so on.

These results confirm the hypothesis of the first scenario – that this narrow ensemble photoluminescence peak is due to the high uniformity of our QDs rather than unusually narrow single-QD photoluminescence peaks. For comparison, the spectral correlations for CdSe/CdS QDs synthesized using a conventional method were also measured using S-PCFS (Fig. 8-4b). Fitting results show that the average single-QD emission FWHM is 65 meV. However, the ensemble emission linewidth is 111 meV (~34 nm), ~60% broader than our QDs, indicating a relatively polydisperse sample.

8.3 Single-NC Linewidth Variations and Synthetic Control

In contrast to the results obtained from different core materials compositions, we discover large batch-to-batch variations in the average single-NC linewidths of three sample batches of commercial CdSe core/shell particles (Qdots®) (Figure 8-5a). Although variation in the room-temperature spectral linewidth of single nanocrystals has been previously observed, this is the first report of variation in the average spectral linewidth of single nanocrystals between synthetic batches. More importantly,
Figure 8-5: a) Single-particle spectral correlation functions $p^{\text{single}}(\zeta, \tau \simeq 5 \mu s)$ for the commercial CdSe particles (Qdots®). There is great variation in the linewidths with no obvious trend according to size or shell morphology. b) Single-particle spectral correlation functions $p^{\text{single}}(\zeta, \tau \simeq 5 \mu s)$ for the CdSe/CdS core/shell particles during shell growth. The linewidth increases monotonically with shell growth. Figure adapted from Ref. 167.

these large single-NC linewidth variations exist despite their same core material composition (CdSe).\textsuperscript{176}

The results from Figure 8-3 and 8-5a reveal that the core material composition does not solely dictate the single-NC linewidth, but instead, that other aspects of the core/shell architecture can have a predominant effect. We can begin to understand the structural origins of these linewidth variations through controlled synthesis in conjunction with S-PCFS.

In our final experiment, we demonstrate that the single-NC linewidth can be altered considerably by the adjustment of a synthetically-controllable structural parameter. In Figure 8-5b, we observe that the single-NC linewidth increases substantially for CdSe/CdS particles undergoing shell growth. In fact, Table 8.1 shows that the single-NC linewidth increases monotonically from 64 meV (1.8 monolayers) to an astonishing 92 meV (10 monolayers). This result does not necessarily imply that all single-NC linewidth variations, such as those observed in the second experiment, are caused by differences in shell thickness. Rather, it provides one instance in which the single-NC linewidth can be strongly influenced by structural features of nanocrystals and brings to light the feasibility of synthetic control over the single-NC linewidth.
8.4 Implications of Single-NC Linewidth Variations

Our findings have far-reaching implications for our understanding of the spectra of both single nanocrystals and nanocrystal ensembles. First, and most importantly, we have shown that the room-temperature single-NC linewidth varies considerably from batch to batch in a synthetically controllable fashion (Figure 8-5). In fact, the broadest single-NC linewidth measured for the CdSe/CdS particles is even broader than the ensemble linewidth for several of the other CdSe particles (Table 8.1). Furthermore, single-NC linewidth synthetic tunability should be possible for nanoparticles with cores other than CdSe because the single-NC linewidth is not dictated solely by the core composition; other aspects of the core/shell architecture can greatly alter the single-NC linewidth.

The direct consequence of these results is that the effect of the single-NC linewidth on the ensemble spectral linewidth cannot be ignored. Throughout the literature,

Figure 8-6: Transmission electron micrographs of: a) Qdot® 545, b) Qdot ® 605, c) Qdot ® 655, d) InP core/shell particle, e) CdSe with 4.0 monolayers CdS shell, f) CdSe with 10.0 monolayers CdS shell. Reprinted from Ref. 167.
changes in the ensemble spectral linewidth have often been attributed to changes in
the size distribution of the particles.\textsuperscript{11} However, Figure 8-5b demonstrates that this
conclusion is unwarranted. In the case of our CdSe particles undergoing CdS shell
growth, the increase in the ensemble linewidth is largely due to broadening of the
single-NC linewidth (Table 8.1).

These insights could not have been conclusively drawn using traditional character-
ization tools. A comparison of Table 8.1 and Figure 8-6 shows that both single-NC
and ensemble spectral linewidths have little correlation with shell morphology in
core/shell particles. Because transmission electron microscopy (TEM) cannot easily
resolve the core from the shell, and because it relies on single-particle examination,
it cannot provide an ideal measure of the degree of inhomogeneity within a synthetic
batch. S-PCFS, on the other hand, provides a quantitative comparison of the single-
NC and ensemble linewidths and is thus a direct probe of the degree of spectral
inhomogeneity within a sample. This technique has allowed us to conclude that the
single-NC linewidth and the sample polydispersity are independent and synthetically
controllable parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Single-NC linewidth (meV)</th>
<th>Ensemble linewidth (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qdot® 545</td>
<td>70</td>
<td>138</td>
</tr>
<tr>
<td>Qdot® 605</td>
<td>42</td>
<td>75</td>
</tr>
<tr>
<td>Qdot® 655</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>InP core/shell</td>
<td>73</td>
<td>178</td>
</tr>
<tr>
<td>InAs/ZnS</td>
<td>76</td>
<td>151</td>
</tr>
<tr>
<td>CdSe/CdS 1.8 ML$\dagger$</td>
<td>64</td>
<td>87</td>
</tr>
<tr>
<td>CdSe/CdS 4.0 ML$\ast$</td>
<td>69</td>
<td>84</td>
</tr>
<tr>
<td>CdSe/CdS 6.5 ML</td>
<td>82</td>
<td>102</td>
</tr>
<tr>
<td>CdSe/CdS 10.0 ML</td>
<td>92</td>
<td>124</td>
</tr>
</tbody>
</table>

$\dagger$This sample is included in Figure 8-1
$\ast$This sample is included in Figure 8-3

Table 8.1: Single-Nanocrystal and Ensemble Effective Spectral Linewidths.

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8.5 Conclusions

In this chapter, we have demonstrated that S-PCFS enables the simultaneous characterization of ensemble and single-emitter spectral properties with unprecedented clarity. With this new class of single-molecule spectroscopy, we have discovered batch-to-batch variability and synthetic tunability in room-temperature single-nanocrystal emission linewidths. Our work highlights the fundamental importance of the single-NC spectral linewidth when characterizing and optimizing nanocrystals for applications. With the use of S-PCFS as a high-throughput characterization tool, synthetic chemists can rapidly and quantitatively assess synthetic methodologies for the rational design of future nanostructures.
Chapter 9

Exciton-Phonon Coupling in Nanocrystals

The average single-NC spectral linewidth variations that we report in Chapter 8 challenge our current understanding of the physical origin of single-nanocrystals emission spectra. As indicated back in Figure 1-3, the breadth of the single emitter spectrum originates from broadening of the lifetime-limited natural emission spectrum by intrinsic and extrinsic interactions with the environment. In the context of nanocrystals, the single-NC linewidth is believed to arise from a combination of photoinduced spectral diffusion (extrinsic) and exciton-phonon interactions (intrinsic). However, in Chapter 7, we found that spectral diffusion is negligible in core/shell particles at these sub-millisecond timescales. Thus, our results directly reflect the intrinsic single-NC spectral broadening mechanisms such as excitonic coupling to phonons within the nanoparticle, to vibrations in the ligands on the surface, and to the bath solvent itself.

A thorough understanding of exciton-phonon coupling is necessary not only for the rational design of nanocrystals for luminescent applications, but also for the future development of nanocrystal-based photovoltaic devices. However, exciton-phonon coupling in quantum dots has been a topic of controversy. S-PCFS offers a unique approach for investigating the spectra of single nanocrystals with large sample statistics, without user selection bias, with high signal-to-noise, and at timescales fast
enough to avoid spectral diffusion. Moreover, S-PCFS probes particles in their native environment with low-intensity CW excitation and short exposure times, thereby minimizing perturbations to the sample.

In this chapter, we discuss our efforts to understand single-nanocrystal spectral linewidths and lineshapes extracted from S-PCFS in the context of exciton-phonon coupling. All nanoparticle samples were synthesized with guidance from José Cordero-Hernandez. The spectral lineshape modeling was largely adapted from the literature by Liam Cleary.

9.1 Spectral Linewidth Broadening with CdS Shell Growth

In Chapter 8, we observed that the average single-NC spectral linewidth broadened considerably as a CdS shell was grown on CdSe cores. In an effort to determine the role of the shell on single-NC spectral linewidths, we conducted an experiment where we compared three different types of shells: ZnS, CdS, and a CdZnS alloy. A single batch of CdSe cores were synthesized and split for three different overcoatings: ZnS, CdS, and CdZnS (50% Cd, 50% Zn). All overcoatings were performed at the same temperature for the same amount of time and with similar organometallic precursors at the same concentration. We drew aliquots during shell growth and performed S-PCFS on the aliquots.

Our results show that the single-NC linewidth depends on the composition as well as the thickness of the shell (Fig. 9-1). In the case of ZnS shell growth, we observed little-to-no broadening of the single-NC linewidth. However, the CdS and CdZnS shell growths led to significant broadening, in accordance with what we observed for CdSe/CdS in Chapter 8. We note that this agreement exists despite using a different CdS overcoating protocols from the one used in the previous chapter.

These results cannot be explained by the idea that induced strain from a greater lattice mismatch leads to broader single-NC linewidths. ZnS has a 12% lattice mis-
Figure 9-1: Single-NC linewidths were measured for a single batch of CdSe cores that were synthesized and split for three different overcoatings: ZnS, CdS and CdZnS (50% Cd, 50% Zn). Aliquots were drawn for shell growth up to ∼10 monolayers.

match with CdSe while CdS has a 4% lattice mismatch with CdSe. If the strain from lattice mismatch were the dominant factor behind spectral broadening, we would expect greater broadening from the ZnS sample, but that is not the case.

This effect is consistent with an increased “Fröhlich-like” exciton-phonon interaction due the incerased spatial separation between the electron and hole wavefunctions in these quasi-type-II heterostructures. CdSe/ZnS core/shell particles are believed to be type-I heterostructures. That is, the electron and hole are largely confined in the core. On the other hand, CdSe/CdS core/shell particles are believed to be quasi-type II heterostructures. Here, the electron leaks far more into the shell than the hole, which remains confined in the core. Because the volume of the shell is so much greater than the volume of the core, there would be very little overlap between the electron and the hole wavefunctions. This spatial separation creates an internal polarization within the crystal lattice that leads to an enhanced Fröhlich-like exciton-phonon interaction, which broadens the spectrum (Fig. 9-2).
9.1.1 Core-Size Dependence

One of the most attractive property of quantum dots for the study of physical properties is the dependence of their photophysical properties on the size of the particle. The size dependence of exciton-phonon coupling in nanocrystals has been a topic of considerable debate and controversy. As discussed in Reference 177, neither theorists nor experimentalists have been able to agree on the size dependence of exciton-phonon coupling. For instance, while most calculations predict $S < 0.1$ for both acoustic and optical phonons, there are conflicting reports on the size dependence of the coupling. Experimentally, there are many conflicts regarding both the strength of coupling and their size-dependence. Moreover, different coupling strengths have also been observed depending on the initial excitonic state.

S-PCFS offers a unique approach for investigating the intrinsic spectra of single nanocrystals with large sample statistics, without user selection bias, and with high signal-to-noise. Moreover, S-PCFS probes particles in their native environment with low-intensity CW excitation and short exposure times, thereby minimizing perturbations to the sample. As mentioned in Chapter 6, each emitter may only undergo a few excitation events during the course of the measurement. Therefore, the effective
spectral linewidth obtained from S-PCFS is an indicator of the overall exciton-phonon coupling in the system – a broader linewidth would indicate stronger overall exciton-phonon coupling.

In an effort to understand the size dependence, CdSe cores were synthesized using the protocol described in Ref. 15. During growth, small aliquots were drawn from the solution and quenched in hexanes. Figure 9-3 shows that the average single-NC effective spectral linewidth appears to have a fairly linear inverse relationship with core size. That is, with increasing size, the single-NC linewidth decreases. However, we note two additional observations.

First, the single-NC linewidth values are very broad. We note that in Figure 9-1, all of the single-NC linewidths decreased initially with shell growth. After several monolayers, the linewidth increased again. This may be due to the shell passivating trap states on the surface of the nanoparticle. As discussed in Ref. 133, the presence of an additional charge on the surface could greatly enhance excitonic coupling to optical phonons because of the additional distortion of the polar lattice. There is also the possibility that excitonic coupling to vibrations in the ligands on the surface of the particle as well as the solvent molecules themselves may lead to additional
spectral broadening. A definitive approach to measuring a proper size series would therefore be to synthesize a core size series and then overcoat each core sample with a ZnS shell such that surface traps are passivated and excitonic coupling is isolated to phonons in the core.

Second, we note that with the largest particle (smallest emission peak energy) in Figure 9-1, appears to have an increase in the single-NC spectral linewidth. While this may be attributed to noise, there is a hypothesis in the literature that is a cross-over region in the size-dependence of LO phonon coupling. The hypothesis rests on the idea that the exciton confinement energy decreases with increasing size. At some point in the size series, the exciton confinement energy becomes less than the Coulombic interaction energy and therefore, the electron-hole wavefunctions would be more spatially separated, leading to enhanced Frölich coupling. Our result may indicate the presence of a cross-over point, but further experimentation with core/shell particles, as described above, is necessary.

9.2 Spectral Lineshape Modeling

The effective spectral linewidth obtained from S-PCFS may be an indicator of the overall exciton-phonon coupling in the system, but it gives little quantitative insight into the strength of coupling or the frequency of the phonons. In this section, we describe a simple physical spectral lineshape model that we have applied to the analysis of the data obtained from S-PCFS in an effort to quantitatively characterize exciton-phonon coupling in quantum dots.

9.2.1 Modeling the Spectral Correlation

In this model, a two-level electronic transition undergoes linear coupling to a bath composed of harmonic oscillators that is modeled as a continuum. We begin with the definition of the spectrum:

\[
s(\omega) = \text{Re} \left\{ \frac{1}{\pi} \int_{0}^{\infty} e^{i\omega t} e^{i(\varepsilon - \lambda) t / \hbar - L^*(t)} \, dt \right\} \quad (9.1)
\]
where $E$ is the excited state energy, $L(t)$ is the lineshape function, defined as:

$$L(t) = \int_{0}^{t} dt' \int_{0}^{t'} C(t'') dt''$$  \hspace{1cm} (9.2)

Here, $C(t)$ is the bath correlation function, which is defined as:

$$C(t) = \int_{0}^{\infty} J(\omega) \left[ \coth(\hbar\beta\omega/2) \cos(\omega t) - i \sin(\omega t) \right]$$  \hspace{1cm} (9.3)

where $\beta = 1/k_B T$ is the inverse of the thermal energy. Now here, $J(\omega)$ is the spectral density of the bath defined as:

$$J(\omega) = \sum_{i} \lambda_{i} \omega_{i} \delta(\omega - \omega_{i}) = \sum_{i} S_{i} \omega_{i}^{2} \delta(\omega - \omega_{i})$$  \hspace{1cm} (9.4)

$J(\omega)$ describes both the frequencies of the phonons in the bath as well as the strength of excitonic coupling to them such that we have the following definitions for the total reorganization energy $\lambda$ and the Huang-Rhys factor $S$:

$$\lambda = \int_{0}^{\infty} \frac{J(\omega)}{\omega} d\omega$$  \hspace{1cm} (9.5)

$$S = \int_{0}^{\infty} \frac{J(\omega)}{\omega^2} d\omega$$  \hspace{1cm} (9.6)

which are indicators for the strength of coupling.

PCFS measures the time-dependent spectral correlation function, which can be defined as follows for any given $\tau$:

$$p(\zeta) = \int_{-\infty}^{\infty} s(\omega) s(\omega + \zeta) d\omega$$  \hspace{1cm} (9.7)

By inserting the definition of the spectrum into the spectral correlation, it can be shown that:

$$p(\zeta) = \frac{2}{\pi} \text{Re} \left\{ \int_{0}^{\infty} e^{i\zeta t - 2L(t)} dt \right\}$$  \hspace{1cm} (9.8)

As expected, $p(\zeta)$ is related only to the spectral lineshape. Therefore, the data
obtained from PCFS can be modeled through the correct selection of a spectral density \( J(\omega) \) for the bath. From this, we can calculate how strongly the exciton couples to different vibrations in the system.

9.2.2 Exciton-Phonon Coupling Mechanisms in Quantum Dots

In order to select a functional form for the spectral density \( J(\omega) \), we turn to the literature. Excitons in quantum dots are known to couple to acoustic phonons through the deformation potential and the piezoelectric potential. Deformation potential coupling arises from the indirect interaction between carriers and modulations of the atomic lattice due to phonons. This tends to dominate in non-polar materials such as silicon. From previous work, the acoustic deformation potential spectral density for a quantum dot can be modeled as:

\[
J_D(\omega) = \frac{4\lambda_D}{\Lambda_D^3} \omega^3 e^{-\left(\frac{\omega}{\Lambda_D}\right)^2}
\]  

(9.9)

where, in general, \( \lambda \) refers to the reorganization energy of the interaction and \( \Lambda \) refers to the inverse of the bath correlation time.

Piezoelectric coupling to acoustic phonons arises from the piezoelectric effect. Here, phonons in the system result in strain on the lattice. When the crystal lacks inversion symmetry, an internal polarization is created that can affect the exciton. Again, from previous work, the piezoelectric potential spectral density for a quantum dot can be modeled as:

\[
J_P(\omega) = \frac{8\lambda_P}{3\Lambda_P^5} \omega^5 e^{-\left(\frac{\omega}{\Lambda_P}\right)^2}
\]  

(9.10)

For simplicity, we combine the above densities into a single spectral density for coupling to the acoustic phonons:

\[
J_{AC}(\omega) = \frac{2\lambda_{AC}}{\Lambda_{AC}^3} \left(\omega^3 + \frac{2\omega^5}{3\Lambda_{AC}^2}\right) e^{-\left(\frac{\omega}{\Lambda_{AC}}\right)^2}
\]  

(9.11)

where we have set \( \lambda_D = \lambda_D \) and introduced \( \Lambda_{AC} = \Lambda_D = \Lambda_P \) and \( \lambda_{AC} = \lambda_D + \lambda_P \).

As discussed above, Fröhlich coupling is the direct interaction between carriers
and the polarization of lattice vibrations. This coupling mechanism is important in materials with polar contributions to their atomic bonds. To treat coupling to the LO phonon in nanocrystals, we turn to a slightly more complicated model for spectral broadening.

### 9.2.3 Multimodal Brownian Oscillator Model

The multimodal Brownian oscillator (MBO) model is good for incorporating the effects of electronic coupling to a single vibrational mode into the spectrum of a single transition. In the MBO model, a two-level system is coupled to a single oscillator, which in turn is coupled to a bath modeled as a continuum of oscillators. This model is attractive for our purposes because it has been used to study phonon progressions in the spectrum as observed at low temperature (Fig. 3-1). For quantum dots, a single underdamped mode describes the well-known coupling to the LO phonon at $\omega_{LO} = 207 \text{ cm}^{-1}$ via Fröhlich coupling. In the MBO model, the spectral density of the LO phonon is:

$$J_{LO}(\omega) = \frac{2\lambda_{LO}\omega_{LO}^2\gamma_{LO}\omega}{\gamma_{LO}^2\omega^2 + (\omega_{LO}^2 - \omega^2)}$$  

(9.12)

Finally, we include all three interaction mechanisms by summing the above spectral densities:

$$J(\omega) = J_D(\omega) + J_P(\omega) + J_{LO}(\omega)$$  

(9.13)

With this, we can calculate the lineshape function and determine the spectral correlation function $p(\zeta)$. We can then fit directly to the PCFS interferogram $\tilde{g}(\delta, \tau)$ as in Chapter 8.

### 9.2.4 Weighted Phonon Density of States

The phonon density of states $J(\omega)$ is somewhat difficult to interpret. Recall that its definition is:

$$J(\omega) = \sum_i \lambda_i \omega_i \delta(\omega - \omega_i) = \sum_i S_i \omega_i^2 \delta(\omega - \omega_i)$$  

(9.14)
A more intuitive spectral density is the weighted phonon density of states:

$$\rho(\omega) = \sum_i S_i \delta(\omega - \omega_i)$$  \hspace{1cm} (9.15)

This is easily interpreted as the density of coupling strengths multiplied by the number of phonons at a given frequency. Moreover, since \(\rho(\omega) = J(\omega)/\omega^2\), the total reorganization energy and Huang-Rhys factors are simply:

$$\lambda_{\text{tot}} = \int_0^\infty \omega \rho(\omega) \, d\omega$$  \hspace{1cm} (9.16)

$$S_{\text{tot}} = \int_0^\infty \rho(\omega) \, d\omega$$  \hspace{1cm} (9.17)

### 9.3 Spectral Lineshape Modeling Results

In Figure 9-4, we have applied our fit to the 1.8 monolayer CdS shell sample from Chapter 8. We see that the model fits well to the PCFS interferogram (Fig. 9-4a). In Figure 9-4b, we also show our spectral density \(\rho(\omega)\). At low frequencies \(\omega\), we have coupling to the acoustic phonons. The sharp peak at 207 cm\(^{-1}\) shows the coupling to the LO phonon in CdSe. Given this spectral density, we can calculate the emission spectrum \(s(\omega)\) at 300 K (Fig 9-4c). We see its shape is slightly asymmetric, but its FWHM of 65 meV is in good agreement with the effective spectral linewidth obtained by fitting to a linear combination of Gaussian functions (Table 8.1). Because temperature is a variable independent of the model fitting parameters, it can easily be tuned to low temperatures where we can observe features in the single-NC spectrum due to phonon-assisted emission (Fig. 9-4).

Unfortunately, fitting this model to the data from S-PCFS does not give unique results. Many different combinations of parameters in the model can lead to the same fit, producing drastically different spectral densities and spectral lineshapes. A key model-independent parameter to adjust and test is temperature. Performing S-PCFS on a temperature range may result in a narrowing of the parameter space to determine quantitative values for the phonon spectral density. Another consideration
Figure 9-4: We apply our continuum spectral lineshape model to the S-PCFS data of the 1.8 monolayer CdS shell sample from Chapter 8. a) Our model fits nicely to the PCFS interferogram obtained for the average single-NC. b) The weighted spectral density $\rho(\omega)$ shows coupling to the acoustic phonons at low frequencies and the LO phonon at higher frequencies. c) The room temperature and d) the low-temperature spectra can be modeled from the spectral density. At room temperature, we have a singly-peaked nearly symmetric function. At low-temperature, the acoustic phonon and LO phonon sidebands can be resolved.

is the solid-state analogue of S-PCFS, where nanoparticles are dispersed on a substrate and the laser beam scanned rapidly over them. At low temperatures, the single-NC spectrum is rich with features due to phonon sidebands. Therefore, fitting to these low-temperature spectra may help us uniquely determine the exciton-phonon coupling parameters.
9.4 Conclusions

The work in this chapter helps emphasize the broad applicability of S-PCFS. Beyond empirical observations of changes in sample heterogeneity or linewidth changes, S-PCFS provides access to rich and unexplored physics. In this chapter, we have discussed the development of a spectral lineshape model based on coupling of electronic transitions to a continuum of phonon modes, that may allow us to extract quantitative information about exciton-phonon coupling from data obtained through S-PCFS. Combining these tools with temperature-dependence measurements and strict synthetic control over the size, structure and composition of nanocrystals, we hope to assemble a global picture of exciton-phonon coupling in nanocrystals along with its synthetic tunability.
Chapter 10

Conclusions and Outlook

In this thesis, we have attempted to deconstruct the room-temperature emission spectra of nanocrystals. While acknowledging the power of single-molecule techniques to the study of nanocrystals, we laid down the theoretical framework for PCFS, FCS, and S-PCFS, in order to go beyond the study of individual particles to understand single-nanocrystal spectra in the context of an entire sample batch. With this technique, we have a direct probe of spectral inhomogeneity as well as a direct probe of spectral dynamics. In nanocrystals, we confirmed the independence between homogeneous and inhomogeneous spectral linewidths. We also discovered the absence of sub-millisecond spectral dynamics and discovered batch-to-batch variation in average single-NC linewidths with some synthetic tunability. Finally, we made strides toward understanding the excitonic coupling to the environment that gives rise to these intrinsic, homogeneous emission spectra.

Perhaps most importantly, S-PCFS has expanded the suite of single-molecule techniques for observing the complex photophysical phenomena found in nanocrystals. This expanded toolbox, in conjunction with ongoing developments in materials synthesis, detection technology and structural characterization, leaves single-nanocrystal studies poised to make an impact in several research directions.

The symbiotic relationship between single-nanocrystal studies and synthesis has been an enduring theme over two decades of nanocrystal research. Because the properties of an ensemble are a convolution of the intrinsic properties of individual particles
and sample heterogeneity, the rational design of nanocrystals requires characterization tools capable of rapid and unbiased measurement of single-nanocrystal properties on a statistically-significant scale. We believe that the success of S-PCFS embodies the role that single-molecule techniques can play in synthetic development and foreshadows further innovation.

Similarly, improved syntheses have been essential for the development of single-molecule spectroscopies and the observation of new phenomena. Spectroscopic practitioners are well aware that signal-to-noise is a constant concern in single-molecule spectroscopy. We cannot overstate the fact that increasingly sophisticated studies have only been made possible by the development of brighter and more stable emitters. Moreover, as amply demonstrated in the reports we have highlighted, novel nanostructures can introduce new phenomena that challenge and expand our understanding of nanoscale physics.

One of the frontiers of this symbiotic relationship is the infrared (>800 nm). While organic dyes are widely used as visible fluorophores, many of the best infrared-emitting organic dyes exhibit quantum yields below 1%. In contrast, nanocrystal syntheses have been extended to infrared materials while maintaining quantum yields as high as 60%. Beyond luminescent applications, these materials are also attractive for optoelectronic devices due their tunable absorption profiles and solution processability.

However, many fundamental properties of infrared-emitting nanocrystals have remained unexplored due to latency in the development of detectors with single-nanocrystal sensitivity. Tantalizingly, recent advances in single-photon detection in the short-wave infrared (∼1–3 μm) have opened the door for single-nanocrystal studies. The first studies of individual infrared-emitting nanocrystals have recently been reported: Figures 2-1 and 2-8 show data obtained from single InAs and PbS core/shell particles. We expect that the virtuous cycle of single-nanocrystal studies and synthetic efforts will help move infrared nanocrystals toward widespread application.

Single-molecule optical techniques have found great utility in the study of many
complex systems. Indeed, for nanocrystals, these techniques have not only been beneficial, they have been necessary. In this way, single-molecule studies of colloidal quantum dots represent an archetype for the elucidation of optical physics at the nanoscale. It is the hope of this soon-to-be PhD that the toolkit of single-molecule techniques described in this thesis, particularly PCFS and S-PCFS, will prove invaluable to the study of other complex or developing microscopic systems.


