ULTRAFAST DYNAMICS OF INDIVIDUAL AIR-SUSPENDED SINGLE-WALLED CARBON NANOTUBE

by

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Abstract

Thorough understanding of the electronic and optical properties of single-walled carbon nanotubes (SWCNTs) will no doubt benefit future technological applications. Since the discovery of band gap photoluminescence from isolated semiconducting SWCNTs, significant progresses in studying the optical properties of SWCNTs have been made (e.g. linear polarization along the tube axis for the absorption and emission of light, excitonic nature in SWCNT excitation). However, there are still several controversial parameters of SWCNTs (e.g. quantum efficiency, absorption cross section, radiative lifetime, and Auger recombination lifetime). With the advancement in SWCNT sample preparation, studies of SWCNT intrinsic properties have shifted from ensemble to a single tube level, in which the ambiguities in elucidating intrinsic properties posed by the assortment of different tube species can be minimized. By examining individual SWCNTs suspended in air, in contrast to micelle-encapsulated SWCNTs, we believe that the environmental effects can be reduced.

This thesis will demonstrate the capability of doing spectroscopy on a single semiconducting air-suspended SWCNT. In continuous-wave excitation, the photoluminescence excitation map and high resolution photoluminescence (PL) image of a SWCNT can be constructed, and PL polarization is proven. Quantum efficiency of 5% is experimentally estimated for (9,8) and (10,8) chiral SWCNTs. Pulse excitation allows us to study the intrinsic exciton dynamics of a SWCNT. To gain insight into exciton nonlinear decay
processes, PL saturation in pump power dependence measurement is investigated and compared to the simulated results from stochastic models of exciton dynamics. Femtosecond excitation correlation spectroscopy with 150 fs time resolution is employed to time-resolve the PL of a single tube suspended in air.
Acknowledgments

This dissertation would not have been possible without the support of many individuals. First and foremost, I am extremely grateful for continual guidance and valuable advice of Dr. James Fraser throughout the entire course of this project. My comprehension of SWCNT theory, and practical skills in an optics lab have been enhanced tremendously during two years working under his supervision.

Secondly, I would like to acknowledge the contribution of two co-workers, Y. F. Xiao and M. W. B. Wilson. In addition to the involvement in developing the optic setup and system characterization, Ms. Y. F. Xiao has also played a leading role in exploring the stochastic model to help interpret the experimental results.

I also wish to acknowledge the funding support by the Natural Sciences and Engineering Research Council and by the Queen’s University Department of Physics, Engineering Physics and Astronomy. The staff and faculty at the Queen’s University also deserve recognition because of their assistance in various aspect of my education.

Finally, I wish to thank my family for their encouragement. To my parents, sister, aunts and Lam: your constant support and love have motivated me to complete this chapter of my life.
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>BP</td>
<td>Band Pass</td>
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<td>BRF</td>
<td>Birefringent</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<tr>
<td>CW</td>
<td>Continuous Wave</td>
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<td>DOS</td>
<td>Density Of States</td>
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<td>FEC</td>
<td>Femtosecond Excitation Correlation</td>
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<td>FWHM</td>
<td>Full Width Half Maximum</td>
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<tr>
<td>GPIA</td>
<td>General Purpose Interface Adapter</td>
</tr>
<tr>
<td>GPIB</td>
<td>General Purpose Interface Bus</td>
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<td>HiPCO</td>
<td>High Pressure Carbon Monoxide</td>
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<td>LIA</td>
<td>Lock In Amplifier</td>
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<td>LN2</td>
<td>Liquid Nitrogen</td>
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<tr>
<td>LWP</td>
<td>Long Wave Pass</td>
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<tr>
<td>MCAPI</td>
<td>Motion Control Application Programming Interface</td>
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<td>MWCNT</td>
<td>Multi-walled Carbon Nanotube</td>
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<td>NA</td>
<td>Numerical Aperture</td>
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<tr>
<td>OPO</td>
<td>Optical Parametric Oscillator</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly Acrylic Acid</td>
</tr>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>PLE</td>
<td>Photoluminescence Excitation</td>
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<td>PPD</td>
<td>Pump Power Dependence</td>
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<td>QE</td>
<td>Quantum Efficiency</td>
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<td>SDBS</td>
<td>Sodium Dedocyl Benzene Sulfonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dedocyl Sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SWCNT</td>
<td>Single-walled Carbon Nanotube</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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Chapter 1

Introduction

Carbon nanostructures play a unique role in nanoscience not only due to their small size (less than 30 nm scale) but also the simplicity of their chemical composition (i.e. consisting only of carbon), allowing theoretical calculation and modeling of their physical properties feasible and convenient for experimental comparison. Among several carbon nanostructures, carbon nanotubes have the smallest length scale. This tubular structure with a nano-sized diameter and length of a few $\mu$m exhibits very large aspect ratio (i.e. three to four orders of magnitude). This makes carbon nanotubes a quasi one-dimensional system where quantum effects are dominant [1]. After the early synthesis of multi-wall carbon nanotubes (MWCNTs) which are concentrically arranged cylinders with outer diameters less 15 nm [2], single-wall carbon nanotubes (SWCNTs) with only one atom thickness of the cylinder wall were achieved. Since then, the synthesis of SWCNTs has seen tremendous progress and now can offer samples of good quality SWCNTs for both experimental studies and fabrication into nano-devices.

SWCNTs exhibit very interesting thermal, mechanical, chemical, electronic and optical properties, which have attracted attention from many researchers for the past decade.
SWCNTs have incredible chemical and environment sensitivity owing to their small radius and large surface. In addition to the natural stability of the $\sigma$-bond, the axial component of the $\sigma$-bond is enhanced due to the cylindrical configuration of the SWCNTs, which increases the tensile strength along the tube axis. The Young’s modulus was found to be as high as 1 TPa for SWCNTs with 1-2 nm diameter [3]. From the optoelectronic point of view, SWCNTs can either be semiconducting or metallic depending on how the tubes are rolled from the graphene sheet. More interestingly, the opening or closure of the band gap under tensile and torsion strain make the electromechanical properties of SWCNTs very applicable [4]. SWCNTs also exhibit band gap modification when a magnetic field is applied either parallel or perpendicular to the tube axis, this is known as Aharonov-Bohm effect [5].

1.1 Research Goals

Understanding of the electronic and optical properties of SWCNTs will benefit future technological applications (e.g. light emitting devices, field effect transistors, photosensitive devices, and bipolar electronics [6, 7, 8, 9]). Since the discovery of band gap photoluminescence from isolated semiconducting SWCNTs [10], significant progresses in the detailed studies of the optical properties of SWCNTs have been made. The correlation between nanotube structure (diameter and chirality) and transition energies (excitation and emission) provides a simple spectroscopic method to decipher the composition of SWCNTs in an unknown sample [11]. The absorption and emission of light from SWCNTs were experimentally observed and reported to be strongly polarized along the tube axis [12, 13, 14]. Experimental evidences of the excitonic nature in excitation of SWCNTs were also significant findings since excitons are the manifestation of enhanced Coulomb interaction and spatial confinement in the 1D system. In other words,
SWCNTs offer an ideal playground to investigate the role of reduced dimensionality in optical absorption and emission and carrier-carrier interaction (e.g. exciton formation, exciton-exciton annihilation).

Despite these recent advances, there are still several controversial and unresolved questions. The mechanisms of exciton dynamics (e.g. radiative and nonradiative relaxation pathways) are still poorly understood. In time-resolved photoluminescence (PL) spectroscopy (one way to probe exciton relaxation mechanisms), the observed PL lifetimes have a broad distribution from 10-180 ps, as reported by several research groups [15, 16, 17, 18, 19]. This could be due to the difference in sample state and/or the surrounding environment of SWCNTs. Absolute fluorescence quantum efficiency (QE) measured by different groups varies from $10^{-4}$ to $7\times10^{-2}$ [10, 11, 16, 18, 19, 20, 21, 22, 23]. One of the causes for the inconsistency in QE is the uncertainty in the absorption cross-section of the SWCNT. Currently, there is a twenty-fold spread in the absorption cross section (from $0.8\times10^{-18}$ to $16.7\times10^{-18}$ cm$^2$/atom [22, 23, 24, 25, 26, 27, 28]), which may be affected by variances in excitation wavelengths, laser mode (continuous-wave (CW) versus pulse), polarization of excitation light (parallel or unpolarized along the tube) and in particular, sample preparation methods.

The scientific community has witnessed the progressive improvement in the synthesis and growth of SWCNTs. The first attempt of synthesis was to separate semiconducting tubes from bundling by vigorous dispersion in various types of surfactant (e.g. Sodium dedocyl sulfate (SDS), Sodium dedocyl benzene sulfonate (SDBS), Poly acrylic acid (PAA)), sonication and centrifugation. Further improvement included chirality enrichment, narrow diameter distribution [29] and alignment of SWCNTs [24]. Individual semiconducting SWCNTs were first obtained by spin-coating and aqueous suspension onto substrates [19]. Another milestone of achieving cleaner individual SWCNTs was by growing them suspended in air to minimize interactions with their environment.
As a result of the advancement in sample preparation, work in studying the intrinsic properties of SWCNTs have also shifted from ensemble to a single tube level, in which the ambiguities in elucidating intrinsic properties posed by the assortment of different tube species can be removed. For the measurements of absorption cross section, experimentalists upgraded the studied system from aligned SWCNT ensemble to single tube dispersed in $\text{H}_2\text{O}$ with SDBS surfactant [23] or DNA-solubilized [22]. Similarly, QE measurement was first done on an ensemble of isolated tubes which were free from the complications of intertube interactions [16]. However, in such analysis of inhomogeneity of ensemble [31], averaging quantum yield for individual tube is unavoidable. Hence, the studied system was promoted to micelle-encapsulated single tube [19], then to single tube suspended in air [21]. In time-resolved PL spectroscopy, rapid relaxation from excited states (e.g. 1 ps) was found in bundling carbon nanotubes due to energy transfer from semiconducting to metallic tubes [32, 33]. In an attempt to study isolated SWCNTs, time-resolved PL studies have shifted from ensemble of different chiralities $(n,m)$ or sub-ensemble of identical structure $(n,m)$ towards the single tube level. Previous single tube work done by Hagen et al. revealed monoexponential decay with lifetimes ranging from 20 ps to 200 ps as tube-to-tube variation [19]. However, those micelle encapsulated SWCNTs might still be susceptible to tube-environment interaction or bundling.

By examining individual tubes of the same chirality suspended in air, we believe that the environmental effects can be eliminated, leaving defects, impurities, and length variation as extrinsic factors and the splitting of bright/dark excitons, Auger recombination (or exciton-exciton annihilation) processes as intrinsic factors to be investigated. However, there are a lot of challenges to overcome. In comparison to SWCNTs synthesized by the high pressure carbon monoxide (HiPCO) process, air-suspended SWCNTs obtained from the chemical vapor deposition (CVD) growth are of higher quality and
CHAPTER 1. INTRODUCTION

...do not require further processing for purification and separation. However, the CVD method typically yields larger diameter SWCNTs. Since the bandgap of a semiconducting SWCNT is inversely proportional to its diameter, working with these large diameter SWCNTs requires us to operate in the IR regime of the emission. Other groups using HiPCO synthesized SWCNTs do not face this problem since their SWCNTs emit PL in the visible region, where the available technology can provide much better detection efficiency compared to IR regime. Furthermore, pulse excitation, which is necessary for time-resolved studies, poses another challenge since it yields much lower signal than CW excitation. Also, air-suspended SWCNTs are susceptible to aging with the degradation in PL emission. Under these constraints imposed on all the measurements of optical properties for these IR emitting SWCNTs, the objectives of this thesis are characterized as follows:

- Spectroscopy of a single tube in CW excitation: constructing photoluminescence excitation (PLE) map (i.e. a measurement of luminescence spectra as a function of excitation energy), examining PL polarization, performing PL imaging to estimate the length of SWCNT.

- Pulse excitation to study the intrinsic exciton dynamics: investigating strong power dependent PL saturation, exploring time-resolved PL dynamics using femtosecond excitation correlation.

1.2 Structure of Thesis

In Chapter 2, the background of SWCNT research will be discussed, including SWCNT discovery, synthesis techniques, and the nomenclature of the SWCNT structure. This chapter also reviews important theoretical discoveries and experimental measurements of
the optoelectronic properties of SWCNTs. Chapter 3 explains the details of our samples, the optical setup as well as the system characterization and design in order to fulfill our specific experimental purposes. Chapter 4 is devoted to describing various LabVIEW programs that were designed by the author to assist the experimental measurements. Chapter 5 presents the evidences of individual isolated SWCNTs used in our experiment, such as the PLE map, high resolution PL image, and PL polarization. Chapter 5 also includes the experimental results on pump power dependence of the PL and time-resolved PL dynamics via femtosecond excitation correlation technique. The intrinsic optical properties (e.g. emission and absorption spectra, the quantum efficiency, and tube length dependence of PL) obtained from our air-suspended SWCNT system are also compared to findings by other groups. Furthermore, exciton dynamics are investigated in this chapter, through the analysis of PL saturation behavior observed from the PPD data and the elucidation of PL decay times from the FEC results. The conclusion chapter will give a summary of all the important results and observations as well as suggestions for future work.
Chapter 2

Background

2.1 Historical Review of SWCNTs

The formation of carbon filaments has been known since 1889, when Edison found them from the thermal decomposition of methane [34]. He originally proposed their applications as light bulb filaments. However, due to limitations in the resolution of the existing microscopy technology (i.e. the highest resolving power was a few $\mu$m), the underlying structure of the filaments was not known. It was not until 1952, after the transmission electron microscope (TEM) was invented and commercialized, that Radushkevich and Kukyanovich showed the morphology of hollow carbon filaments with nanometer-sized diameter in their TEM images. Since then, many scientists (e.g. Baird, Baker, Boehm, Endo, Harris, Oberlin, Robertson, Walker) have been successful in growing MWCNTs [34]. At the frontier of nanoscience, the work on MWCNTs started to capture the interest of fundamental physicists after the publication by Iijima in 1991 [35]. From his original synthesis of bucky-ball $\text{C}_{60}$ and other fullerenes, Iijima found a “new type of finite carbon structure consisting of needle-like tubes”. Coaxial tubes were found to
grow from the anode in an arc-discharge evaporation apparatus used for the mass production of $C_{60}$. In 1993, scientists were able to synthesize the first single-walled carbon nanotubes; these were found independently by Iijima and Ichihashi at NEC, Japan [36] and by Bethune et al. at IBM, California [37].

2.2 SWCNT Growth Techniques

This section will discuss the three prevalent techniques used to grow SWCNTs: arc discharge, laser ablation, and chemical vapor deposition (CVD). Samples for this thesis work were prepared by collaborators at NRC Institute for Microstructural Sciences (NRC-IMS) using the CVD technique.

2.2.1 Arc Discharge

This method is considered to be the easiest and cheapest way to produce SWCNTs although the products are less pure than those synthesized from other methods [38]. Similar to the facility for fullerene production, the carbon arc chamber consists of two vertical electrodes. The anode is a graphite carbon rod of up to 10 mm in diameter while the cathode is another graphite rod with its tip drilled into a dimple and packed with metal-graphite powders [36]. The most commonly used metallic mixtures are Ni/Y and Co/Ni catalysts. A gas mixture (e.g. CH$_4$, Ar, He) is purged into the evaporation chamber. Carbon arc discharge is achieved when a direct current is run across the two electrodes. The high temperature leads to the evaporation of the graphite and metal. This causes the deposit on the cathode to grow while the anode is gradually consumed.

SWCNTs produced by arc discharge tend to aggregate into bundles of 20-40 tubes. Their diameters ranges from 1.2 nm to 1.5 nm range [37]. The tube diameters were found to be dependent on the temperature at the catalytic site. Factors that result in
high yield of SWCNTs are: environmental temperature, choice of metal catalyst, ratio of metals in catalyst mixture, gas pressures, arc currents and gap widths [38].

2.2.2 Laser Ablation

In this technique, a solid target of graphite that contains a small amount of metal catalyst (e.g. Ni, Co) is housed in an oven at high temperature (e.g. 1200°C) [39]. The furnace is filled with inert gas (e.g. Ar) compressed to 500 Torr. Under the illumination of a CW or a pulsed laser, the surface of the carbon-metal composite target is evaporated, causing the plasma of atoms and molecules of C, Ni, Co and their ions to leave the target at supersonic velocity (e.g. $10^6$ cm/s). These initial ejecta are further dissociated and ionized when colliding with the inert gas. It was found from various in situ imaging and spectroscopy techniques (e.g. optical emission spectroscopy, laser-induced fluorescence and Rayleigh scattering) that the ablation plume after interacting with the inert gas forms a swirling vortex ring [40]. This “microreactor”, containing condensed phase metal and carbon nanoparticles, is where the actual SWCNT growth takes place. The length of these SWCNTs can be controlled by adjusting the lifetime of the plume in the furnace, and the growth rate was found to be 0.5-5 $\mu$m/s [39]. Although laser ablation can yield high quality SWCNTs, it is more expensive for large-scale production. It is noted that HiPCO SWCNTs are produced using this method.

2.2.3 Chemical Vapor Deposition (CVD)

The first attractive feature of this method is the potential for an industrial-scale production with low price per unit ratio [38]. Secondly, unlike the two previously discussed techniques where SWCNTs need to be collected, this CVD method allows the SWCNTs to be grown directly on a substrate.
In this method, the substrate (~1 inch thick) is deposited with a catalyst mixture (e.g. Co, Ni, Fe). The structure of composition of the catalysts are essential for nanotube yield. More importantly, the size of these catalyst particles dictates the diameter of nanotubes. For instance, Fe$_3$O$_4$ catalyst particles of 1.7 nm diameter result in SWCNTs of diameter ranging from 0.6-2 nm and centered around 1 nm [41]). The substrate is heated in a chamber that is purged with a process gas (e.g. NH$_3$, H$_2$, N$_2$) and carbon feedstock gas (e.g. CO, CH$_4$, C$_2$H$_2$, C$_2$H$_4$). Upon bond breaking, the C atoms land on the catalyst particles and initiate the growth of SWCNT. Depending on the adhesion between the catalyst particles and the substrate, the former species can either stay sandwiched between the substrate and the nanotube (base growth), or stay on the tip of the growing nanotube (tip growth). SWCNTs grown by the CVD method are of high quality (less impurities, reduced bundling). Longer SWCNTs are also possible by this method (e.g. a 4 cm long SWCNT has been achieved [42]). However, the CVD method tends to yield SWCNTs of larger diameter compared to other methods.

2.3 Structure of Carbon Nanotube

2.3.1 Atomic Bonding

A carbon atom has six electrons. Two electrons occupy the inner 1s orbital, while the other four electrons in an outermost shell can fill either $sp^3$ (four $\sigma$ covalent bonds), $sp^2$ (three $\sigma$-bonds and one $\pi$-bond) or $sp$ (two $\sigma$-bonds and two $\pi$-bonds). For instance, the tetrahedral geometry in diamond, with each of its carbon having four valence electrons connecting to four other carbons, is due to the $sp^3$ hybrid orbital [43]. In contrast, graphite can be viewed as stacking multiple hexagonal sheets. Graphite’s $sp^2$ hybrid
orbital consists of three in-plane $\sigma$ bonds that form a hexagonal network and one out-of-plane $\pi$-bond that connects adjacent sheets via weak van der Waals interaction [44]. From this viewpoint, a SWCNT is formed by rolling a graphene sheet into a seamless cylinder, hence, inheriting the overall $sp^2$ bonding characteristics. However, the circular curvature generates quantum confinement and $\sigma$-$\pi$ rehybridization in which three $\sigma$-bonds are slightly out of plane and the $\pi$ bond is more delocalized outside the tube [38].

2.3.2 Chirality

In theory, there are infinite ways of wrapping a graphene sheet into a seamless cylinder, resulting in different diameters and microscopic structures of SWCNT. As illustrated in Figure 2.1, a chiral vector $\vec{C}$ is introduced as a conventional way to define the wrapping orientation of a particular SWCNT:

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2$$  \hspace{1cm} (2.1)

where $n$ and $m$ are integers, $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors in the graphene hexagonal lattice, with their angle of $60^\circ$ (e.g. with the nearest neighbor C-C distance $a_{C-C} = 1.421$ Å, $a = |\vec{a}_1| = |\vec{a}_2| = \sqrt{3}\times a_{C-C} = 2.461$ Å). If $n = m$, the SWCNTs are characterized as armchair. If $m = 0$, the SWCNTs are of zigzag type; and its chiral vector $\vec{C}$ in this case aligns with the unit vector $\vec{a}_1$.

The diameter of a (n,m) SWCNT is:

$$D = \frac{1}{\pi} |\vec{C}| = \frac{1}{\pi} a(n^2 + nm + m^2)$$  \hspace{1cm} (2.2)

The chiral angle $\theta$ is the angle between the chiral vector $\vec{C}$ and the unit vector $\vec{a}_1$. Therefore, $\theta = 30^\circ$ and $\theta = 0$ for the armchair and zigzag types, respectively. For a tube
of regular chirality, its chiral angle is given by:

$$\theta = \tan^{-1}\left(\frac{\sqrt{3} \, m}{m + 2n}\right)$$

(2.3)

To specify a SWCNT, we can use the pair of indices \((n,m)\) or the equivalent pair of tube diameter and its chiral angle. In this thesis, SWCNTs will be identified by their chiral indices only.

Figure 2.1: Defined chirality SWCNT on the graphene’s hexagonal lattice. \(\vec{a}_1\) and \(\vec{a}_2\) are the graphene’s unit vectors. \(\vec{C}\) and \(\vec{T}\) are the chiral vector and translation vector of a SWCNT. OBB’A outlines the unit cell of the SWCNT. [Adapted from “Carbon Nanotubes: Basic Concepts and Physical Properties”[45]].

### 2.4 SWCNT Electronic Structure

The electronic structure of carbon nanotubes is usually derived from that of graphene. The unit cell of graphene is a rhombus that contains two carbon atoms. It is illustrated
in Figure 2.2(a) as a dash zone with sites A and B. Figure 2.2(b) shows the corresponding Brillouin zone (BZ) of graphene as a hexagon outlined in red, with the reciprocal lattice vectors \( \vec{b}_1 = \left( \frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right) \) and \( \vec{b}_2 = \left( \frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a} \right) \). These two vectors have been rotated from the real space basic vector \( \vec{a}_1 \) and \( \vec{a}_2 \) by 30°. Three points Γ, K, and M labelled in the BZ are the high symmetry points where the electronic band structure is usually investigated.

Figure 2.2: Real space (a) and reciprocal space (b) lattice of graphene with their corresponding unit vectors. High symmetry points Γ, K, and M are shown in the Brillouin zone in the reciprocal space. [Adapted from “Unusual Properties and Structure of Carbon Nanotubes” [2]].

Since a SWCNT is rolled up from a graphene sheet along the chiral vector \( \vec{C} \), the unit cell of the SWCNT is then defined in the graphene’s hexagonal lattice as a region outlined by the chiral vector \( \vec{C} \) and a translation vector \( \vec{T} \) (i.e. OBB’A region in Figure 2.1). The translation vector \( \vec{T} \) (the vector \( \overrightarrow{OB} \)) is the shortest repeating distance along the tube axis. It can be written in terms of \( \vec{a}_1 \) and \( \vec{a}_2 \) as follow:

\[
\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2
\] (2.4)
where

\[ t_1 = \frac{2m + n}{d_R} \quad (2.5) \]

\[ t_2 = -\frac{2n + m}{d_R} \quad (2.6) \]

with \( d_R \) being the greatest common divisor of \((2n+m, 2m+n)\). The translation vector has the magnitude of \(|\overrightarrow{T}| = \frac{\sqrt{3}\pi}{d_R} |\overrightarrow{C}|\).

The number of hexagons, \( N \), contained in a unit cell of a SWCNT is given by [2]:

\[ N = \frac{2(m^2 + mn + n^2)}{d_R} \quad (2.7) \]

As suggested from the above, the real space unit cell of the SWCNT is much larger than the unit cell of graphene (i.e. a single two-atom rhombus). In the reverse manner, the BZ of the SWCNT is much smaller than the BZ of graphene. Vector \( \overrightarrow{K_1} \) and vector \( \overrightarrow{K_2} \) are defined as the two unit vectors of the SWCNT in the reciprocal lattice. Vector \( \overrightarrow{K_1} \) is associated with the chiral vector \( \overrightarrow{C} \) along the circumference, and \( \overrightarrow{K_2} \) is corresponding to the translation vector \( \overrightarrow{T} \) along the tube axis. For clarity, Table 2.1 summarizes all the notations for the unit vectors of graphene and SWCNT in the real and reciprocal space.

<table>
<thead>
<tr>
<th>Real space</th>
<th>Graphene</th>
<th>SWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1, a_2 )</td>
<td>( C, T )</td>
<td></td>
</tr>
<tr>
<td>Reciprocal space</td>
<td>( b_1, b_2 )</td>
<td>( K_1, K_2 )</td>
</tr>
</tbody>
</table>

Table 2.1: Notations for unit vectors of graphene and SWCNT in real and reciprocal space.
The relationships among $\vec{K}_1$, $\vec{K}_2$, $\vec{C}$ and $\vec{T}$ are as follows:

$$\vec{C} \cdot \vec{K}_1 = 2\pi \quad (2.8)$$
$$\vec{C} \cdot \vec{K}_2 = 0 \quad (2.9)$$
$$\vec{T} \cdot \vec{K}_1 = 0 \quad (2.10)$$
$$\vec{T} \cdot \vec{K}_2 = 2\pi \quad (2.11)$$

This yields:

$$\vec{K}_1 = \frac{1}{N}(-t_2\vec{b}_1 + t_1\vec{b}_2) \quad (2.12)$$
$$\vec{K}_2 = \frac{1}{N}(m\vec{b}_1 - n\vec{b}_2) \quad (2.13)$$

where $N$ has been defined in Equation 2.7. With the periodic boundary condition imposed on the circumference of the SWCNT [46, 47], there are $N$ discrete wave vectors $\vec{k}$ along $\vec{K}_1$ direction (i.e. $\vec{k} = \mu\vec{K}_1$, with $\mu = 0, 1, ..., N-1$). Meanwhile, along the tube axis, the reciprocal lattice vector $\vec{K}_2$ has its length as:

$$|\vec{K}_2| = \frac{2\pi}{|\vec{T}|} \quad (2.14)$$

For a finite length tube, there will be a discrete number of wave vectors along $\vec{K}_2$ direction, and the spacing between these wave vectors is $\frac{2\pi}{|\vec{T}|}$ [2]. However, if the tube is infinitely long, the wave vectors along $\vec{K}_2$ are continuous (i.e. infinite number of wave vectors). Since a SWCNT has very large aspect ratio of length to diameter (3-4 orders of magnitude), the approximation of infinite length is applied. Consequently, the allowed wave vectors for a SWCNT are $N$ lines parallel with $\vec{K}_1$.

As shown in Equation 2.12 and 2.13, the reciprocal lattice vectors $\vec{K}_1$ and $\vec{K}_2$ of a $(n,m)$ SWCNT have a characteristic relation with the fixed reciprocal unit vectors $\vec{b}_1$ and $\vec{b}_2$. This means that different $(n,m)$ SWCNTs have their $\vec{K}_1$ and $\vec{K}_2$ mapped out differently on the hexagonal BZ of the graphene. Figure 2.3 shows the orientation of the reciprocal lattice vectors $\vec{K}_1$, $\vec{K}_2$ of a $(7,7)$ armchair SWCNT with the respective to $\vec{b}_1$, $\vec{b}_2$. [Note: Figure 2.3 should be included here to illustrate the orientation of the reciprocal lattice vectors.]
\( \vec{b}_2 \) in the BZ of graphene. The red lines parallel to \( \vec{K}_2 \) are the allowed \( \vec{k} \) wave vectors of the (7,7) armchair SWCNT. These allowed \( \vec{k} \) vectors are then superimposed on the 2D electronic band structure of graphene and used as “cutting lines” to approximate the electronic properties of SWCNT. This technique is known as the zone folding approximation. Despite its simplicity and convenience, this approach is only valid for SWCNTs of large diameter, where the curvature effects (e.g. the rehybridization between the \( \sigma \) and the \( \pi \) states) can be neglected. For a very small diameter SWCNT (\( d \leq 0.8 \) nm), we need to go beyond the zone folding approach [45].

Figure 2.3: 2D Brillouin zone of graphene with its unit vectors \( \vec{b}_1, \vec{b}_2 \). The reciprocal unit vectors \( \vec{K}_1 \) and \( \vec{K}_2 \) and allowed \( \vec{k} \) vectors (red lines) of a (7,7) SWCNT are mapped onto graphene’s BZ. [Adapted from “Carbon Nanotubes: Basic Concepts and Physical Properties”[45]].

To apply zone folding, we first need to understand the electronic structure of graphene. Using the tight-binding approximation approach, the electronic band structure of graphene was calculated [1]. Figure 2.4 shows the tight-binding electronic band structure along the high symmetry \( \Gamma-K-M \) directions. In contrast to the \( \sigma \) bands where the energies are well separated, the fact that the \( \pi \) valence and \( \pi^* \) conduction bands are very close to the Fermi surface and cross at the \( \textbf{K} \) points of the BZ makes graphene metallic. With
a total of six \( K \) points in its hexagonal BZ, the 2D energy surfaces of graphene can be visualized with a valence band and a conduction band touching at these six edges, as illustrated in Figure 2.5(a).

![Graphene Band Structure](image)

Figure 2.4: Tight binding electronic band structure of graphene along directions going through the high symmetry points \( \Gamma \), \( K \), and \( M \). The \( \pi \) and \( \sigma \) hybridization of the 2s valence states are indicated next to the electronic bands. The Fermi level is at zero eV. The \( \pi \) valence and \( \pi^* \) conduction band cross at the \( K \) point of the Brillouin zone. Meanwhile, the bonding \( \sigma \) and anti-bonding \( \sigma^* \) bands are well separated. [Reproduced from [2] with the permission of M. S. Dresselhaus and A. Jorio].

On the 2D energy surfaces of graphene, one can superimpose the allowed \( \vec{k} \) vectors designated for a SWCNT of a particular \((n,m)\) chirality to obtain the electronic band structure of the SWCNT. The number of “cutting lines” (associated with the SWCNT diameter) and their orientations in the BZ (dependent on the rolling direction) will dictate the electronic band structure of the SWCNT. A SWCNT can be classified as metallic or semiconducting tube, depending on whether its allowed wave vectors go through \( K \) points. If any \( \vec{k} \) vectors pass through any \( K \) points, a SWCNT is a metal. Otherwise, it is a semiconductor, with the band gap increasing inversely with the diameter. Figure 2.6 shows the mapping of allowed \( \vec{k} \) vectors (red lines) onto the 2D graphene Brillouin
Figure 2.5: (a) A 2D electronic constant-energy surface of $\pi$ and $\pi^*$ bands of graphene. Thick lines are the cutting curves defined by allowed $k$ vectors of a (4,2) SWCNT. (b) The corresponding electronic band structure of (4,2) SWCNT obtained from those cutting lines from (a). (c) Van Hove singularities density of states of (4,2) SWCNT appear as sharp peaks of the valence bands and conduction locating symmetrically over Fermi level at zero energy. Peaks below the Fermi level are the valence bands (labelled as $i=1, 2, ...$). Peaks above the Fermi level are the conduction bands (labelled as $j=1, 2, ...$). [Reproduced from [48] with the permission of M. S. Dresselhaus].
zone for three different chiral SWCNTs: (5,5), (7,1) and (8,0). The first two are metallic since at least one of $\vec{k}$ vectors crosses the K point. Whereas, none of the wave vectors pass through K points in (8,0) SWCNT, which makes it semiconducting. Overall, the general rule for any (n,m) tube is: if $(m - n) \mod 3 = 0$, it is metallic; if $(m - n) \mod 3 = 1$ or 2, it is semiconducting. This indicates that one third of the tubes are metallic and two thirds are semiconducting.

![Figure 2.6: Allowed $\vec{k}$ vectors of the (5,5), (7,1) and (8,0) SWCNTs labelled as red lines mapped onto the 2D graphene Brillouin zone. [Adapted from “Unusual Properties and Structure of Carbon Nanotubes” [2]].](image)

From the dispersion relation of its energy band structure, the density of states (DOS) of a SWCNT (i.e. the number of available electrons for a given energy interval) can be calculated. The details of this calculation are beyond the scope of this thesis, and can be found elsewhere [45]. Nevertheless, the SWCNT density of states appears as several van Hove singularities with sharp peaks in the valence and conduction bands locating symmetrically over the Fermi level at zero energy. Different electronic band structures leads to distinct van Hove singularities DOS for each (n,m) chirality. Figure 2.5(b) and 2.5(c) present the electronic band structure and the corresponding DOS of a (4,2) SWCNT, which is of semiconducting type. Zero energy in Figure 2.5(c) is the Fermi level. Peaks below this Fermi level are the valence bands (labelled as $i=1, 2, ...$) while those peaks above the Fermi level are the conduction bands (labelled as $j= 1, 2, ...$).
The energy band gap $E_{11}$ between the valence and conduction band is indicated by the magenta double-arrow.

### 2.5 Optical Measurements of SWCNTs

The van Hove singularities in the SWCNT density of states give rise to many interesting optical phenomena. Under optical excitation with energy of the incident photons matching with the energy difference between the valence band $i$ to the conduction band $j$, where $i, j = 1, 2, ..., $, an $E_{ij}$ transition can be made, given that the selection rules are obeyed. Under the conservation of the total angular momentum of the system, the selection rules depend on the relative polarization of the electric field vector to the nanotube axis. For the light polarized perpendicular to the tube axis, only transitions between the $i$ valence and the $i \pm 1$ conduction bands are allowed. For the light parallel to the tube axis, transitions are always allowed between the valence and conduction bands of the same index (i.e. $i = j$, or $E_{ij}$ transition).

Using the nearest-neighbor tight-binding approximation to calculate the energy transitions $E_{ii}$, researchers have found the dependence of the energies on SWCNT diameter ($E \sim \frac{1}{d}$) and presented these results on a Kataura plot [49]. Raman spectroscopy, optical absorption, and PL have been used to verify these $E_{ii}$ values in association with the chirality and tube diameter. In particular, as illustrated in Figure 2.7a, the $E_{22}$ of semiconducting SWCNTs are explored from the absorption at the second band under the excitation, and $E_{11}$ can be probed from the PL after the relaxation of the carriers from the higher excited state to the lowest one. However, early studies found that these absorption spectra were very broad and no PL was detected. This is because carbon nanotubes tend to aggregate into bundles and the energy transfer from semiconducting to metallic tubes will quench any PL from the semiconducting tubes. To restrain
isolated tubes from bundling, raw nanotubes produced from the HiPCO method (i.e. gas-phase reactions of carbon monoxide at high pressures, refer to Section 2.2) were ultrasonicated and dispersed in an aqueous surfactant (e.g. SDS, SDBS). The samples were then centrifuged at high g. Due to the difference in their density and mass, the centrifugation process brought bundles to the bottom, leaving a supernantant enriched in isolated SWCNTs [50]. With the attainment of isolated SWCNTs in a soap micelle, PL was observed from these semiconducting tubes [10]. Although their emission spectra from this work showed narrow linewidth (25 meV) at room temperature, later investigations by Lefebvre et al. revealed two or three times narrower linewidth for air-suspended SWCNTs ([14]. Studies at low temperature showed that the emission spectra were further reduced from 10 meV to 4.4 meV when cooled from 25 K to 4.2 K [51].

In 2002, Bachilo et al. reported the spectrofluorimetric measurements for the absorption and emission transitions (i.e. $E_{11}$ and $E_{22}$) for 33 different micelle-encapsulated SWCNT species in solution [11]. The measurement of luminescence spectra as a function of excitation energy (i.e. $E_{22}$ versus $E_{11}$) was presented on a 2D plot, called the photoluminescence excitation (PLE) map. On this map, each intensity peak corresponds to an absorption and emission of SWCNTs of the same chirality. Full assignment of these peaks to systematic chiral indices was done by matching particular chiral indices of a few SWCNTs with their signature radial breathing mode (RBM) frequency in the Raman scattering measurements and deriving chiral indices of the rest according to the family pattern of $(m - n) \mod 3$ in the PLE map. This is a significant breakthrough since it provides a simple spectroscopic method to analyze the composition of SWCNTs in ensemble consisting of numerous chiralities. In 2004, published data by Lefebvre et al. showed the blueshifts in the emission and absorption peaks (28 meV and 16 meV, respectively) for their air-suspended SWCNTs as compared to the micelle-encapsulated
SWCNTs.

The experimental measurement of $E_{11}$ and $E_{22}$ also revealed an interesting problem: the ratio of $\frac{E_{22}}{E_{11}}$ was less than the value of 2 that was predicted by the tight binding theory. This indicated the presence of excitons in SWCNTs, which will be explained in Section 2.6.1. Additionally, the power dependence of PL emitted from SWCNTs showed that the linearity of PL only occurred at very low pump powers. When the power was moderately high, sublinear excitation dependence was observed. Ma et al. regarded a square root dependence of PL on the intensity for their SWCNT ensemble measurements [52]. Recently, Högele et al. reported a PL “hard” saturation behavior for the pump power dependence measurement on a single SWCNT encapsulated in SDBS [51]. By considering the amount of PL associated with the absorbed power by a SWCNT in the linear regime, quantum efficiency was reported to be very low (e.g. the highest value ever reported was 7% [21]). Low photoluminescence quantum efficiency indicated that the excited state relaxation of SWCNT is dominated by other nonradiative decay channels (e.g. traps at impurities, or dark excitonic states).

2.6 Excitonic Nature of SWCNT

2.6.1 Evidence of Excitons

Although the optical transitions of SWCNT are commonly attributed to the van Hove singularities in the 1D DOS (see Figure 2.7(a)), a complete picture should consider the optically produced electron-hole pairs that are strongly bound under their mutual Coulomb interaction and lead to the formation of excitons. From the wave vectors of the electron and hole ($\overrightarrow{k}_e$ and $\overrightarrow{k}_v$), the wave vector for the center of mass of an exciton and
the relative coordinate are defined as:

$$\vec{K}_{cm} = \frac{\vec{k}_c + \vec{k}_v}{2}$$  \hspace{1cm} (2.15)$$

$$\vec{K}_r = \vec{k}_c - \vec{k}_v$$  \hspace{1cm} (2.16)$$

Using the Bethe-Salpeter equation written in terms of $\vec{K}_{cm}$ and $\vec{K}_r$, researchers were able to derive the energy dispersion of excitons [48]. Because the Coulomb interaction is related to the relative coordinate of an electron and a hole, the center of mass wave vector $\vec{K}_{cm}$ can be treated as a good quantum number, and the energy dispersion of exciton can be described as a function of $\vec{K}_{cm}$.

The binding energy of an exciton, calculated by the hydrogenic model with reduced effective mass and a dielectric constant, can be as large as 500 meV for a SWCNT, as compared to only 10 meV for 3D bulk semiconducting materials [53]. This binding energy gives rise to discrete exciton energy levels lying below the continuum band as shown in Figure 2.7(b). While it requires very low temperatures to observe this small excitonic effect (e.g. a few meV) for most bulk semiconductors, it can be detected at room temperature in a SWCNT system. Two factors causing such a strong excitonic effect in SWCNT are: (1) the reduced dimensionality leads to very small separation of the electron and hole, hence, greatly enhancing their Couloumb interaction; (2) the dielectric screening is less effective compared to bulk materials since the electric field lines originating from the electron-hole pair extend outside the tube [53].

Experimental studies have found evidence of excitons in semiconducting SWCNTs. The first one is the “ratio problem” for $E_{22}/E_{11}$ of semiconducting SWCNTs, as mentioned in Section 2.5. Theoretical calculations from the tight-binding model suggests that the ratio should be 2. However, with the inclusion of very strong Coulomb interaction, this ratio should be 1.8 [54, 55], which has been confirmed by experimental observation [11]. The second experimental evidence for the excitonic nature of optical
transition in semiconducting SWCNT is the access of excited states of exciton using non-linear two-photon absorption [53]. Unlike one-photon excitation processes, a two-photon transition is allowed according to the selection rules for the wavefunction parity of these excitonic states. An intense laser pump power with energy above $E_{11}/2$ was used to excite the SWCNTs and PL was observed at $E_{11}$. The result, in form of a contour plot of two-photon excitation spectra, revealed the intensity peak of (7,5), (6,5) and (8,3) SWCNTs with two photon excitation energy blueshifted by 300 meV compared to the emission energy $E_{11}$ (refer to Figure 2.7(b)). This emission energy level (depicted as a red arrow in Figure 2.7(b)) is the lowest-energy excitonic state, while other excited excitonic state has energy higher than $E_{11}$.

Different symmetries of exciton wavefunctions result in the dark and bright excitons. The dark exciton is the lowest energy state below the lowest bright excitons. From both theoretical calculation [56] and experimental observation at low temperature [31], the energy splitting between these two states were found to be 3-5 meV. In context of the diagram shown in Figure 2.7(b), the dark exciton state is 3-5 meV below the lowest yellow line.

### 2.6.2 Study of Exciton Dynamics

Time-domain studies of optical transients are capable of elucidating exciton or carrier dynamics in photo-excited SWCNTs. Two commonly used techniques on ensemble systems are: transient absorption spectroscopy and time-resolved PL spectroscopy. In the first method, the induced absorption and induced transmission kinetics are investigated, while the second technique examines the PL decay mechanisms. The tentative picture of exciton dynamics (refer to Figure 2.8) suggested from optical transient measurements can be summarized as follows:
1. Excitons in $E_{22}$ are created under resonant optical excitation in which electrons are generated in the conduction band and holes in the valence band.

2. This is followed by interband relaxation from $E_{22}$ to $E_{11}$ within 100 fs [57, 58].

3. The intraband relaxation in $E_{11}$ occurring in less than 30 fs will bring the exciton to the bottom of this band [59].

4. Exciton-exciton annihilation might occur under an Auger recombination process (i.e. e-h recombination energy is nonradiatively transferred to a third particle that is re-excited to a higher-energy state [60]). We expect the Auger recombination phenomena to be dramatically enhanced for SWCNT as compared to bulk semiconductors, due to the 1D spatial confinement. In fact, experiments have confirmed the evidence of Auger recombination in SWCNT from the excitation intensity dependence of PL decay [61, 62]. In addition to the Auger recombination process,
another mechanism known as Auger ionization that was proposed by Barzykin et al. can lead to the annihilation of two excitons [63].

5. There might also be the exchange of population between bright and lower-lying dark exciton states (3-5 meV below the lowest-energy bright exciton as mentioned in Section 2.6.1). From the observation of PL quenching at low temperatures, Berger et al. proposed that the bright state is coupled to the ground state through radiative and nonradiative recombination processes. The dark state is only coupled to the ground state through a nonradiative processes. These two states are coupled to each other at a much faster rate than both radiative and nonradiative decays. At room temperature, however, both states are very close to being equally populated, therefore trapping at the dark state can be neglected [31].

6. Ground-state recovery of the exciton can happen via (a) radiative decay or (b) nonradiative decay.

Figure 2.8: Possible decay channels for exciton dynamics. [Adapted from “Exciton Dynamics in Structurally Sorted Carbon Nanotubes and Nanotube Aggregates” [64]].
In this tentative picture, there remain several controversial issues and unresolved questions. First, while the Auger lifetime suggested by Wang et al. was as short as 1.2 ps for 400 nm SWCNTs [16], the most recent value (in 2008 by Högele et al.) for tubes of comparable lengths was found to be an order of magnitude higher (i.e. 15 ps) [51]. Since the latter measurement was carried out at low temperature, they reasoned that much slower Auger rate is due to temperature driven exciton localization. Secondly, the detailed mechanisms of nonradiative decay and its kinetics are still unclear. The PL monoexponential decay lifetimes measured on individual micelle-encapsulated (6,4) SWCNTs revealed tube-to-tube variations (from 20-200 ps). Hagen et al. speculated that the nonradiative decay of excitons is facilitated by trapping at a low-lying optically inactive state via phonon-assisted processes [19]. However, Metzger et al. claimed that there is a conflict between this model and their findings on tube diameter dependence of nonradiative lifetime. Instead, they suggested the recombination kinetics are influenced by multiple excitonic states, including a dark lower state [65]. On the other hand, Hirori et al. supported a model that includes the localized and free excitons of different nonradiative lifetimes [66]. With the radiative lifetime experimentally determined from the nonradiative lifetime and quantum efficiency, there is a large range for this value (i.e. from 10 ns to 10 µs) as reported by different research groups [16, 18, 19, 20].

2.6.3 Stochastic Model of Exciton Dynamics

By considering the competition between different decay processes as discussed in Section 2.6.2, the average number of excitons per SWCNT at any time $t$ can be simulated using the stochastic model proposed by Barzykin and Tachiya [63]. For excitation into $E_{22}$, due to very fast dynamics (less than 100 fs), the interband and intraband relaxations (i.e. processes (2) and (3) in Figure 2.8) are assumed to be instantaneous. As explained
in the last section, the thermalization process between dark and bright excitonic states
(i.e. process (5)) allows us to assume a constant distribution of these two states at
room temperature. Three decaying processes remain for the investigation are Auger
recombination or exciton-exciton annihilation (i.e. process (4)), radiative decay \( \gamma_r \) (i.e.
process (6a)) and nonradiative decay (i.e. process (6b)). Their rate constants are notated
as \( \gamma_A \), \( \gamma_r \) and \( \gamma_{nr} \), respectively. The latter two are linear processes, hence, can be
combined as \( \gamma = \gamma_r + \gamma_{nr} \). Meanwhile, Auger recombination is a nonlinear process. The
rate equation that dictates the time-dependent probability density \( \rho_n(t) \) of finding \( n \)
excitons in a nanotube at time \( t \) can be expressed as follow:

\[
\frac{d}{dt}\rho_n(t) = -[\gamma + \frac{1}{2}(n-1)\gamma_A]n\rho_n(t) + (\gamma + \frac{1}{2}n\gamma_A)(n+1)\rho_{n+1}(t) 
\]  
(2.17)

For the ensemble measurement, Barzykin and Tachiya used the Poissonian distribu-
tion to account for the initial probability distribution of excitons in the system. In our
analysis where an individual isolated SWCNT is examined, we excite the tube with a
train of 150 fs pulses (76 MHz repetition rate). While some pulses succeed in generating
excitons, some may not. Thus, the Poissonian distribution remains valid in describing
the initial distribution of excitons:

\[
\rho_n(0) = \frac{\bar{n}_0^n}{n!}exp(-\bar{n}_0) 
\]  
(2.18)

where \( \rho_n(0) \) is the probability of having \( n \) excitons in the system at time \( t = 0 \) and \( \bar{n}_0 \)
is the average number of initially generated excitons in the tube. For a SWCNT of length
\( L_T \) and diameter \( D_T \), the average number of excitons created under the exposure to the
pump fluence \( \phi_{exc} \) is given by:

\[
\bar{n}_0 = \pi\phi_{exc}AD_TL_T 
\]  
(2.19)

where \( A \) is a unitless absorption coefficient, denoting the product of absorption cross
section of C atom (nm\(^2\)/atom) and the surface density of C atoms in graphene (i.e. \( A = \))
σ_{ab} \times σ_s\). The value of 37 atom/nm\(^2\) is used for σ_s [21], and σ_{ab} ranges from 0.8 \times 10^{-18} to 16.7 \times 10^{-18} cm\(^2\)/atom as reported by different groups [22, 23, 24, 25, 26, 27, 28]).

By numerically solving the rate equation (i.e. Equation 2.17) with the initial condition established in Equation 2.18, the average number of excitons per nanotube at any time \(t\) can be calculated as:

\[
\bar{n}(t) = \sum_{i=1}^{\infty} n_i \rho_i(t)
\] (2.20)

Since the observable fluorescence emission rate at certain time is proportional to the average number of excitons at that time \(\bar{n}(t)\), the total PL detected over a period of time is given by:

\[
P_{L, \text{total}} = K \int_0^{\infty} \bar{n}(t) \, dt
\] (2.21)

where K is a constant.

### 2.6.4 Time-resolved Measurements of Exciton Dynamics

Aside from the commonly-used transient absorption spectroscopy [15, 27, 29, 52, 62, 67, 68, 69], another robust method for probing exciton relaxation mechanisms is time-resolved PL spectroscopy. Conventional techniques (e.g. PL upconversion [62], time-correlated single-photon counting [15, 19], optical Kerr gating [16, 61], synchro-scan streak camera [17]) have been employed by different groups to perform PL dynamics measurement on SWCNT ensembles. However, these techniques are not feasible for our single tube studies due to the very low output signal. Another challenge comes from the emission wavelength of our air-suspended SWCNT species. Unlike the visible range emitted by a (6,4) SWCNTs, which allowed Hagen et al. to study the PL dynamics from an individual tube using the time-correlated single-photon counting method [19], we worked with IR emitting SWCNTs (e.g. 1380-1440 nm). Detecting low IR PL signal from a single tube poses a very challenging task.
CHAPTER 2. BACKGROUND

We employed a femtosecond excitation correlation spectroscopy to study PL dynamics of our SWCNTs. Although this FEC technique has been used to measure the recombination lifetimes of free and bound excitons in CdSe [70], it is not a well-established procedure for detecting very fast dynamics. Nevertheless, the employment of this technique to SWCNT ensembles has been demonstrated by Hirori et al. [66]. By collinearly focusing two beams that are separated by delay time $\tau$ onto the same 10 $\mu$m spot on the SWCNT sample, total PL is recorded as a function of $\tau$. The intensity of both pump pulses are high enough so that PL response is nonlinear. Due to the relaxation of the system between two pulses, the total PL increases as $\tau$ increases. They interpreted this FEC signal to be proportional to PL decay from single pulse excitation. The PL lifetime was extracted by fitting the data with a single exponential function $Ae^{-\tau/\tau_{PL}} + B$. Their normalized FEC signals at two different pump powers showed no dependence on excitation intensity. From the variance of PL lifetimes for SWCNTs in D$_2$O solution versus those in gelatin film (e.g. 22 ps versus 31 ps), they attributed the environment dependence of $\tau_{PL}$ to the interplay between localized excitons and free excitons as:

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_L} + \frac{1}{\tau_F}e^{-\Delta/k_B T}$$

(2.22)

where $k_B$ is the Boltzmann constant, $\Delta$ is the thermal activation energy, and $\tau_L$ and $\tau_F$ are the PL lifetimes of localized excitons and free excitons.

Applying the same FEC technique for an individual isolated air-suspended SWCNT, we expect that the environmental effect can be reduced. By fitting our FEC signal data with a biexponential decay, we also hope to gain insight into Auger recombination process that was not seen by Hirori’s group.
Chapter 3

System Design and Experimental Setup

3.1 SWCNT Growth

The samples used for our studies were prepared at the NRC Institute for Microstructural Sciences (NRC-IMS) as follows [71]: the substrate consists of 1 nm thick Co film deposited on a 1 µm thick thermal oxide layer of a Si wafer. Standard wet chemical photolithography technique was employed to etch a trench pattern through the Co film. Initially, the substrate heating process was carried out inside a CVD chamber by flowing a mixture of Argon/Hydrogen (ratio 48:1) gas. Upon reaching the growth temperature of 850°C, ethanol was purged at the rate of 0.3 l/min via a bubbler for 45 minutes. The growth was completed by cooling the sample to room temperature.

A scanning electron microscopy (SEM) image in Figure 3.1 illustrates the structure of the sample. The cobalt ridge appears rough with catalyst nanoparticles, most of which failed to grow nanotubes. The top of the image reveals two single SWCNTs that start from the cobalt ridge and attempt to make their way to the next ridge. However,
they fail and fall onto the Si or SiO$_2$ substrate. The bright spots are due to the charging effect when the SWCNT makes contact with the surface. Using atomic force microscopy (AFM), Dr. Robert Knobel also confirmed the height of the cobalt ridge to be 500 nm.

Figure 3.1: SEM of our sample: SiO$_2$ substrate, cobalt ridge and nanotubes landing on the trenches.

PL images provided by our collaborators (K. Kaminska, J. Lefebvre, and P. Finne) at NRC-IMS, as shown in Figure 3.2, display various scenarios of PL response from failed and successfully suspended SWCNTs that are illuminated under a large excitation spot size. In these frames, the dark thin lines are ridges and the remaining reddish area is the substrate. Firstly, it is noted that the thickness of these ridges varies from frame to frame. This is because the Co film was etched in an interleaved-finger configuration, which was confirmed via AFM and also observed with our imaging system. Secondly, the suspension of the SWCNTs can occur in different ways: one end of the SWCNT is on the ridge and the other end falls on the substrate; or two ends are on two adjacent ridges; or the suspension continued over several ridges. However, only those SWCNTs that successfully suspend in air will show up as a bright segment. Dark segments are due to parts of the SWCNT either resting on the ridge or touching the substrate. Thirdly,
although some SWCNTs might tilt in the direction of the gas flow during the growing process, most of them orient perpendicular to the ridges. This is very useful in identifying the SWCNT orientation, since the ridges can be seen easily with optical microscopy while the SWCNTs cannot.

Figure 3.2: Images of bright SWCNTs by illuminating large areas of the sample with a large spot size. The spatial PL was recorded using a 2D InGaAs array.
3.2 Schematics of Optical Setup

With the main goal of detecting micro-photoluminescence from a SWCNT, our optical setup was designed such that a SWCNT on the nanotube sample is excited with a tunable wavelength from the laser source and the PL emission from the SWCNT is detected for further analysis. The complete setup, including optical components, signal detection and data acquisition system, is shown in Figure 3.3. The laser source will be described in Section 3.4. As depicted in the diagram, the beam path is as follows: the excitation beam emerges from the laser source passing through lens L1. This lens serves to maintain the collimation of the beam down the line. The first beam splitter splits the beam into two paths: a transmitted beam that makes a fixed arm, and a reflected beam that follows a variable delay line. This delay line is required to timely separate two pulses for the time-resolved PL experiment, which will be discussed in Section 5.3. It is composed of a retroreflector mounted on a 1D translation stage and moved by a stepper motor as shown in Figure 3.4. After being spatially recombined at the second beam splitter, the recombined beam passes through an optical chopper as required by our signal detection technique. Following redirection via several mirrors, the beam then goes through lens L2. This lens can be removed from the beam path easily to change the excitation spot size on the sample.

The details of the beam path at the two periscopes are depicted in Figure 3.5. At the first periscope, the glass window partially reflects the excitation beam parallel to the optic table downwards. The aspheric lens focuses the beam onto the sample held on a 3D translation stage. Both the reflected excitation beam and the emitted PL from the nanotube sample are collected by the aspheric lens and transmitted through the glass window. Three consecutive mirrors are mounted on the two periscopes to redirect the outgoing beam parallel to the optics table. The third mirror also ensures the beam is at
the right height before entering the spectrometer. A flip mirror is inserted to offer the flexibility of either sending the beam to the imaging system or to the spectrometer. For the former case, the beam is focused by lens L4 onto a digital camera. For the latter option, lens L3 focuses the collimating beam (including the reflected excitation light and PL signal from the sample) to the entrance slit of the spectrometer. A long pass filter (LWP) preceding the spectrometer allows wavelengths above 1200 nm (e.g. PL emitted from a nanotube) to enter, filtering out 99.9% of wavelengths below that cutoff point (e.g. to attenuate the excitation light). The polarization analyzer can be placed prior to the LWP to study the polarization of PL, which will be discussed in Section 5.1.4. By rotating the $\lambda/2$ waveplate and using the polarizer to select the component of the PL projected on the polarization axis, the PL intensity was recorded as a function of the angle between the SWCNT axis and a linear polarizer. After this stage, signal detection and data acquisition take place using the spectrometer, liquid nitrogen (LN$_2$) cooled InGaAs detector, lock-in amplifier and optical chopper as discussed in Section 3.5.

Figure 3.3: The schematic of the experimental setup.
Figure 3.4: Components of the delay line.

Figure 3.5: The side view of the periscopes.
3.3 Characteristics of Optical Components

Below is an outline of the characteristics and functionalities of each optical component employed in the setup.

- **Mirrors (Thorlabs M01)**: protected gold mirrors, average > 97.5% reflection throughout IR region 0.8-10 \( \mu \)m, to reduce power loss and maintain the quality of the beam profile.

- **Beam splitters (Thorlabs BS011)**: 700-1100 nm broadband, 10 mm beamsplitter cube, antireflection coating for entrance and exit faces, 50:50 splitting.

- **Retroreflector (Newport UBBR1-2I)**: 25.4 mm diameter, antireflection coating, gold protected surface. The benefit of this hollow retroreflector is to maintain the parallelism between the incoming beam and the emerging beam (less than 1 arc sec deviation).

- **Lens (L1, L2, L3, and L4) (Thorlabs LA1509-C)**: plano-convex lens, BK7 \( (n = 1.515 \text{ at } 633 \text{ nm}) \), C-coating (1050-1620 nm). Lens L1 \( (f = 1 \text{ m}) \) serves to maintain the collimation down the line of the beam emerging from the laser cavity. Lens L2 \( (f = 125 \text{ mm}) \) is placed in a translation stage which allows the precise tuning of the spot size on the sample; this lens could be removed to adjust the spot size on the sample. Lens L3 \( (f = 100 \text{ mm}) \) serves to focus the beam into the spectrometer. Lens L4 \( (f = 75 \text{ mm}) \) serves to focus the beam into the imaging system.

- **Aspheric Lens (Thorlabs C110TM-C)**: 0.4 NA, \( f = 6.24 \text{ mm} \), 9.2 mm diameter, anti-reflection coating for 1050-1550 nm range. The alternative of this optic is the conventional microscope objective which is usually much thicker. Too much glass could temporally chirp the beam in an undesired manner. Furthermore, since they
are generally used for visible wavelengths, microscope objectives are not commonly found for the IR regime.

- Glass window (Thorlabs WG11050): BK7 broadband window, 25.4 mm diameter, uncoated.
- LWP filter (Thorlabs FEL1200): cutoff wavelength of 1200 nm, 0.01% transmission in the rejection region.

3.4 Laser Source

3.4.1 Overall Configuration

Figure 3.6 displays the complete laser system. In brief, its operation is as follows:

1. Laser diode: Laser light is converted from low-voltage high-current electrical power. The output from the laser diode is used to pump the Verdi.

2. Verdi V-18: This is a unidirectional and single-frequency ring cavity. It employs Nd:YVO₄ (Neodymium-doped Yttrium orthovanadate) as the gain medium with a characteristic lasing wavelength of 1064 nm. A second harmonic generation process via the birefringent crystal lithium triborate (LBO) produces a 532 nm output.

3. Mira 900: When the Mira 900 is pumped by the green light from the Verdi, its Titanium:sapphire gain medium (Ti:Al₂O₃) lases over a tunable range of 710-1000 nm. It can be operated either in continuous-wave (CW) mode (low peak power, narrow bandwidth of ~ 1-2 nm) or pulse mode (high peak power, broad bandwidth of up to 10 nm). The latter is achievable by a Kerr-lens modelocking mechanism [72]. The pulse has a duration of 150 fs and a repetition rate of 76 MHz (or 13
ns delay between pulses). Since the output from the Mira can be used directly for SWCNT excitation, Section 3.4.2 will focus on the laser optimizing process to obtain a good output beam (in terms of the spatial profile and the output power) as well as to achieve modelocked operation.

4. Optical parametric oscillator (OPO): Once the Mira is modelocked, its pulse train is used for direct SWCNT excitation or to optically pump the OPO. Being synchronously pumped, the nonlinear crystal (periodically poled) in the OPO cavity down-converts the pump photon into two photons of lower energy: the signal beam of 1050-1600 nm and the idler beam of up to 3.4 µm. In this process, both the photon energy and the momentum must satisfy the equations below:

\[ \mu_p = \mu_s + \mu_i \]  \hspace{1cm} (3.1)
\[ n_p \mu_p = n_s \mu_s + n_i \mu_i \]  \hspace{1cm} (3.2)

where \( \mu_p, \mu_s \) and \( \mu_i \) are the frequencies of the pump, signal and idler beam, respectively; \( n_p, n_s \) and \( n_i \) are their refractive indices [73]. It should be noted that although we did not use the OPO for SWCNT excitation, the signal beam from the OPO was used in the calibration of the spectrometer.

Figure 3.6: Schematics of the laser system.
3.4.2 Optimizing the Mira Output

The output power, the beam profile and the modelocked stability for the Mira are controlled by adjusting mirror M7, prism BP2, birefringent BRF, the starter, and the slit (see Figure 3.7). For the daily routine operation, the Verdi is stabilized at 10.5 W and diode current of 47 A. After the system has warmed up, the Mira lases in CW mode. The output power or the beam profile can be modified by tweaking the M7 mirror. To achieve modelocked operation, the following steps are needed:

- The switch on the Mira controller front panel must be toggled from “CW” to “Modelocked” in order to initiate vibration of the starter.

- The detection of modelocked operation is done by the Wavescan spectrometer or by the oscilloscope that is connected to the fast photodiode located inside the Mira.

- The output slit must be centered on the output beam (by adjusting the H knob) and have its width sufficiently narrowed (by adjusting the adjacent knob) so that only the modelocked beam can pass through while the CW component is spatially rejected.

- The prism BP2 can be tweaked to add more glass to the beam path, which helps correct any chirping effects introduced by group velocity dispersion and self-phase modulation. By this means, the adjustment of the spectral bandwidth is possible.

- The birefringent filter BRF is used to set the central wavelength. This capability plays an important role in the PLE mapping experiment (see Chapter 5.1).

The experiments with SWCNT of (9,8) and (10,8) chiralities required pulses with central wavelengths of 800 nm and 860 nm, respectively. It is recommended that the
BRF and BP2 be set to the values recorded in the Mira log book before any other changes are made to achieve modelocking. Although the first attempt at modelocking requires several tweaking steps, switching back and forth between CW and Pulse mode during later trials become more convenient by simply toggling the starter control. It is also noted that for the initial trial of modelocking at 800 nm, it is best to obtain modelocking at 830 nm first and then tune the wavelength down to 800 nm using the BRF. At the same time, tweaking M7 can stabilize the output power and maintain modelocked operation.
CHAPTER 3. SYSTEM DESIGN AND EXPERIMENTAL SETUP

3.5 Signal Detection and Data Acquisition System

3.5.1 Spectrometer and Detector

A HoribaJobin Yvon iHR320 imaging spectrometer is used to analyze the wavelength composition of the photoluminescence.

Optical Design

The optical design of the iHR320 is depicted in Figure 3.8. In brief, a well-focused beam at the entrance slit is collimated by the collimating mirror. After reflection from the grating attached to the turret, the beam is dispersed such that different wavelength components are spatially separated according to the grating equation [74]:

\[ \sin \theta_m(\lambda) - \sin \theta_i = m \frac{\lambda}{d} \]  

where \( \theta_i \) is the angle of the incident beam made with the normal of the grating, \( \theta_m(\lambda) \) is the diffracted angle at order \( m^{th} \) (where \( m \) is an integer). We work with \( m = 1 \) in particular. After the grating, the focusing mirror and reflecting mirror then ensure that the collimating beam is refocused at the exit slit. An elliptical mirror at the side exit window reflects the beam onto the IR photodetector.

Spectrometer Specifications

The major specifications provided by the company are summarized in Table 3.1. Although the iHR320 has dual entrance and exit ports, we currently use the front entrance port and side exit port for inputing the focused beam and collecting the dispersed beam, respectively. The widths of both entrance and exit slits, which determine the throughput and wavelength resolution of the spectrometer, are adjustable from 0 to 7 mm via computer control.
Currently, we have only two gratings on the turret: 900 grooves/mm (wavelength range 600-1700 nm) and 1200 grooves/mm (wavelength range of 300-1200 nm). For nanotube spectroscopy, the former is used with monochromator operation for our spectral analysis. In this mode, the grating is driven by a gear wheel mechanism under stepper motor control to select a certain wavelength hitting the detector. With the direct USB connection to the computer, we can select the entrance and exit ports, the gratings, and set the slit widths using the USB Spectrometer Control Software (provided by iHR HoribaJobin Yvon). The standard settings to initialize the spectrometer for our experiments are as follows:

- Choose spectrometer: iHR320

- Wavelength controls: Position → 1380 nm or 1400 nm (depending on specific wavelength to be detected), Grating → (950, 900, 38535)

- Slits: Entrance → Front → 7; Exit → Side → 7
• Mirrors: Exit → Side

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length</td>
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</tr>
<tr>
<td>Entrance Aperture Ratio</td>
<td>f/4.1</td>
</tr>
<tr>
<td>Spectral Range</td>
<td>600-1700 nm for 900 grooves/mm grating</td>
</tr>
<tr>
<td>Grating Size</td>
<td>68 mm x 68 mm</td>
</tr>
<tr>
<td>Number of Gratings on Turret</td>
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</tr>
<tr>
<td>Minimum Spectral Resolution</td>
<td>0.06 nm *</td>
</tr>
<tr>
<td>Spectral Dispersion</td>
<td>3 nm/mm</td>
</tr>
<tr>
<td>Magnification</td>
<td>1.1</td>
</tr>
<tr>
<td>Stray Light</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Scan Speed</td>
<td>159 nm/s for 1200 grooves/mm grating</td>
</tr>
<tr>
<td>Minimum Drive Step Size</td>
<td>0.002 nm</td>
</tr>
<tr>
<td>Computer Interface</td>
<td>USB 2.0</td>
</tr>
</tbody>
</table>

* This value is claimed by HoribaJobin Yvon. The author verified up to 0.2 nm resolution (see Figure 3.9) for 900 grooves/mm grating with 0.075 mm entrance and exit slit widths.

Table 3.1: Spectrometer specifications [75].

The spectrometer can also be programmed and controlled in a LabVIEW environment based on ActiveX technology (refer to Chapter 4). The subroutines that are used to control the grating for spectral scanning purposes are listed in Table A.1 in the Appendix A.

Specifications of the Detector

A LN$_2$-cooled InGaAs single element detector (DSS-IGA020L) is used in tandem with the spectrometer. Table 3.2 lists the specifications of the detector.

Calibration of Wavelength Setting

The initial grating calibration was completed by a co-worker (Ms. Y. F. Xiao) using a mercury lamp [77]. The author further verified the correctness of the wavelength setting by scanning the spectral lines of a mercury argon calibration source (Ocean Optics
Operating Temperature (°C) | 22 | -196
---|---|---
Spectral Range (μm) | 1.0-1.7 | 1.0-1.5
Responsivity (V/W) | 9x10⁹ (low gain) | 2x10⁹ (low gain)
NEP (W/√Hz) | 5x10⁻¹⁴ | 1x10⁻¹⁵
Detector Type | 2 mm diameter InGaAs photodiode | Dual Gain Transimpedence
Amplifier | | LN₂ Downview Dewar
Package | | 12 Hours Nominal
Hold Time | | BNC Output; Shielded Power Cable
Connections | | Table 3.2: Detector specifications [76].

HG-1) for the range of 900-1500 nm with the iHR320 spectrometer and confirming the consistency of these peaks with predetermined values from the “National Institute of Standards and Technology (NIST) Atomic Spectra Database Lines Form” [78] and the list of Ar strong emission lines provided by the HG-1 light source manufacturer [79]. In this test, both the entrance slit and the exit slits were set to their smallest widths of 0.075 mm in order to achieve the highest resolution. Figure 3.9(a) and 3.9(b) are examples of a 900-950 nm and 1345-1400 nm range spectral scans for the HG-1 light source obtained by the iHR spectrometer. These spectral scans not only reveal the narrow peaks (less than 1 nm FWHM) but also the consistency (less than 0.5 nm) in wavelength values corresponding to strong Ar and Hg emission lines (marked as red star symbols) that are specified in the databases and summarized in Table 3.3. The accuracy in wavelength setting of the spectrometer is sufficient for our studies.

Calibration of Spectrometer Bandpass

The bandpass (BP) of the spectrometer is defined as: BP = Linear Dispersion × Exit Slit Width, or Image of Entrance Slit Width (whichever is greater) [75]. The linear dispersion for the 900 grooves/mm grating is 3 nm/mm. Hence, with the entrance slit set to 0.075 mm, the BP is expected to be 3, 6, 12 and 21 nm for exit slit widths of...
<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral Line (nm)</th>
<th>Database Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>912.297</td>
<td>HG-1 Manufacturer [79]</td>
</tr>
<tr>
<td>Ar</td>
<td>922.450</td>
<td>HG-1 Manufacturer [79]</td>
</tr>
<tr>
<td>Ar</td>
<td>1371.858</td>
<td>NIST [78]</td>
</tr>
<tr>
<td>Hg</td>
<td>1350.268</td>
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<td>Hg</td>
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<td>NIST [78]</td>
</tr>
<tr>
<td>Hg</td>
<td>1395.055</td>
<td>NIST [78]</td>
</tr>
</tbody>
</table>

Table 3.3: List of strong Ar and Hg emission lines for a 900-950 nm and 1345-1400 nm wavelength range provided from the NIST database and the HG-1 light source manufacturer.

Figure 3.9: Spectral scan of mercury argon calibration light source for (a) 900-950 nm and (b) 1345-1400 nm wavelength range acquired by the iHR spectrometer. Red stars represent the positions of Ar and Hg strong emission lines as retrieved from the databases and summarized in Table 3.3.
1, 2, 4 and 7 mm, respectively. These tests were carried out by the author using a monochromator source (HeNe at 633 nm). Figure 3.10(a) shows the experimental BP measurement for four exit slit widths. The BP as a function of exit slit width is plotted in Figure 3.10(b) and compared to predictions. The measured BP is $\sim 3\%$ smaller than the predicted values, suggesting the exit slit width might be slightly off.

Figure 3.10: Calibration of the spectrometer bandpass: (a) Spectral scans of HeNe line with various exit slit widths (1-7 mm) to measure the spectrometer bandpass; (b) The comparison between the spectrometer bandpass theoretically calculated and FWHM measured from (a).

### 3.5.2 Measurement with a Lock-in Amplifier

A lock-in amplifier (Stanford Research Systems SRS530) is used to detect the low voltage signal from the transimpedance amplified InGaAs detector, resulting from the low PL emission from the nanotube. It behaves as an electronic filter with a very narrow bandpass tuned to the chopping frequency of the input signal.
CHAPTER 3. SYSTEM DESIGN AND EXPERIMENTAL SETUP

Front Panel Setting for LIA

With an input signal coming from the detector and an external reference from the optical chopper, the parameters on the LIA’s front panel are set as follows:

1. Signal Input: A

2. Signal Filters: Bandpass = In, Line = In, Line × 2 = In

3. Sensitivity: 500 µV

4. Dynamic Reserve: Low

5. Display Select: Use X(Rcosθ) and Y(Rsinθ)

6. Reference: Input → the optical chopper provides the oscillating signal for the reference input (in particular, we use 20 Hz and 70 Hz setting for the optical chopper for high gain and low gain settings of the InGaAs detector, respectively); Reference Phase → This is set such that the Y component of the output signal is zero and the X component of the output signal is maximized; Mode → f; Trigger → square wave

7. Time constant: Post → 0.1 s; Pre → 1 s (for a 20 Hz chopping rate and a high gain for the detector) or 300 ms (for 70 Hz and a low gain for the detector). Since 100 s time constant gives a bandpass of 0.0025 Hz centered at the reference frequency input [80], we expect our setting for the time constants will result in band passes of 0.25 Hz and 0.85 Hz.

Communicating with the LIA

With a 4 MHz microprocessor, the LIA can be programmed from the computer via the RS232 and IEEE-488 digital communication standards. The major commands to
CHAPTER 3. SYSTEM DESIGN AND EXPERIMENTAL SETUP

interact and control the LIA in our experiments are listed in Table A.2 in Appendix A. To systematically test the LIA response to any command sent from the computer, the author used RS232 with an ASCII terminal. Eight configuration switches of the SW2 bank on the rear panel of the LIA are responsible for the communication parameters (baud rate, parity and stop bits). However, for regular experimental measurements, we employ the GPIB interface for higher speed communication. A 1 MHz GPIA (General Purpose Interface Adapter) interrupts the 4 MHz microprocessor whenever a GPIB transaction occurs and requires the CPU’s response. The GPIB address of the LIA is set by the SW1 configuration switches. Using the GPIB controller for High Speed USB 2.0 (National Instruments GPIB-USB-HS), we can transform the computer with a USB port into a plug-and-play IEEE 488.2 controller to program the LIA through the GPIB. The communication from computer to the LIA via high speed USB 2.0 allows up to 1.8 MB/s with the standard IEEE 488 handshake.

After the installation of the GPIB controller, the Measurement and Automation Explorer (National Instrument NI-MAX) application was used to detect the device, scan for the LIA instrument and test the communication line. Once the GPIB interface is properly configured, GPIB functions (e.g. Read, Write, Initialization, Status, Wait) in the Instrument I/O library provided by LabVIEW VI Development System are called to handle the communication with the LIA.

3.5.3 Calibration of System Throughput

The overall throughput of the signal detection and data acquisition system (from the spectrometer to the LIA) was calibrated at 800 nm by the author and at 1380 nm by a co-worker (Ms. Y. F. Xiao) [77]. Since the latter wavelength has more relevance to the experiment, the calibration result at this wavelength using the OPO beam will be
explained in detail. The output of the OPO (central wavelength: 1380 nm, spectral bandwidth: 15-20 nm was focused into the entrance slit of the spectrometer. The reflection coefficient of the beam from the collimating mirror, focusing mirror and reflecting mirror is measured to be 0.93, which agrees with the specification values. Furthermore, the diffraction grating’s relative efficiency at 1380 nm is also consistent with the 0.8 value presented on the calibration curve provided by the manufacturer at the wavelength range of 1300-1500 nm for TM mode. Hence, the total throughput of the spectrometer immediately after the elliptical mirror that focuses the beam from the exit slit into the light sensitive element of the detector is 0.59, ignoring clipping of the exit slit. However, after the dispersion at the grating, 15 nm bandwidth light is partially clipped by the exit slit (even at 7 mm size), resulting the total throughput of only 0.42.

The verification of the detector sensitivity was first performed for a DC signal by measuring the power input into the detector using a thermal optical power sensor (Thorlabs S210A) and comparing it with the DC voltage detected by the oscilloscope when the detector was set at low gain. It was found to be 0.89 times less than the value claimed on the specification document (2×10^9 V/W at low gain setting). Nevertheless, a ten-fold improvement was observed when switching from the low gain to the high gain setting. To calibrate the detector sensitivity with lock-in amplification (i.e. oscillating signal at chopping frequency), the incident OPO beam is chopped at 70 Hz and the output signal was monitored by both the oscilloscope and the LIA (which is our main data acquisition tool). With the detector set to low gain, the voltage signal (peak-to-peak) detected by the oscilloscope is 3.1 times higher than that on the LIA. Furthermore, the detector sensitivity at high gain and a 20 Hz chopping rate (which is used in our experiment to achieve a higher signal-to-noise ratio) was found to be 3.4 times higher than the sensitivity achieved with low gain and a 20 Hz chopping rate, due to limited
electronic bandwidth of photodetector and transimpedance amplifier. The overall efficiency, in terms of the input signal entering the detector and the output signal of the LIA, is summarized in Table 3.4.

<table>
<thead>
<tr>
<th>Input Power</th>
<th>LIA Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>1380 nm central wavelength</td>
<td></td>
</tr>
<tr>
<td>15-20 nm bandwidth</td>
<td></td>
</tr>
<tr>
<td>0.1 pW</td>
<td></td>
</tr>
<tr>
<td>Low gain</td>
<td>70 Hz</td>
</tr>
<tr>
<td>High gain</td>
<td>20 Hz</td>
</tr>
<tr>
<td>60 µV</td>
<td>200 µV</td>
</tr>
</tbody>
</table>

Table 3.4: Overall efficiency of the detector and the LIA.

3.6 Motion Control

3.6.1 Sample Stage DC Servo Motor

To facilitate automated 2D motion of the translation stage holding the SWCNT sample, we used two DC servo actuators (Thorlabs Z625B). Driven by 12 volts, each motor has an optoelectronic feedback device (Quadrature Incremental Encoder), with a light source (LED) and photosensor pickup to detect markings on a glass scale. The high precision optical rotary encoder offers: 48 Count Encoder × 256:1 Gear Head = 12288 counts/revolution [81]. They support a 25 mm travel range, 40 nm minimum incremental movement and backlash of less than 8 µm. The motor also has mechanically built-in limit switches to provide overdrive protection.

The DC servo motors are controlled by DCX modules installed on a DCX-PCI100 motherboard. The motherboard with 192 MHz processor is mounted on the PCI slot of the computer and dynamically addressed into the PC memory map, and programmed to perform motion control tasks. Each DCX module provides circuitry to control one motor and its associated axis I/O (home, limit switch, servo encoder, and amplifier). Although the DCX Modular Motion Control system could manage up to eight servo
motors simultaneously, we only make use of two motion control modules (DCX-MC110) to coordinate x and y axis for 2D motion. The cable interface (Thorlabs Z600-CAB2) connects the servo motor to its designated motion control module. The Motion Control Application Programming Interface (MCAPI) provides support for visual programming like LabVIEW. Accuracy of motion control system was tested. The Motor Mover program (part of the Motion Integrator development tool in the Motion Control package) is used to instruct the motion of these motors manually and monitor their positions and status. For each axis, we can also set the maximum velocity and acceleration, or reset the zero position. In our experiment, two servo motors are used to move the nanotube sample around the excitation beam. To coordinate the control of the DC servo motors along with other instruments (e.g. the LIA, the spectrometer) for automatic sample scan in LabVIEW programming, we employ MCAPI functions (sub VIs) provided by the Motion Control package. All MCAPI subVis that are used in our LabVIEW programs are listed in Table A.3 in Appendix A.

3.6.2 Delay Line Stepper Motor

Our initial implementation of the delay line was to use a manual 1D translation stage to displace the retroreflector. When the retroreflector is displaced by $\Delta x$, the corresponding delay time is $t_d = \frac{2x\Delta x}{c}$, where $c$ is the speed of light. By stacking two 1D translation stages to obtain a total traveling range of 3 inches, the maximum delay time we were able to achieve was 500 ps. However, manually controlling the delay time throughout the full range of 500 ps for several scans in the FEC experiment was time consuming. We therefore used the stepper motor for the automatic control of the translational motion. The benefit of this stage included: more accurate setting of the delay time, decreased scanning time due to higher speed of the motor, longer delay time (1.3 ns) thanks to a
wider range of the translational motion, and automation of FEC experiment (for time-resolve PL study as mentioned in Section 2.6.4) using computer control.

Specifications

The stepper motor (American Precision Industries, Inc 23D-6108A) has the following specifications:

- Resolution: 400 steps per revolution or 0.9° step angle.
- Speed: 1 to 6000 steps/sec in 1 step/sec increment.
- Index distance: ±1 to ±1048575 steps.

The Velmex NF90 is a programmable controller to manage the stepper motor. RAM on the controller’s electronic circuit stores any user-entered commands and motion parameters. The main features of the controller include [82]:

- A digitizing function allows readout of motor position from host terminal.
- The motor position can be read while the motor is in motion.
- Zero position is programmable.
- Backlash compensation can be set automatically.

Using the serial port (RS-232-C standard), the host computer can send commands in ASCII characters to the motor controller, post data poll for status and read out the position of the motor. Specific settings for this communication are: 7 data bits, 2 stop bits, even parity, and 9600 baud rate. Primary commands used in my LabVIEW programs to control the stepper motor are summarized in Table A.4 in Appendix A.
Calibration of the Stepper Motor

With the stepper motor driving the 1D translation stage to control the delay line (see Figure 3.11), it is desirable to attain high accuracy and reproducibility in linear motion control. However, this system was formerly used by other research group, hence required cleaning and thorough calibration. The following tests were performed by the author and another co-worker (Ms. Y. F. Xiao) to ensure reliable operation of this system.

![Image of stepper motor and controller for the delay line](image)

**Figure 3.11:** Stepper motor and controller for the delay line.

1. **Transverse distance and maximum speed in operation:** although the translation stage originally had a full traveling range of 32 inches, the current functional range of the stepper motor is limited to 12 inches due to the mechanical problem. This region was marked on the shaft of the translation stage. Furthermore, although the maximum speed of the motor was claimed to be 6000 steps/s [82], in practice, the motor should be operated below 4000 steps/s to ensure smooth translational motion.

2. **Repeatability in motion and backlash of the stepper motor:** using a microscope with...
200× magnification, images of two consecutive division bars on a ruler separated by 500 µm were zoomed in and used for distance measurement. A clamp was mounted on the stepper motor and its sharp edge was then imaged by the microscope. When the stepper motor was instructed to move in either direction and return to the initial position, the edge was observed to have been shifted by one-seventieth of 500 µm, or 7 µm. Furthermore, with large back and forth traveling movements made several times, the shift of the sharp edge compared to its initial position was localized within a 28 µm range. The uncertainty of 28 µm implies the setting of delay time is reliable beyond 200 fs.

3. **Conversion ratio from steps to millimeter**: the conventional unit used in motion control software for the stepper motor is steps, but we used millimeter (or inch) for linear motion of the translation stage. The conversion ratio from steps to millimeter was calculated as follows: the threaded rod connecting the translation stage to the motor has 10 threads/cm, the stepper motor has 400 steps/thread (or steps/revolution), hence, we expect the conversion ratio to be 4000 steps/cm.

### 3.7 Imaging System

It is desirable to image the sample surface optically (to gain insight into the orientation and spacing of trenches and ridges as discussed in Section 3.1) and view the excitation spot on the sample (to inspect the symmetry of the beam profile or estimate the spot diameter). We illuminate the sample with 800 nm light from the Mira oscillator; the reflected light from the sample surface follows the same path as the PL but is then redirected at the flip mirror (refer to Figure 3.3). Another lens (i.e. lens L4) collects the reflected beam and creates an image that is detected and captured by a CCD camera (PixeLINK PL-A741). This camera has a resolution of 1280×1024 and pixel pitch of 6.7
Once the vertical separation between the sample and the aspheric lens is fixed (e.g. after optimal PL is achieved), the magnification of the image is controlled by varying the position of lens L4. The camera position should also be adjusted until a sharp image of the sample surface is obtained. The field of view can be measured by moving any distinctive feature on the sample from one end of the field of view to the other along the x (or y) axis with Motor Mover software and measuring the total traveled distance. This measurement also allows us to calculate the equivalent $\mu$m per pixel in each direction. Therefore, when the image of the excitation spot on the sample is acquired, its FWHM (in the unit of pixels) from the analyzed image profile could be reconverted into $\mu$m unit. A more accurate spot size measurement will be described in Section 5.1.2.

### 3.8 Optical Setup of 4f Grating Pair Configuration

In our study of the pump power dependence (PPD) of PL with the pulse excitation, it is desirable to explore the dependence of emitted PL with pulse durations. This allows us to investigate the intermediate excitation processes between two extreme cases: short pulse excitation (150 fs) and “infinite duration” excitation (CW). A 4f grating pair configuration was employed to control the duration of the excitation pulses. As schematically shown in Figure 3.12, the input beam from the Mira is spectrally dispersed by the first grating G1 and focused by lens L1. A second lens L2 refocuses the dispersed light onto the second grating G2, which in turn brings the dispersed spectrum back into short pulse. Two gratings (Thorlabs GR25-1208) with 1200 grooves/mm and two lenses (Thorlabs LA1708-B) of focal length $f = 20$ cm are separated from one another by $f$. To control the temporal duration of the output pulse, a hard aperture is positioned at the focal area between lens L1 and lens L2, to filter the spectral content of the dispersed
beam. This system was originally set up by a previous graduate student, Mr. Matt Muller, to manipulate pulses with 830 nm central wavelength [83]. However, for the purpose of our experiment, the re-alignment of the two gratings was performed in order to operate at 800 nm central wavelength. Moreover, we also replaced the previously-used adjustable iris with a micrometer-controlled slit. This offers a greater cutoff in bandwidth, equivalent to greater stretch in pulse duration. One disadvantage imposed by this 4f grating pair system, however, is the dramatic loss in output power emerging from the system since the beam is physically clipped by the hard aperture. With the smallest slit width with sufficient power for PPD measurements, the corresponding temporal duration is 4 ps. The output pulse spectrum is acquired by a spectrometer (APE Wavescan spectrometer) and pulse autocorrelation trace is measured by a two-photon autocorrelator (APE GmbH MINI autocorrelator). Figure 3.13 shows the power spectra and the associated autocorrelation traces for various slit widths. Resulting values for spectral bandwidth FWHM, Gaussian fit FWHM of the autocorrelator trace and the output power available for the PPD experiment are listed in Table 3.5.

Figure 3.12: 4f grating pair schematics. G1 and G2 are dispersive gratings; L1 and L2 are focusing lens; S is the manually controlled slit.
Figure 3.13: 4f grating pair normalized power spectrum and autocorrelator trace at different slit widths. The deconvoluted FWHM of pulse duration assuming a Gaussian shaped pulse for each case is shown on the legend.

<table>
<thead>
<tr>
<th>Output Spectral Bandwidth FWHM (±0.1 nm)</th>
<th>Autocorrelation Trace Gaussian fit FWHM (ps)</th>
<th>Output Power (±1 mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>0.15±0.01</td>
<td>135</td>
</tr>
<tr>
<td>0.9</td>
<td>2±0.1</td>
<td>20</td>
</tr>
<tr>
<td>0.5</td>
<td>4±0.5</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3.5: Temporal broadening of pulse duration by spectral filtering with 4f grating pair.
Chapter 4

LabVIEW Programs

Six different LabVIEW programs designed by the author to assist in various experimental measurements will be discussed in this chapter.

4.1 Sample Scan

4.1.1 Sample Rapid Scan

The purpose of this LabVIEW program is to raster scan a new sample over a large area (e.g. 4×8 mm²) to search for approximate positions of SWCNTs of a specific chirality. The sample is placed on the translation stage and exposed to an excitation spot (e.g. 20 µm diameter) at the resonant wavelength for the SWCNT chirality (e.g. 800 nm for (9,8) chirality). The spectrometer is set to select the emission wavelength (e.g. 1380 nm for (9,8) chirality), and the InGaAs detector in tandem with the LIA records the PL signal. With two DC servo motors controlling the translation stage, the sample is scanned under the illumination of the fixed excitation beam. While the current positions of the two motors, which are equivalent to a point (x,y) on the sample, are read out from the Motion Control modules, the associated PL signal is acquired from the LIA
and streamed into the computer via GPIB interface. A full 2D raster scan is achieved by assigning one servo motor to operate the “Rapid Axis” (x) and the other to control the “Step Axis” (y). The former ensures that every line in the scanning area is scanned from one end to another, and access to the next line is provided by the latter. The scanning result is a list of three columns: x, y, and associated PL. In order to operate this program, the following input fields in the front panel of the LabVIEW VI are needed:

1. GPIB parameters including **GPIB Address**, **Number of Bytes to Read**, and **Timeout (ms)**: these values have been initially set during the installation and configuration of the GPIB interface. Their default values are: 19, 20, and 5000, respectively.

2. **Wait Time (ms)**: this controls the time elapsed between the acquisition of two consecutive [x,y,PL] entries. Ideally, minimizing **Wait Time** increases the size of the [x,y,PL] list, hence revealing more details of the sample. However, **Wait Time** should be comparable to the time constant set for the LIA and the transfer rate from the LIA’s microprocessor to the GPIB.

3. **File Name**: This user-defined **File Name** is appended to a predetermined folder name and a specific date and time of the experiment to create a full file path where the output data will be stored.

4. “Rapid Axis (X)” allows Motor 1 (or 2) to be selected. The associated parameters for this axis are: **X Initial Position**, **X Scan Range**, and **X Backlash**.

5. “Step Axis (Y)” allows Motor 2 (or 1) to be selected. The associated parameters for this axis are: **Y Step size**, **Y Initial Position**, **Y Scan Range**, and **Y Backlash**.
The flow chart in Figure 4.1 describes the structure of the program. Once the assignment of the servo motor for the “Rapid Axis” or “Step Axis” is decided by the user and essential scanning parameters (scanning range, initial position, final position and backlash compensation) in each axis are converted from user-input unit $\mu m$ to the motor encoder’s unit $counts$, both motors are set to their initial positions to begin the 2D raster scan. The program also keeps track of the starting and finishing time of the entire scanning process. The outer “While loop” ensures that the program is terminated either by the completion of the Step Axis or cancellation from the user (e.g. hitting the Stop button). For each y position of the “Step Axis”, the “Rapid Axis” is scanned either from its initial or final position to the other end. Backlash correction is also executed every time the motion of the “Rapid Axis” is reversed. Delayed by $Wait\ Time$, the PL signal (in $\mu V$) is obtained using the GPIB Read function and the current (x,y) positions of the two motors are read out from their modules and reconverted from $counts$ to $\mu m$). A complete stack of the [x,y,PL] entries forms a 2D array which is displayed as an intensity profile on the front panel and stored as .xls and .dat format files. For the latter format, the original 2D array of data is maintained. However, due to the limited number of rows supported by Excel (i.e. 65535 rows), the LabVIEW program needs to check whether the length of the output 2D array exceeds the limit. In such a case, the original 2D array is fragmented into several sub-2D arrays and appended side by side. The important settings of the LIA (e.g. sensitivity, dynamics response, and time constant) are also acquired by the GPIB and stored in the same file.

4.1.2 Sample Step Scan

Once a SWCNT is identified from the sample scan, it is desirable to record a high resolution PL image of the SWCNT, in order to estimate its length and determine its
orientation. This LabVIEW program is therefore designed to perform a 2D scan around a nanotube in stepping mode of both DC servo motors for high resolution imaging purpose. The overall scheme of this scanning process (i.e. optical setup, parameter setting, and data output) is similar to the sample raster scan. However, two distinct features implemented in this program are:

- With the conversion of the “Rapid Axis” into another “Step Axis”, the program waits at each discrete points in the x axis for a certain amount of delay time then records the associated PL signal.

- To completely avoid any backlash issues, the x axis is step scanned in only one direction (e.g. if the first row is scanned from left to right, when the next row is accessed, Motor x will quickly scan from right to left, overshoot the starting point, reverse its direction, return to the starting point and step scan this second row from left to right).

Figure 4.1: Flow chart of the “Sample Rapid Scan.vi” LabVIEW program.
In addition to the GPIB settings and “File Name” input mentioned in the previous program, new input fields in the front panel required in this program are:

1. **Wait Time (ms)**: this ensures that the PL values at each discrete (x,y) position are averaged by the LIA for noise reduction before being read out.

2. “Axis X” (replacing “Rapid Axis”) allows Motor 1 (or 2) to be selected. The associated parameters for this axis are: **X Stepsize, X Initial Position, X Scan Range**, and **X Backlash**

3. “Axis Y” (replacing “Step Axis”) allows Motor 2 (or 1) to be selected. The associated parameters for this axis are: **Y Stepsize, Y Initial Position, Y Scan Range**, and **Y Backlash**

The “Sample Step Scan.vi” program shares similar initialization and file-saving steps with the previous “Sample Rapid Scan.vi” program. The key difference lies in the control of the 2D step scan, as presented in Figure 4.2. The second “While loop” controls the stepping motion in the x direction. The program ensures that once each step is made and the (x,y) positions are recorded, a certain amount of delay time is spent at that position before acquiring the associated PL signal.

### 4.2 Spectral Scan

It is desirable to acquire the emission spectrum from a SWCNT for the analysis of its linewidth, lineshape and peak wavelength (e.g. for a (9,8) chirality, we examine a 80 nm range, from 1340 nm to 1420 nm). The spectrometer needs to be instructed to step from one wavelength to another over the range of interest and the PL signal is recorded at each wavelength component. This program provides automated spectrum recording by incorporating spectrometer control and LIA data acquisition. The program also allows
for several scans of the same wavelength range to be acquired and averaged for the reduction of noise. The control fields in the front panel needed to be input by the user are:

1. **GPIB setting:** GPIB Address, Number of Bytes to Read, and Timeout (ms).

2. **Spectrometer setting:** Spectrometer ID (Mono1 is applicable in our case).

3. **Spectral scan parameters:** Number of Scans (to support multiple-scan), Set Starting WL ($\lambda_{\text{min}}$), Set Stop WL ($\lambda_{\text{max}}$), Step Size (increment in wavelength), Wait Time (ms) (to allow the LIA to settle to a new value).

4. **File name:** to specify the storage location for the spectral scan results.

The flow chart in Figure 4.3 illustrates the structure of this LabVIEW program. Based on the user-input values ($\lambda_{\text{min}}, \lambda_{\text{max}}$ and step size $\Delta \lambda$), the number of visited points in wavelength is calculated and used as a threshold value to signify the scanning limit. In particular, for each spectral scan starting from $\lambda_{\text{min}}$, the spectrometer is commanded
to make an increment in wavelength ($\Delta \lambda$) via the “MoveToWavelength” subroutine, and the program waits for a specified amount of time for the LIA to average the PL signal. The inner “While loop” is responsible for the completion of each spectral scan, with a plot of PL versus wavelength being updated on front panel’s “Current scan” display and a list of $[\lambda, PL]$ is stored in an .xls file titled “File Name” + “current scan number”. The outer “While loop” verifies the completion of the multiple scans specified by the “Number of Scans” field. At the exit of this “While loop”, an “Average scan” obtained by averaging all the acquired spectral scans is displayed and its list of $[\lambda, Averaged PL]$ is saved into a .xls file labelled “File Name + -1”. The status of the LIA settings for the experiment are retrieved via GPIB Read and recorded as the header of these saved files.

4.3 Data Recording

This program automates data acquisition from the LIA for PPD experiments (in which PL from a SWCNT is measured as a function of the manually controlled excitation power). Aside from the primary parameters required for GPIB interface (GPIB Address, Timeout and Number of Bytes to Read) and “File Name” for the storage location of the output data, the user needs to specify these parameters:

- **Number of data points for each setting**: how many data points to be collected at each excitation power.

- **Wait for next data**: the delay in time (ms) between the acquisition of two consecutive data points. The length of this waiting time should be based on the currently set LIA time constant.

- **Wait until the next setting**: the separation in time (ms) between two sets of
Figure 4.3: Flow chart of the “Spectral Scan.vi” LabVIEW program.
data associated with different excitation powers. The length of this waiting time should be sufficient for the user to manually change the excitation power on the SWCNT.

The flow chart shown in Figure 4.4 describes the implemented structure of the program. Data recording is continued until the user decides to terminate using the Stop button on the front panel. The completion of each data set associated with a distinct excitation power is monitored by a “For loop”. The program forces consecutive data points to be separated in time so that LIA can settle to the new PL value. Upon completion of data acquisition for the current set, the program generates a beeping sound to notify the user to set a new excitation power. The program waits a specified amount of time for the setting of new power before a new associated data set is acquired. The output file stores data in a 2D format in which each column is associated with PL signals from the SWCNT under a particular excitation power.

### 4.4 Automated FEC Measurement

This program combines motion control of the stepper motor and data acquisition from the LIA to automate the FEC experiment. It controls the delay time, speeds up the measurement (compared to manually controlling the 1D translation stage) and has multiple-scan capability (for several scans of the same delay times to be recorded and averaged). In addition to the default settings for the GPIB interface as in previous programs, the following parameters for the stepper motor and serial connection are also kept fixed:

- **Serial Port Number**: COM1
- **Motor Number**: Motor 1
- **Motor Speed**: 2500 steps/s
Figure 4.4: Flow chart of the “Data Recording.vi” LabVIEW program.
• Conversion ratio from Delayed Time (ps) to Stepper Motor position (steps): 60

• Motor Position at Zero Delay: 0

The user needs to specify the following parameters on “Settings for Data Acquisition” section in the front panel:

• “Range of delay time”: Measurements by other research groups suggested that PL dynamics of a SWCNT has a very fast decay component (less than 5 ps) and slow decay component (100-200 ps) [51, 61]. Therefore, with the maximum delay time of 1.3 ns accessible in our system (refer to Section 3.6.2), it is essential to investigate the early time (less than 5 ps) in a linear scale for high resolution, while the later time (from 5 ps to 1.3 ns) can be examined in a log scale for the overall decaying trend. To support these two different time scales, the LabVIEW program prompts the user for five relevant inputs: From(ps) for the starting of linear scale; To(Linear)(ps) for ending linear scale and starting log scale; To(Log)(ps) for ending log scale; Total number of delay time data points for total visited time delay of the entire range; Number of delay time data points in log scale is input by the user. Therefore, the number of delay time data points in linear scale should be the difference of the previous two values.

• Number of scans: allows multiple scans of the same range of delay time to be recorded. These scans are averaged in the end to reduce scattering in the signal.

• At each delay time, the user can set these following parameters: Number of data points collected at each delay time (N_{recorded}) to specify number of PL values to be recorded, Wait Time between data, and Number of data points
for averaging \( N_{\text{average}} \) to specify how many PL values among all the values recorded will be averaged, hence \( N_{\text{average}} \leq N_{\text{recorded}} \).

As summarized by the flow chart in Figure 4.5, the program first configures the GPIB interface with the LIA, establishes the serial connection with the stepper motor controller, initializes the stepper motor and creates a file path for data saving. Based on the user inputs for the limits of delay time in log and linear scale, and the number of delay time points in these two domains, the program generates a full list of delayed time values (in ps) and the equivalent positions of the stepper motor, from which the displacement between two adjacent points (\( \Delta d = \text{next position} - \text{current position} \)) is extracted for the relative motion of the motor. The outermost “For loop” keeps track of the number of completed scans. For each scan, a series of delay times are visited in an increasing or a decreasing order (e.g. when \( \Delta d \) is input for \( x \) in the “ImMx” command (refer to Table A.4), the sign of \( x \) informs the motor to rotate clockwise or counter clockwise). At each delay time, the program reads out several PL values and averages them for mean value and standard deviation. A complete record of FEC data in a 2D array format is saved in an .xls file: the first two columns are the list of delay times and the corresponding positions of the stepper motor, other columns of associated data (i.e. average PL and its standard deviation) from several scans are appended side by side.
Figure 4.5: Flow chart of the “Automated FEC Measurement.vi” LabVIEW program.
Chapter 5

Experimental Results and Analysis

Using the setup described in Chapter 3 with the control programs introduced in Chapter 4, various experiments performed on single air-suspended SWCNT will be presented in this chapter. Section 5.1 describes a typical sample scanning process in order to search and select a specific SWCNT and also provides the evidence of an isolated individual SWCNT including high resolution PL imaging of a SWCNT, its PLE map and PL polarization data. Since nonlinear dependence on the pump power of PL from SWCNT was observed for both ensembles and a single SDBS-encapsulated SWCNT, we would like to conduct this pump power dependence measurement on an individual air-suspended SWCNT. As a focus of Section 5.2, this work will allow us to verify the existence of nonlinear processes intrinsic to the SWCNT system. Directly from the PPD measurements, quantum efficiency can be estimated and its correlation with tube length can be elucidated. The time-resolved PL experiment using the FEC technique for single air-suspended SWCNT, as presented in Section 5.3, will allow the PL decay times to be measured and compared with values found for other SWCNT systems (e.g. ensemble, micelle-encapsulated single tube). This study will shed light on the presence of intrinsic and extrinsic decay channels that contribute to exciton dynamics.
5.1 Single Tube Identification

5.1.1 Sample Scan

To roughly identify locations of SWCNTs of a certain \((n,m)\) chirality over large areas of a substrate, we performed a rapid 2D scan of the sample by illuminating it with the resonant excitation wavelength (i.e. \(E_{22}\) transition of the SWCNT) while constantly monitoring the PL level of the emission wavelength (i.e. \(E_{11}\) transition).

The sample was placed firmly at the corner of a groove etched on an aluminum plate that rests on a 3D translation stage (refer to Figure 3.5). We first ensured that the sample was at the correct distance away from the aspheric lens so that the PL signal is maximized. To do this, we used the phase adjusters to move the sample around the excitation spot (~ 20 \(\mu m\)) to manually search for any SWCNT. Once a SWCNT was detected, we then varied the \(z\) axis of the translation stage to raise or lower the sample until the PL signal was optimized. We then used the DC servo motors for automatic 2D motion control, as explained in Section 3.6.1. Any location on the sample can be specified based on the positions of the servo motors (called \(x\) and \(y\) axes). The \((0,0)\) coordinate for these two axes was set by bringing the left bottom corner of the sample under the illumination of the excitation beam. The “Sample Rapid Scan.vi” LabVIEW program (refer to Chapter 4) was used to control the 2D motion of two DC servo motors to scan the sample under the excitation spot and record the PL signal.

In terms of the parameters in the “Sample Rapid Scan.vi” LabVIEW program to perform a sample scan, the scanning ranges in both axes were set comparable to the size of the sample (e.g. usually up to 8000 \(\mu m\) long and 4000 \(\mu m\) wide). The step size for "Step Axis" was set comparable to the excitation spot size (e.g. 20 \(\mu m\) in diameter). Backlash compensation for both axes was 8 \(\mu m\). The waiting time was set to 50 ms when the speed of the two DC servo motors were set in the Motor Mover program to
4000 counts/s and 9000 counts/s for the “Rapid Axis” and “Step Axis”, respectively, and the LIA’s time constant was set to 300 ms. Two controlling factors that determined the scanning time were the step size of the stepping axis and the motor speed of the rapid axis. On average, it took approximately 1.5 hours to completely scan a 8×2 mm² sample.

The scanning results were stored in a spreadsheet in form of three columns that correspond to x, y and PL values. By sorting the spreadsheet according to the PL values, the locations of the brightest tubes were identified. Thus, a map containing the positions of bright SWCNTs on the sample and their associated brightness can be constructed. As long as the physical location of the sample on the aluminum plate remained unchanged, one could always go back to the scanning records and access a specific nanotube. Figure 5.1 and 5.2 are maps of (9,8) SWCNTs (done by a co-worker, Ms. Y. F. Xiao) [77] and (10,8) SWCNTs (done by the author) that were constructed from the scanning results. These maps suggest the our sample has a very low density of SWCNTs, which is beneficial for single tube study.

Figure 5.1: An example of the sample map of bright (9,8) SWCNTs taken by a co-worker (Ms. Y. F. Xiao).
5.1.2 High resolution PL Imaging of SWCNT

In order to estimate the length of a SWCNT and identify its orientation on the sample, we performed high resolution PL imaging of the tube. Following the same principles as the sample scanning process, however, we focused the excitation spot size down to 2 \( \mu \text{m} \) and scanned an area of 30\( \times \)30 \( \mu \text{m}^2 \) in the proximity of the SWCNT. The automatic stepping motion in both x and y axes was performed by “Sample Step Scan.vi”. The ability to control the excitation spot size was provided by placing a 125 mm convex lens before the aspheric lens. To measure the spot size, we captured the image of the spot on the sample surface using the imaging system as discussed in Section 3.7 and analyzed its profile to extract the FWHM.

For this 2D high resolution imaging scan, the speed of both DC servo motors were set to their maximum value of 9000 counts/s. The “Sample Step Scan.vi” LabVIEW program’s inputs for the initial positions and scanning ranges in the x and y axis were determined by moving the excitation spot away from the tube in both directions until the PL signal drops to the background level. The waiting time in the LabVIEW program
was set comparable to the LIA’s time constant, allowing the PL signal at each visited point on the scanning area to settle before readout.

Similar to 2D sample scan, the data here were stored as [x,y,PL] form in a spreadsheet. This original format was converted into a matrix form to plot the contour map for the image of the tube. The initial version of “Sample Step Scan.vi” allowed the transverse motion along the x axis in both directions (e.g. if the first row was scanned from left to right, the second row would proceed in the opposite direction). This scanning scheme was efficient, yet caused a backlash issue which manifested itself as an 8 \( \mu \text{m} \) shift of the bright peak for every other row along the x axis in the 2D image of the SWCNT (see Figure 5.3(a)). The first attempt to solve this problem was to artificially compensate for backlash by correcting the position of the motor by 8 \( \mu \text{m} \) every time its direction along x was reversed. However, this did not completely remove the problem. The final version of “Sample Step Scan.vi” required a longer scanning time to ensure that every single row in the x axis was approached in the same direction. If the first row in the x axis was scanned from left to right, when the next row was accessed by a step in y, the DC servo motor controlling x axis would resume to the left, overshoot the starting point by 8 \( \mu \text{m} \), then reverse the direction to approach the starting point and scan this second row from left to right. Consequently, the 2D images no longer suffered from any backlash effect as illustrated in Figure 5.3(b).

From the 2D contour map of a SWCNT, the spot size and tube length were estimated from the intensity profiles that were cut along and across the SWCNT map, respectively. Figure 5.4 is an example of an PL image of a (10,8) SWCNT being scanned with a 2 \( \mu \text{m} \) spot diameter. The x slice through the peaked PL (6 \( \mu \text{V} \)) in the contour map confirms the small spot size \( s = 2 \pm 0.5 \mu \text{m} \). The y slice, which also crosses the peak, has its FWHM of 7\( \pm 1 \mu \text{m} \). Since this value \( c = 7 \mu \text{m} \) was a result of the convolution between the intrinsic length \( l \) of the tube and the spot size \( s \), by deconvoluting using
l^2 + s^2 = c^2 \text{ relation, the length of the tube in this case was } l = 7 \pm 1 \, \mu\text{m}.

From this high resolution imaging, some SWCNTs exhibited inhomogeneous PL with several segments of different brightness, as shown in Figure 5.5. The dark segment could be the result of its contact to the substrate or resting on the ridges as previously discussed in Section 3.1. Furthermore, in two images of the same SWCNT segments recorded on different days, we observed a SWCNT segment that was originally bright became completely dark. The evidence is demonstrated in Figure 5.6, with absence of the bottom segment (i.e. y = 2400-2410 \, \mu\text{m}) in the second image. This could be due to the change in the environment around the sample or the tube segment was pushed down onto the substrate by the optical field as observed by our collaborators at NRC [84].

5.1.3 PLE Map of SWCNT

To maximize PL signal from the nanotube, we opened both the exit and the entrance slits of the spectrometer to 7 mm. Since the incoming beam is well-focused down to
Figure 5.4: A 2D PL image of a (10,8) SWCNT. The intensity profiles obtained from cutting the image along the x and y direction at the peak correspond to the spot size and tube length, respectively.

Figure 5.5: Examples of tubes with inhomogeneous PL segments revealed by 2 µm resolution 2D PL imaging.
less than 1 mm diameter spot at the entrance slit, the widely open entrance slit does not affect the lineshape of the emission spectrum. However, the open exit slit will result in the convolution between the intrinsic lineshape of nanotube emission spectrum and the bandpass of the spectrometer (refer to Section 3.5.1). To verify this, the author simulated the convolution between a top hat function of 3 nm and 21 mm widths (which accounts for spectrometer bandpass at 1 mm and 7 mm exit slit widths, respectively) with a Lorentzian and Gaussian peak function of 15 nm FWHM (which is comparable to the expected intrinsic emission linewidth of a SWCNT). As demonstrated in Figure 5.7, the 3 nm top hat width convoluted curves (black squares) retain a similar FWHM with their original peak functions (red diamonds). Meanwhile, two curves (blue triangles) resulting from the convolution of the original peak functions of 15 nm FWHM with a 21 nm width top hat function exhibit a broadening: $\sim 50\%$ for the Lorentzian and $\sim 20\%$ for the Gaussian.

However, from the experimental test, the author found that the 7 mm wide exit slit did not dramatically modify the intrinsic lineshape of the SWCNT emission spectra.
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Figure 5.7: The comparison of the original peak function of 15 nm FWHM Lorentzian in (a) and Gaussian in (b) and their convolution with a 3 nm and 21 nm width top-hat function.

This was done by closing the entrance slit down to 1 mm and recording the emission spectra at different exit slit widths (from 1 mm to 7 mm). The results in Figure 5.8(a) show the signal increase when going from 1 mm to 7 mm. With the normalized spectra in Figure 5.8(b) fit with a Lorentzian and Gaussian profile, the FWHM values show broadening of less than 18% when exit slit widths were increased from 1 mm to 7 mm (refer to Table 5.1). Therefore, spectra taken with the exit slit widely opened are acceptable when high resolution spectra are not required.

<table>
<thead>
<tr>
<th>Exit slit width (mm)</th>
<th>Spectrometer Bandpass (nm)</th>
<th>Lorentzian FWHM (nm)</th>
<th>Gaussian FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>$15 \pm 2$</td>
<td>$15 \pm 1$</td>
</tr>
<tr>
<td>7</td>
<td>21</td>
<td>$18 \pm 1$</td>
<td>$17 \pm 1$</td>
</tr>
</tbody>
</table>

Table 5.1: FWHM values from fitting the emission spectra at different exit slit widths of the spectrometer to Lorentzian and Gaussian functions.

Photoluminescence excitation spectroscopy (PLE) was then performed with the entrance and exit slits of the spectrometer opened to 7 mm. The PLE map is composed of numerous PL spectra (100 nm range) at various excitation wavelengths in the proximity
Figure 5.8: The emission spectra of a SWCNT with various exit slit widths of the spectrometer.

of the resonance. The Mira laser beam in CW mode was tuned over a range of 100 nm with 5-10 nm incremental steps. A Si detector was used to monitor the pump power for all excitation wavelengths and the “Nanotube Spectral Scan.vi” LabVIEW program (refer to Section 4.2) was run to record the emission spectra. Figure 5.9 illustrates the contour maps of the PLE spectra for a (9,8) and (10,8) SWCNT. The assignment of (9,8) chirality (see Figure 5.9(a)) for SWCNT with $\lambda_{11} = 1380$ nm (or $E_{11} = 0.9$ eV) and $\lambda_{22} = 800$ nm (or $E_{22} = 1.55$ eV) was based on the existing database by Lefebvre et al. in their work comparing the PL from suspended and micelle-encapsulated SWCNTs [85]. For the peak at $\lambda_{11} 1440$ nm (or $E_{11} = 0.86$ eV) and $\lambda_{22} 860$ nm (or $E_{22} = 1.44$ eV) in the PLE map shown in Figure 5.9(b), the author assigned a (10,8) chirality to this tube by considering the blueshift in both excitation and emission peaks (20 meV and 10 meV, respectively) of suspension compared to micelle-encapsulation (refer to Section 2.5), and the original chirality assignment for various micelle-encapsulated SWCNTs by Weisman and Bachilo [11]. Particularly, in comparison to their findings: $E_{11} = 0.841$ eV, and $E_{22} = 1.428$ eV, our suspended SWCNT has its excitation and emission peaks
blueshifted by 20 meV and 12 meV, respectively.

The excitation and emission spectra were obtained by cutting in the x and y directions of the PLE map at the peaked PL. In these profiles, the x axis represents energy (eV), instead of wavelength (nm). It is also noted that bin-size correction was made in the conversion from wavelength to energy for the emission spectra. Figure 5.10 and Figure 5.11 show the result for the (10,8) SWCNT, with the excitation linewidth $\sim 44$ meV and the emission linewidth $\sim 13$ meV. A much broader linewidth and asymmetry of the excitation spectrum as compared to the emission spectrum can be explained by very efficient coupling of $E_{22}$ to $E_{11}$, with the relaxation time less than 100 fs as mentioned in Section 2.6.2. As compared to 25 meV observed on the ensemble measurement [10] or 23 meV noted from the work done on a single SWCNT that was suspended in soap and spun onto the substrate [12], our emission spectra showed a 50% narrower linewidth. This strongly indicates that the ensemble average measurement in the first case and the environment effects (e.g. the surrounding dielectric constant or the presence of
adsorbate) in the latter case could introduce a significant inhomogeneous broadening.

Emission spectra of micelle-encapsulated individual SWCNT were also reported to exhibit a symmetrical emission lineshape that can be well-described by a single Lorentzian function. By contrast, our data show an asymmetric spectrum with a gradual falloff at high energy and a steeper rise at low energy. Lefebvre et al. suggested that this asymmetry might have some connection with the van Hove singularities DOS [86]. Trial fit of the emission spectrum to a Lorentzian function (Figure 5.11(b)) or a Gaussian function (Figure 5.11(a)) also indicates a pure peak function cannot fully describe our emission spectrum. Instead, it is a mixture of both Lorentzian and Gaussian profile: the former homogeneous broadening stemming from the intrinsic lifetime and phonon coupling, and the latter inhomogeneous broadening possibly due to environmental influences of exciton relaxation.

![Graph](image)

Figure 5.10: Excitation spectrum of a (10,8) SWCNT recorded at $E_{11} = 0.86$ eV.

Previous work on temperature dependence of PL (5 K to 700 K) showed changes in the peak emission energy, linewidth, and intensity, which reflect a deformation or shift in the optical band gap $E_{11}$ [87, 88]. Although our experiments were carried out at room temperature, the pump power dependence study of PL required the sample
be exposed to a sequence of different excitation powers. In order to ensure that the heating effect did not occur during this process, the author compared emission spectra at various excitation powers, from 20 W/cm$^2$ up to the highest pump intensity in CW accessible with the system (500 W/cm$^2$). This was followed by the acquisition of five emission spectra for a (10,8) SWCNT, the background was measured by taking the corresponding spectra at another location on the sample (e.g. 100 µm away from the SWCNT) with the same pump power. Five background-corrected spectra are shown in Figure 5.12(b) corresponding to pump intensities of 20, 40, 60, 150, and 500 W/cm$^2$. Their spectra before normalization demonstrate signal increase corresponding to higher excitation intensity. The peak PL values (at 1440 nm) scale linearly for the first three lowest excitation intensities, and become nonlinear beyond 60 W/cm$^2$. This nonlinear power dependence of PL will be explored in detail in Section 5.2. More importantly, the normalized spectra in Figure 5.12(b) overlap without any distinguishable modifications in their lineshapes and FWHMs. Therefore, this suggests that heating effects were negligible.
Figure 5.12: Emission spectra of a (10,8) SWCNT for different excitation intensities.

5.1.4 PL Polarization

The absorption and emission of light from a single straight SWCNT were experimentally observed and reported to be strongly polarized along the tube axis [6, 12, 13, 14]. In our studies, by knowing the polarization of the excitation light from the laser and relying on the fact that most tubes were suspended perpendicular to the trenches on the sample, we oriented the sample in such a way that excitation light is parallel to the SWCNT axis. We then verified the presence and orientation of an individual single tube via the polarization of its emitted PL. The emitted PL from the SWCNT was examined using a polarization analyzer system which consisted of a $\lambda/2$ waveplate preceding the linear polarizer (refer to Figure 3.3). Figure 5.13 demonstrates the PL signal as a function of the angle between the SWCNT axis and the linear polarizer. The maximum and minimum of the emission correspond to the electric component of the light field parallel and perpendicular to the SWCNT axis, respectively. The red curve is a sine square function $y = B + A\sin^2(x + x_C)$ that was fit to the experimental data points. The fitting parameters for $A$, $B$, and $x_C$ as $55 \pm 2 \mu V$, $7 \pm 1 \mu V$, and $68 \pm 1$ degree, respectively.
Figure 5.13: Polarization of photoluminescence from a SWCNT.

5.2 Pump Power Dependence (PPD) Studies

As previously discussed in Chapter 2, PL from SWCNT ensembles exhibited a non-linear dependence on the pump power and a more dramatic effect was observed for a single SDBS-encapsulated SWCNT. This indicates the evidence of nonlinear decay processes. Conducting PPD measurement on an individual air-suspended SWCNT is one way of studying exciton dynamics. Since the total experimentally detected PL, $PL_{total}$, is related to the average number of excitons per SWCNT at any time $t$, $\bar{n}(t)$, (refer to Equation 2.21), and $\bar{n}(t)$ can be determined from the initial number of excitons, $\bar{n}_0$, using the stochastic model that has been explained in Chapter 2, we can simulate the $PL_{total}$ as a function of $\bar{n}_0$. This simulated curve is then compared against our experimental PPD data.
5.2.1 Experimental Procedure

SWCNTs selected for this experiment were based on their defined chirality (confirmed by the PLE map) and tube lengths (estimated from the high resolution 2D PL imaging). PL saturation studies were done with SWCNTs of (9,8) and (10,8) chiralities. For the (9,8) SWCNT, we pumped at 800 nm ($E_{22} = 1.55 \text{ eV}$) and detected the PL at 1380 nm ($E_{11} = 0.9 \text{ eV}$). For the (10,8) SWCNT, we pumped at 860 nm ($E_{22} = 1.44 \text{ eV}$) and detect PL at the 1440 nm ($E_{11} = 0.86 \text{ eV}$). Both CW and 150 fs duration pulse excitation were performed. In CW excitation, the signal was sufficient for detection with the low gain mode of the detector. The optical chopper modulated the signal at 70 Hz and the LIA’s time constant was set to 300 ms. In the pulse excitation, to enhance the signal to noise ratio, we usually operated at the high gain mode of the detector, 20 Hz for the chopper and 1 s for LIA’s time constant. The neutral density attenuator wheel was used to adjust the pump power and the “Data Recording.vi” LabVIEW program read out the associated PL signal from the LIA at specific power settings.

To verify if the SWCNT’s PL experienced any hysteresis, PL was recorded for both increasing and decreasing pump powers. After the PL was recorded with the excitation spot centered on the SWCNT, the background signal as a function of pump power was also measured at a location away from the tube (e.g. 100 µm). The PPD PL curves were averaged from several scans and subtracted from the linear fit of the background data. Figure 5.14 shows an example of PL and background measurements taken for a (9,8) tube in CW mode. The pump power in the x axis is not measured at the tube, instead immediately before the glass window (refer to Figure 3.5). This “experimentally convenient” entity will be converted to the excitation intensity on the sample, following the procedure explained in Appendix B. Dark blue diamonds and magenta squares are PL data recorded at the SWCNT as a function of increasing and decreasing pump
powers, respectively. The error bars are calculated from the standard error of all the original data recorded at each pump power. The overlapping of these two data sets of less than 9% in the uncertainty confirms that there were negligible hysteresis effects. The background PL were also obtained with pump powers being varied in both ways (e.g. green diamond and cyan triangle for increasing and decreasing powers, respectively). The background data were then fit to a linear function $y = 0.423 \times x$ (dashed line) and subtracted from the PL data at the SWCNT. Since the background PL was relatively small compared to the PL measured at the SWCNT, the background corrected curve (brown circle) is similar to the original PL curves (dark blue diamonds and magenta squares).

Similar PPD measurements performed in pulse mode (see Figure 5.15) also show PL signals (dark blue diamonds and magenta squares) and the background PLs (green triangles and cyan circles) taken with the increasing and decreasing powers. Both data sets agree with each other within their error bars. It should be noted that this measurement in pulse mode was run with the high gain setting of the detector, compared to low gain used for Figure 5.14. The main features observed in Figure 5.15 are the much lower PL signal compared to previous CW excitation, and a “hard” saturation at high pump power displayed by the background corrected PPD curve (brown circles). The contrast of PL saturation between CW and 150 fs duration pulse suggests the PPD study at some intermediate excitation schemes (i.e. with other pulse durations longer than 150 fs) should be addressed. This will be discussed in Section 5.2.5.

5.2.2 Geometric Effect

Conforming to the previously described experimental procedure to obtain PL data, we explored whether inhomogeneous excitation affects the PL saturation measurement. To
Figure 5.14: An example of background corrected PPD curve (labelled as brown circles) for a (9,8) SWCNT in CW excitation. Dark blue and magenta bullets are the PL data recorded at the SWCNT as a function of increasing and decreasing pump powers, respectively. Green diamond and cyan triangle symbols represent the background PL as a function of increasing and decreasing pump powers. The dashed line is the best linear fit to the background PL data.
Figure 5.15: An example of background corrected PPD curve (labelled as brown circles) for a (9,8) SWCNT that was excited by 150 fs duration pulse. Dark blue and magenta bullets are the PL data recorded at the SWCNT as a function of increasing and decreasing pump powers, respectively. Green diamond and cyan triangle represent the background PL as a function of increasing and decreasing pump powers. The dashed line is the linear fit to the background PL data.
address this geometric effect, we introduced two distinctive scenarios:

1. The SWCNT is completely contained inside the excitation spot, hence experiences uniform intensity at every part of the tube.

2. The excitation spot size is comparable to the tube length, hence, nonuniform intensity is experienced by different parts of the tube (e.g. a Gaussian spatial distribution of the excitation spot results in high intensity at the middle of the tube and much lower intensity at its ends).

Figure 5.16(b) and 5.16(a) show in log-log scale the normalized PPD measurement carried out for a 7.7 ± 1 µm long (10,8) tube and 5 ± 0.8 µm long (9,8) with 20 ± 2 µm (magenta) and 2 ± 1 µm (blue) excitation spot sizes. In these graphs, the pump intensity is calculated as the excitation power divided by the area of the excitation spot (e.g. $A = \pi r^2$, where $r = 1$ and 10 µm). It is noticeable that the magenta curves approach saturation faster than the blue curves (i.e. the “turnover” point of the pump intensity, where PL starts saturating, is at 100-1000 W/cm$^2$ for the first scenario and beyond 1000 W/cm$^2$ for the second scenario). We attribute the delay in saturation of the latter to the nonuniform excitation experienced by different parts of the SWCNT. At the same pump intensity point where no further PL can be enhanced from the SWCNT in the case of homogeneous excitation, the SWCNT in inhomogeneous excitation can emit more PL with higher input power. We speculate that only the middle part of the SWCNT experienced saturation, while its ends are still in the linear regime (i.e. PL is linear with the input power). If we treat the pump intensity differently for two scenarios (i.e. peak intensity for the 20 µm case and average intensity for the 2 µm case), the difference between saturated pump intensity in these two excitation schemes is reduced. Nevertheless, it is still recommended to use a spot size larger than the SWCNT to ensure uniform excitation.
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(9,8) SWCNT

(10,8) SWCNT

Figure 5.16: Normalized PL for different excitation spot sizes (20 µm diameter (magenta) and 2 µm diameter (blue)) for: (a) SWCNT of (9,8) chirality and (b) SWCNT of (10,8) chirality.

5.2.3 Intrinsic PL Saturation Curves

After the geometric effect was determined to be a problem for spot sizes smaller than the nanotube, we used a 20 µm diameter spot to excite each of five individual isolated SWCNTs (of (9,8) and (10,8) chiralities) with 150 fs duration pulse and measured their PL as a function of pump intensity (refer to Figure 5.17). Each of these PPD curves was obtained after background correction. All of them exhibit the same PL saturation trend: at first, PL increases with elevating pump intensities, up to a threshold (i.e. saturating pump intensity) where no improvement of PL is further obtained regardless of higher pumping. We even observed the declining trend of PL at very high pump intensity (e.g. 5-10% from highest PL value). As mentioned earlier, this PL “hard” saturation behaviour was not seen in previous ensemble measurement by Ma et al. [52]. Instead, they observed PL that scaled linearly with the square root of the excitation intensity. We believed that this is not the intrinsic pump power dependence of PL for a SWCNT. In fact, a recent measurement in 2008 by Høgele et al. on a single SWCNT encapsulated in SDBS show very similar PL saturation behaviour and a substantial decrease (25%)
in PL at high power [51].

With the saturated PL level for each PPD curve defined as the average of all the PLs at pump intensities higher than the saturated intensities, we normalized the original PL data of all five SWCNTs to their saturated PL level for comparison purposes. Figure 5.17 shows normalized PL data plotted against the pump fluence (unit of photons/pulse/cm$^2$) in a log-linear scale for the three (10,8) SWCNTs and two (9,8) SWCNTs. The details of conversion for the x axis (from the pump intensity to pump fluence) can be found in Appendix B. Interestingly, these five PPD curves trace the same pattern and consistently group into a single cluster regardless of their chiralities. The “knee” of these curves occur around $0.1 \times 10^{13}$ photons/pulse/cm$^2$. As compared to similar work by Hagen et al. (i.e. resonantly exciting an individual (6,4) SWCNT), the saturated intensity point for our SWCNT is lower by three orders of magnitude [19]. However, as their SWCNTs are encapsulated in micelle and their excitation polarization did not align to the tube, we believe excitation photons might not be efficiently absorbed by the SWCNT.

Figure 5.17: Normalized PPD curves of several (9,8) and (10,8) individual SWCNTs.

Using the the stochastic model described in Section 2.6.3, we simulated the PL saturation curve by plotting $PL_{total}$ as a function of the initial number of excitons per
nanotube. Recall that the $P_{L_{\text{total}}}$ is calculated using Equation 2.21 and $n_0$ is proportional to the pump fluence as given in Equation 2.19. This simulation was done by a co-worker (Ms. Y. F. Xiao) [77]. For $\tau = \frac{1}{\gamma} = 150$ ps, and $\tau_A = \frac{1}{\gamma_A} = 10$ ps (where $\gamma$ and $\gamma_A$ are the linear and nonlinear decay rates, respectively, defined in Section 2.6.3, the simulated curve agrees with our experimental PL saturation curve up to moderate pump intensities. At high pump intensities, however, the simulated curve remains saturated, which is inconsistent with the declining trend of the experimental curve. This suggests the possibility of some other decay mechanisms annihilating the excitons at very high power that was not included in the stochastic model.

5.2.4 Calculation of Quantum Efficiency

From the linear regime of PPD measurement, the power of light absorbed, $P_{\text{absorb}}$, and emitted, $P_{PL}$, by a SWCNT allows the calculation of quantum efficiency $\eta$. Defined as the ratio of the number of emitted photons $\Phi_{PL}$ to the number of absorbed photons $\Phi_{\text{absorb}}$ by a SWCNT, the quantum efficiency can be written as:

$$\eta = \frac{\Phi_{PL}}{\Phi_{\text{absorb}}} = \frac{P_{PL}\lambda_1}{P_{\text{absorb}}\lambda_2}$$ (5.1)

where $\lambda_2$ and $\lambda_1$ are the excitation and emission wavelengths (associated with $E_{22}$ and $E_{11}$) for the SWCNT.

For a $5 \pm 1 \, \mu m$ long $(9,8)$ SWCNT and the average excitation intensity $I_{\text{exc}} = 1 \pm 0.2 \, W/cm^2$, the PL signal detected by the LIA at high gain setting of the detector and 20 Hz chopping rate of the optical chopper was $11 \, \mu V$. The power absorbed by the SWCNT was calculated as:

$$P_{\text{absorb}} = \pi I_{\text{exc}} AD_T L_T$$ (5.2)

where $A$, $D_T$, and $L_T$ are the absorption coefficient, the diameter and the length of the SWCNT, respectively. We considered $A = 0.059$, which was used by Tsyboulski et al.
for a SWCNT of comparable absorption bandwidth to our studied SWCNT [23]. With $D_T = 1$ nm, $L_T = 5 \pm 1 \mu m$, the $(9,8)$ SWCNT would absorb $P_{\text{absorb}} = 9.3 \times 10^{-12}$ W for 1 W/cm$^2$ excitation intensity. Considering the calibrated throughput value of our detection system (i.e. including the spectrometer, the InGaAs detector and the LIA) mentioned in Section 3.5.3 and the transmittance of other PL capturing optics that are summarized in Appendix B, PL signal of 11 $\mu$V detected under such condition described above is equivalent to the power of $200 \times 10^{-15}$ W emitted from the SWCNT. With $\lambda_1 = 1380$ nm and $\lambda_2 = 800$ nm for the $(9,8)$ SWCNT, the value of $\eta$, as calculated from Equation 5.1, was 5%. The total uncertainty of this calculation was 30%, calculated from the measure uncertainties in PL signal, the input power, the excitation spot size, the tube length and the calibrated detection efficiency. With $P_{PL}$, $P_{\text{absorb}}$ values found in the linear regime of the PPD curve and the $\frac{\lambda_1}{\lambda_2}$ ratio evaluated at $\lambda_1 = 1400$ nm and $\lambda_2 = 800$ nm, being comparable to those values in $(9,8)$ SWCNT, the quantum efficiency was found to be similar for a 6.5 $\mu$m long $(10,8)$ SWCNT.

However, the estimation of quantum efficiency is only valid under the following assumptions:

- The total intensity at the SWCNT is the sum of incident and reflected intensity (20 %) from the Si/SiO$_2$ substrate. We neglect the possibility of constructive or destructive interference between the incident and reflected beam.

- SWCNT PL intensity is spatially isotropic, and the collection efficiency is 0.136 (refer to Appendix B).

- By varying the distance between the sample and the aspheric lens until PL is optimized, the PL is collimated and well-focused by lens L3 (refer to Figure 3.3) and captured by the spectrometer.
With QE being an intrinsic and constant value for a SWCNT of certain chirality, Equation 5.1 and Equation 5.2 show that the emitted PL should be proportional to SWCNT length. This has been observed by Fagan et al. by sampling a large number of (6,5) SWCNTs of 50-600 nm length [89]. The analysis for (10,2) SWCNTs of lengths ranging from 500 nm to 4000 nm by R. Bruce Weisman showed SWCNTs of the same length might have variation in PL emission intensity, yet, the maximum PL scales linearly with tube length [90]. In our experiments, most SWCNTs were measured on different days with different separations between the SWCNT and the aspheric lens, hence resulting in different PL collection efficiencies. For two (9,8) SWCNTs and one (10,8) SWCNT on the same sample with identical PL collection efficiency, the author compared the slopes of their PPD curves in the linear regime with their lengths. The inset of Figure 5.18 shows the three linear fits for the original PPD data of these SWCNTs at low pump power. The slopes found from these fit are used to represent PL intensity and plotted against the tube length, as illustrated in Figure 5.18. Despite the small variation in tube length and the small number of SWCNTs studied, the expected trend of tube length dependence of PL intensity is observed.

5.2.5 PPD Measurement with Various Pulse Duration

From the earlier description in Section 5.2.1, PPD results from CW excitation (refer to Figure 5.14) show very different PL saturation behaviour from that of 150 fs pulse excitation (refer to Figure 5.15). By further investigating the PPD of PL at some intermediate excitation processes between a short duration pulse (150 fs) and a “pulse of infinite duration” (CW), we wish to gain insight into nonlinear processes of exciton dynamics in SWCNT.

Preliminary pulse chirping was introduced by sending the beam through glass (SF66
Figure 5.18: Slope of PL as a function of tube length for two (9,8) SWCNTs and one (10,8) SWCNT. The inset shows the linear fit to the PPD data in the linear regime for each of the SWCNT. The slope of each fit represent PL intensity in the main plot.

type). There are four configurations: no glass, 6 mm thickness of glass, 12 mm thickness of glass, and the presence of both. As verified using the autocorrelator, the corresponding pulse durations for the excitation beam passing through these four different configurations are: 150 fs, 165 fs, 200 fs and 250 fs, respectively. Since only pump power (instead of the intensity) was monitored and controlled, we had to ensure that there were no changes in the excitation spot size on the sample when the glasses were introduced in the beam path. 2D scans around a (9,8) with different excitation configurations are shown in Figure 5.19. These results suggested that the spot size remained the same.

Original PPD data for the (9,8) SWCNT (see Figure 5.20) presented very interesting results: in linear regime (low pump fluence) the four PPD curves were well-overlapped; however, at high excitation regime, PL was enhanced with additional glass present. This suggested the existence of fast exciton dynamics. However, further investigation
Figure 5.19: 2D raster scan of a (9,8) SWCNT for different excitation configurations.

(a) No glass

(b) 6 mm glass

(c) 12 mm glass
by other co-workers (Ms. Y. F. Xiao and M. W. B. Wilson) confirmed that the observed enhancement in PL was due to the response of the SWCNT to the second pulse reflected from the second surface of the glass. By tilting the glass in such a way that the second pulse was separated from the same path of the initial pulse, the co-worker (M. W. B. Wilson) found that the PPD signal remained the same without any improvement in PL when the pulse was stretched from 140 fs to 250 fs.

![Figure 5.20: Preliminary PPD data for four different amount of glass present in the beam: no glass, 6 mm thickness of glass, 12 mm thickness of glass, and the presence of both.](image)

The author then explored whether a much longer duration pulse (up to 4 ps) would show any effects in PPD curves. Since glass is inconvenient in stretching pulses to such extreme, a 4f grating pair configuration (described in Section 3.8) was employed. With the capability of temporally stretching the pulse to 4 ps, the author ran a PPD experiment on a single (9,8) tube under three distinctive conditions: 150 fs pulse, 4 ps pulse and CW excitation (equivalent to pulse stretched to infinity). The results for all three cases are shown in Figure 5.21(a). The PL intensity in the y axis is presented on a log scale due to the large contrast in PL level between the CW case (green data points) and the pulse cases (blue and magenta data points). Two important conclusions are
drawn from this result.

First, the two data sets (blue and magenta) associated with two distinctive pulse duration (of 150 fs and 4 ps, correspondingly) confirm there is no increase in PL even when the pulse is stretched to 4 ps. With the CW data excluded, the y axis set to a linear scale and the x axis converted from pump intensity (unit of W/cm$^2$) to pump fluence (unit of photons/pulse/cm$^2$), the two curves associated with 150 fs and 4 ps pulse duration excitation are presented in Figure 5.21(b). At each pump fluence, the two PL data points fall within their error bars. This overlapping in PL up to $0.7 \times 10^{13}$ photons/pulse/cm$^2$, in contrast to the misperceived PL enhancement as previously shown in Figure 5.20, implies that there are no fast dynamics of excitons occurring in the first 4 ps. It is also noted that these PL saturation curves share a consistent power saturation point (at $0.1 \times 10^{13}$ photons/pulse/cm$^2$) with the results presented in Figure 5.17 and Figure 5.20.

Secondly, Figure 5.21(c) shows the results for the low excitation intensity regime (up to 30 W/cm$^2$) with a linear scale. All three PPD curves (CW, 150 fs and 4 ps pulse duration excitation) overlap at very low pump intensity (below 2 W/cm$^2$). The dashed line was a fit to data points of low pump intensities, defining the linear regime where the estimation of quantum efficiency can be made (refer to Section 5.2.4).

By adopting and extending the original work by a co-worker (Ms. Y. F. Xiao) [77], the author simulated the PPD curves for these three scenarios of different pulse duration excitation. In the simulation by Xiao, a Poissonian distribution of excitons (refer to Equation 2.18) is generated instantaneously upon the excitation pulse hitting the SWCNT, and serves as the initial condition for the rate equation model (refer to Equation 2.17). To account for the excitation by different pulse durations, the author modified the rate equations to include the generation terms as follows:

$$\frac{d}{dt}\rho_n(t) = -\left[\gamma + \frac{1}{2}(n-1)\gamma_A\right]n\rho_n(t) + (\gamma + \frac{1}{2}n\gamma_A)(n+1)\rho_{n+1}(t) + G(\rho_{n-1}(t) - \rho_n(t)) \quad (5.3)$$
Figure 5.21: Comparison of PPD measurement for three extreme cases: 150 fs duration pulse, 4 ps duration pulse, and CW excitation. (a) The results for all three cases are shown with a log scale for the PL intensity. (b) With the exclusion of CW case, only the two curves associated with 150 fs and 4 ps pulse duration excitation are presented. (c) All three PPD curves are shown at very low pump intensity.
where $G$ is the rate of exciton generation, and can be calculated by the initial number of excitons, $n_0$, created by a pulse divided by the pulse duration.

This simulation is split into two parts:

**Part One**: for the entire pulse duration (e.g. $t = 0$ to $t = T_1$ = the end of the pulse duration), the rate equation above (Equation 5.3) is applied to solve for $\rho_n(t)$, with the initial condition of $\rho_0(0) = 1$, and $\rho_n(0) = 0$ for $n \neq 0$.

**Part Two**: after $T_1$, the original rate equation (refer to Equation 2.17) is applied for the rest of the dynamics, with the distribution $\rho_n(T_1)$ established in “Part One” serving as the initial condition.

Using Equation 2.21, the total PL can be calculated for any arbitrary initial number of excitons $n_0$ created by the pulse. The correctness of the simulation was verified through the following tests:

- The total probability $\sum_{n=0}^{\infty} \rho_n(t) = 1$. However, it is noted that the simulation truncates $n$ to 100 (i.e. $\sum_{n=0}^{100} \rho_n(t) = 1$).
- If $\gamma$ and $\gamma_A$ are set to zero in Equation 5.3, the distribution $\rho_n(t)$ at the end of the pulse duration should follow a Poissonian distribution.
- To account for $t \to \infty$ in “Part Two”, the upper limit in time, $T_2$, should allow for the average number of excitons in the SWCNT ($\pi(t)$ as evaluated using Equation 2.20) to converge to zero. For pulses of 150 fs and 4 ps duration, $T_2 = 1.4$ ns is sufficient.
- With $\gamma_A$ set to zero for both rate equations (Equation 5.3 and 2.17), the total PL must be independent of the pulse duration.

The simulation described above was used to generate PPD curves for pulse duration of 150 fs and 4 ps. In the CW excitation case, since the system reaches a steady state, we
can set $\frac{d}{dt} \rho_n(t) = 0$. Therefore, Equation 5.3 was solved analytically for $n = 0, 1, 2, 3$. For $n \geq 4$, $\rho_n(t) \approx 0$. Figure 5.22(a) shows the simulated PPD curve for 150 fs and 4 ps pulse duration excitation, with the following parameter set: $N = 20$, $\tau = \frac{1}{\gamma} = 180$ ps, and $\tau_A = \frac{1}{\gamma_A} = 1$ ps. It is noted that the y axis represents time-average exciton density, which scales with the total PL and is written as:

$$n_{\text{average}} = \frac{1}{T} \int_0^\infty \bar{n}(t) dt \quad (5.4)$$

where $T$ is a period of integration time. To account for the periodicity due to the repetition rate of excitation pulse, $T = 13$ ns is adopted. The experimental data for 150 fs and 4 ps pulse durations, as previously shown in Figure 5.21(a), are presented again in Figure 5.22(b) and placed next to the simulated curves for the comparison. The experimental data exhibit a declining trend of PL at pump intensity higher than 15 W/cm$^2$, whereas the simulated curves show an increase in $n_{\text{average}}$ for greater initial number of excitons generated by the pulse (10-30 excitons/pulse). On the same graph (see Figure 5.23), the simulated curve is imposed onto the experimental curve of 150 fs pulse duration and their x and y axes are rescaled, until the best match is obtained. From this way, the absorption coefficient $A$ can be extracted. The best match of these two curves suggests that pump intensity of 15 W/cm$^2$ will generate 5 excitons/pulse in the SWCNT. With $D_T = 1$ nm and $L_T = 2$ µm, $A$ was found to be 0.15, using Equation 2.19. This value is 2.5 times larger than $A = 0.059$ as suggested by Tsyboulski et al. [23]. Matching the saturation level in the y axis of PL signal (from experimental data) and $n_{\text{average}}$ also requires the scaling factor between these two entities to be 2250. With $A = 0.15$ and the scaling factor of 2250, the simulation curve for CW case (with $\tau = \frac{1}{\gamma} = 180$ ps, and $\tau_A = \frac{1}{\gamma_A} = 1$ ps) is generated and placed on the same graph with the experimental data, as shown in Figure 5.24. The simulation traces the experimental curve quite well in both the linear (i.e. average pump intensities below 50 W/cm$^2$) and
nonlinear (i.e. average pump intensities greater than 50 W/cm$^2$) regimes.

Figure 5.22: PPD curves for 150 fs and 4 ps pulse duration excitation: (a) Simulation results using the stochastic model. (b) Experimental data.

5.3 Time-resolved PL dynamics by FEC technique

The PL saturation at high pump power in PPD measurement is consistent with the occurrence of exciton-exciton annihilation via an Auger recombination process. If the instantaneous $PL(t)$ is proportional to the number of excitons in the SWCNT at that time, performing the time-resolved PL spectroscopy will allow us to directly investigate the exciton dynamics in SWCNT. Using the FEC method, we resonantly excited a SWCNT with two pump pulses of the same intensity and measure the total PL as a function of their delay time ($t_d$). The PL lifetimes are extracted from the analysis of the FEC signal.
Figure 5.23: Matching the simulated PPD curve (gray and black squares) with the experimental curve (blue diamonds and magenta squares) for 150 fs and 4 ps pulse duration.

Figure 5.24: Imposing the simulated PPD curve (gray squares), with $\tau = 180$ ps, $\tau_A = 1$ ps, onto the experimental curve (green triangles) in CW excitation.
5.3.1 FEC Implementation

For the (9,8) chirality, we used 800 nm ($E_{22} = 1.55$ eV) pulses from the Ti:sapphire system, while the (10,8) SWCNT was excited with the 860 nm ($E_{22} = 1.44$ eV) pulses. The creation of two pulses by the fixed arm and the delay arm is explained in Section 3.2. The implementation of the delay line for the control of the delay time between two pulses (ranging from 0 to 1.3 ns) is also discussed in Section 3.6.2. The two excitation beams (from the fixed and delay arms) were modulated at 20 Hz by the optical chopper. Under exposure to the two spatially-overlapped excitation spots, the PL emitted from the SWCNT was dispersed by the spectrometer, collected with the InGaAs detector and detected by the LIA at 20 Hz. The recording of total PL signal as a function of delay time was automated by running the “Automated FEC Measurement.vi” LabVIEW program.

5.3.2 Interpretation of FEC signal

As previously mention in Section 2.6.4, the FEC signal had been interpreted by Hirori et al. as a direct consequence of exciton dynamics. By fitting their FEC signal to a single exponential decay, the decay time (which was found to be 22 ps and 31 ps for SWCNTs in D$_2$O solutions and gelatin films, respectively) was assigned to PL lifetimes. When applying this analysis onto our FEC signal, as illustrated in Figure 5.25(a), the author found the decay time to be 90 ps. However, the residuals between the single exponential fit and the actual data (refer to Figure 5.25(c)) have large amplitudes. Random scattering of the residual from bi-exponential fit trial (as shown in Figure 5.25(b)) suggests it is a better candidate for fitting the FEC signal.

To understand why Hirori et al. can claim FEC provides PL decay times consider the schematic in Figure 5.26. If we assume that the PL dynamics of a SWCNT follows a bi-exponential decay [51, 91], we can describe the response of the system to the first
Figure 5.25: (a) Mono-exponential fit for FEC data of a (10,8) SWCNT. (b) Bi-exponential fit for FEC data of a (10,8) SWCNT. (c) The residual between the fit and actual data.
excitation pulse as:

\[ PL_1(t) = C_1 e^{-\frac{t}{\tau_1}} + C_2 e^{-\frac{t}{\tau_2}} \]  

where \( C_1, C_2 \) are the amplitudes for each decay component and \( \tau_1, \tau_2 \) are their associated decay times. The second pulse at delay time \( t_d \) will create a new number of excitons in the system. A complete analysis must include the total of these newly generated excitons and leftover ones due to the previous pulse for the decay. This complicated analysis has been tackled by a co-worker (Ms. Y. F. Xiao) [77], using the stochastic model to simulate the dynamics of excitons. By considering the interaction (linear decay process, Auger recombination, diffusion) of excitons remained from the first pulse with those generated from the second pulse at a certain delay time \( t_d \), the FEC signal can be simulated and compared with the experimental result.

However, the following qualitative analysis is undertaken by the author with the assumption that the leftover excitons from the first pulse are annihilated instantaneously upon the arrival of the second pulse. Therefore, the PL decay due to the second pulse, \( PL_2(t) \), will be independent from the first pulse. Since the FEC signal is the total PL due to these pump pulses (crossed-area in Figure 5.26), we write:

\[ PL_{FEC}(t_d) = \int_0^{t_d} PL_1(t)dt + \int_{t_d}^{\infty} PL_2(t)dt \]  

For two pump pulses of equal intensity, we have \( PL_1(t) = PL_2(t) \). Hence,

\[ PL_{FEC}(t_d) = \int_0^{t_d} (C_1 e^{-\frac{t}{\tau_1}} + C_2 e^{-\frac{t}{\tau_2}})dt + \int_{t_d}^{\infty} (C_1 e^{-\frac{t}{\tau_1}} + C_2 e^{-\frac{t}{\tau_2}})dt \]

\[ = (C_1 \tau_1 - C_1 \tau_1 e^{-\frac{t_d}{\tau_1}} + C_2 \tau_2 - C_2 \tau_2 e^{-\frac{t_d}{\tau_2}}) + (C_1 \tau_1 + C_2 \tau_2) \]

\[ = -C_1 \tau_1 e^{-\frac{t_d}{\tau_1}} - C_2 \tau_2 e^{-\frac{t_d}{\tau_2}} + 2(C_1 \tau_1 + C_2 \tau_2) \]  

The total PL due to one pulse, \( C_1 \tau_1 + C_2 \tau_2 \), is notated as \( PL_1 \). At zero delay (when the two pulses are temporally overlapped), the evaluation of Equation 5.7 yields \( PL_{FEC}(0) = C_1 \tau_1 + C_2 \tau_2 = PL_1 \). When the two pulses are far apart (i.e. \( t_d \to \infty \)), \( PL_{FEC}(\infty) = \)
CHAPTER 5. EXPERIMENTAL RESULTS AND ANALYSIS

2(C_1\tau_1 + C_2\tau_2) = 2PL_1. Thus, we can see \( PL_{FEC}(\infty) = 2PL_{FEC}(0) \), which is an expected feature: the total PL emitted in the case two pulses are completely overlapped should be equivalent to that due to a single pulse; meanwhile, when the two pulses are completely separated, the total PL emitted is the combination of PL intensity from each pulse. As depicted in Figure 5.26, the FEC signal starts at \( PL_1 \) at zero delay, gradually increasing to approach \( 2PL_1 \) as \( t_d \rightarrow \infty \).

![Figure 5.26: Illustrative schematic of the femtosecond excitation correlation spectroscopy technique.](image)

### 5.3.3 FEC results and analysis

The PPD measurement was first performed for a (10,8) SWCNT, with the result shown in Figure 5.27. The FEC measurements were followed at different excitation powers as indicated in the PPD graph. Three FEC data sets corresponding to the excitation powers of 120 \( \mu \)W, 240 \( \mu \)W, 1600 \( \mu \)W are presented in Figure 5.28. The FEC data set for the highest excitation power (2400 \( \mu \)W) has been shown in Figure 5.25(b). These data sets reveal the ratio of 2 between the asymptotic PL level (i.e. \( t_d \rightarrow \infty \)) compared to PL level at zero delay as expected.

As mentioned earlier, the bi-exponential function will be used for fitting. As comparing data sets at higher excitation powers to lower powers (e.g. 2400 \( \mu \)W in Figure 5.25(b) versus 120 \( \mu \)W in Figure 5.28(a)), a much higher signal to noise ratio is observed.
for the former. Therefore, the bi-exponential function \( y = A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}} + y_0 \) is fit on the FEC data of the highest excitation power (2400 µW in Figure 5.25(b)) with five free parameters: \( A_1, A_2, t_1, t_2 \) and \( y_0 \). Their relationships to those conventional parameters in Equation 5.7 are listed in Table 5.2. With the best fit values of 13 ps and 270 ps for \( t_1 \) and \( t_2 \), respectively, these time decays are then fixed and imposed on the latter fits for other FEC data sets. As illustrated in Figure 5.28(a), 5.28(b) and 5.28(c), only the amplitudes \( (A_1, A_2) \) and the DC level \( (y_0) \) are varied for each fit while \( t_1 \) and \( t_2 \) are forced to constant values. Table 5.2 summarizes the output values of \( A_1, A_2 \) and \( y_0 \) from these fits for different powers.

<table>
<thead>
<tr>
<th>Fit Parameters</th>
<th>Parameters in Equation 5.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1, t_2 )</td>
<td>( \tau_1, \tau_2 )</td>
</tr>
<tr>
<td>( A_1, A_2 )</td>
<td>(-C_1\tau_1, -C_2\tau_2)</td>
</tr>
<tr>
<td>( y_0 )</td>
<td>( 2PL_1 = 2(C_1\tau_1 + C_2\tau_2) )</td>
</tr>
</tbody>
</table>

Table 5.2: Matching the fit parameters to the notation used in Equation 5.7

Figure 5.27: PPD data for the (10,8) SWCNT. The excitation powers used in the FEC measurements are also indicated by the inverted triangles.

As indicated in Table 5.2, the DC level \( y_0 \) should match with \( 2PL_1 \) where \( PL_1 \) is the PL intensity due to single pulse excitation. This value \( PL_1 \) can be referred from the
Figure 5.28: FEC data and associated bi-exponential fits for the (10,8) SWCNT at three different excitation powers.
Table 5.3: The results for $A_1$, $A_2$ and $y_0$ parameters obtained from bi-exponential fits of the FEC data at different excitation powers.

<table>
<thead>
<tr>
<th>Excitation Power ($\mu$W)</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$y_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>-3.5±1.1</td>
<td>-2.76±1.2</td>
<td>20.6±0.6</td>
</tr>
<tr>
<td>240</td>
<td>-4.9±0.7</td>
<td>-7.23±0.7</td>
<td>28.8±0.4</td>
</tr>
<tr>
<td>400</td>
<td>-5.5±1.0</td>
<td>-9.30±1.1</td>
<td>32.3±0.6</td>
</tr>
<tr>
<td>800</td>
<td>-6.0±1.3</td>
<td>-10.67±1.1</td>
<td>34.9±0.5</td>
</tr>
<tr>
<td>1600</td>
<td>-6.4±1.0</td>
<td>-10.79±1.1</td>
<td>33.9±0.5</td>
</tr>
<tr>
<td>2400</td>
<td>-6.8±1.1</td>
<td>-10.20±1.0</td>
<td>32.5±0.6</td>
</tr>
</tbody>
</table>

PPD result. Using the PL signal associated with half of the total excitation power used in FEC measurement to account for $PL_1$, the relation of $y_0 = 2PL_1$ can be verified. For instance, $y_0$ value of 20.6 $\mu$V for 120 $\mu$W total excitation in FEC measurement is compared to PL signal of 10.6 $\mu$V at 60 $\mu$W suggested from the PPD curve. A ratio of 2 is observed. In fact, this relationship is satisfied for the rest of the FEC excitation powers listed in Table 5.3.

With the equivalence of $A_1$ and $A_2$ to $-C_1\tau_1$ and $-C_2\tau_2$, respectively, their absolute values represent the integrated PL emission of the fast and slow components of the PL decay dynamics. The dependence of these PL components as a function of the excitation pump fluence has been explored by Wang et al. [61]. They observed PL contribution from the fast component continues to increase, in contrast to the saturation for slow emission component at high pump fluences. They ascribed these features to the dominant role of Auger recombination process, which quickly deplete the population of excitons at high pump fluences. With only one exciton surviving after this process, its decay accounts for the constant PL emission of the slow component. With the magnitude of $A_1$ and $A_2$ that were extracted from our FEC experiment plotted against the excitation power (refer to Figure 5.29), the slow component contribution (red circles) exhibits saturation at high pump power. On the other hand, considering the large error...
bars, it is not clear whether the fast component (blue square) for high pump powers is still increasing or has also saturated.

![Graph](image)

**Figure 5.29**: The dependence of integrated PL emission of the fast ($A_1$) and slow ($A_2$) components of the PL decay dynamics as a function of the excitation pump fluence.

Despite the unclear trend of $A_1$ corresponding to pump power, $\tau_1 = 13$ ps is interpreted as Auger lifetime $\tau_A$ of two excitons. This value is an order of magnitude longer than that reported by Wang et al. However, we note that SWCNTs in their study have lengths of $\sim 400$ nm. Since Auger lifetime is expected to be proportional to tube length [61], the value of $\tau_A$ emerged from this analysis is reasonable since our SWCNTs are 2-4 $\mu$m long. On the other hand, $\tau_A = 13$ ps is comparable to value of 15 ps reported by H"ogele et al. for low-temperature time-resolved PL for a single (6,4) tube [51]. With their SWCNTs of comparable lengths to those in Wang et al., the low temperature was attributed to such low Auger rate.

From the saturation behaviour of $A_2$ as observed in Figure 5.29, we interpreted the associated decay time $\tau_2 = 270$ ps as the linear decay process, associated with $\gamma$.
introduced in Section 2.6.3. This value of \( \tau_2 \) is comparable to 250 ps reported by Högele et al. from the slow component of bi-exponential trial fit on their direct time-resolved PL measurement on a (6,4) SWCNT [51]. These values are longer than the decay times of 24-60 ps measured on individual (6,4) micelle-encapsulated SWCNTs [19]. However, it is noted that their time-resolved PL data were fit to a mono-exponential decay, where the fast component might have convoluted with the intrinsic linear decay lifetime and resulted in a single shorter value.
Chapter 6

Conclusion and Recommendations for Future Work

In this thesis work, the capability of doing spectroscopy on a single air-suspended SWCNT has been demonstrated, considering the challenges that had to be overcome (e.g. low signal at a single tube level, IR emission, and aging phenomenon). We would like to emphasize that we were successful at performing multiple studies on the same SWCNT without any blinking behavior from its PL. The optical setup has been implemented to conduct photoluminescence excitation spectroscopy and time-resolved PL (femtosecond excitation correlation spectroscopy) experiments. In order to assist these measurements, LabVIEW programs were also designed to integrate data acquisition and automatic control of the apparatus (e.g. stepper motor, DC servo motors, spectrometer). As a result, a SWCNT sample can be scanned easily to search for approximate positions of SWCNTs of a specific chirality. A high resolution PL image of a SWCNT can also be recorded to estimate its length and determine its orientation. The pump power dependence of PL and time-resolved PL can be studied conveniently with the “Data Recording” and “Automated FEC Measurement” LabVIEW programs, respectively.
Findings for air-suspended SWCNTs of (9,8) and (10,8) chirality have been illustrated in Chapter 5. The maps obtained from sample scans show very low density of SWCNTs, which is crucial for single tube study. By deconvoluting the observed tube length from its high resolution 2D image with the spot size (e.g. 2 µm), the intrinsic length of the tube can be extracted. The PLE maps reveal $E_{11} = 0.9$ eV (or 800 nm) and $E_{22} = 1.55$ eV (or 1380 nm) for a (9,8) SWCNT; whereas $E_{11} = 0.86$ eV (or 860 nm) and $E_{22} = 1.44$ eV (or 1440 nm) for a (10,8) SWCNT. The excitation and emission peaks of our SWCNTs are blueshifted by 20 meV and 12 meV, respectively, with respect to peaks found for micelle-encapsulated SWCNTs of the same chirality. Our air-suspended SWCNTs also exhibit narrower linewidths (44 meV for excitation and 13 meV for emission) as compared to micelle-encapsulated species. PL polarization data confirm that the emitted light from our air-suspended SWCNTs is strongly polarized along the tube axis as expected from previous studies by other research groups.

Under uniform excitation with 150 fs pulse duration, emitted PL increases with elevating pump intensities. Up to a threshold (i.e. saturating pump fluence of $0.1 \times 10^{13}$ photon/pulse/cm$^2$, which is lower by 2-3 orders of magnitude compared to values reported by other groups), PL exhibits “hard” saturation, with no improvement of PL regardless of higher pumping. We even observed the declining trend (5-10%) of PL at very high pump intensity. These features are consistent with the occurrence of exciton-exciton annihilation via Auger recombination process. Furthermore, PPD measurement with various pulse durations show no increase in PL even when the excitation pulse is stretched to 4 ps. The stochastic model of exciton dynamics was considered in order to simulate PPD curves associated with different excitation pulse durations. By superimposing the simulated results onto the experimental data, the absorption coefficient is suggested to be 0.15, which is 2-3 times greater than the value reported by Tsyboulski et al. for SWCNTs of comparable absorption bandwidth [23]. With $\tau$ and $\tau_A$ set to 180
ps and 1 ps in the rate equations, the simulation result using the stochastic model is simultaneously consistent with pulse and CW excitation experimental data. From the linear regime of PPD measurement, the quantum efficiency was estimated to be $5\% \pm 30\%$ for both (9,8) and (10,8) SWCNTs if $A = 0.059$ is adopted. The trend of tube length dependence of PL intensity was also observed.

With the FEC signal fit to a bi-exponential decay, two time constants were extracted and interpreted as PL decay times. The fast component $\tau_1 = 13$ ps is interpreted as Auger lifetime $\tau_A$ of two excitons. This value is longer than 1.2 ps predicted by Wang et al. for their 400 nm long SWCNTs [61]. Considering the expected proportionality of $\tau_A$ to tube length, our finding is reasonable for 2-4 $\mu$m long air-suspended SWCNTs. The slow component $\tau_2 = 270$ ps accounts for the linear radiative decay and nonradiative decay processes. This value is longer than the decay times of 24-60 ps extracted from mono-exponential fit on time-resolved PL data of individual (6,4) micelle-encapsulated SWCNTs. On the other hand, our $\tau_2$ value is comparable to 250 ps reported by Högele et al. for the slow component of bi-exponential trial fit on their direct time-resolved PL measurement of a (6,4) SWCNT [51].

The findings presented in this thesis are on SWCNTs of (9,8) and (10,8) chirality. The future work should extend to other chiralities that are accessible with the present system. Variety in chiralities will allow to examine the diameter dependence of SWCNT optical properties (e.g. quantum efficiency, PL lifetimes). Considering that the present work is conducted at room temperature, another interesting aspect that can be investigated in the future is the temperature dependence of SWCNT optical properties (e.g. signature and role of dark exciton revealed at low temperature). The dependence of PL intensity on tube length has so far been observed for three SWCNTs of small variations in length. For a more comprehensive conclusion, a larger number of SWCNTs with varying length should be studied.
The FEC technique presented in this thesis is not a direct measurement of PL lifetimes. Other time-resolved PL techniques that are feasible for IR emitting single tube should be investigated. Two possibilities are:

- **Nonlinear time-gating:** output PL from a SWCNT is gated with a short pulse. Upconverted signal resulted from sum frequency generation of the input PL and the gating pulse is analyzed. The essence of this technique is the conversion of SWCNT IR emission to visible regime where detection technology works better.

- **Plasma shutter:** plasma generated when a high intensity pulse hitting a GaAs wafer can induce the change in reflectivity of the material. It can serve as a “knife-edge” to time-resolve the incident PL.
Bibliography


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[91] M. Jones, W. K. Metzger, T. J. McDonald, C. Engrakul, R. J. Ellingson, G. Rum-
Appendix A

Subroutines for Equipment Control

Spectrometer subVIs

<table>
<thead>
<tr>
<th>SubVI</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibrate</td>
<td>Perform the calibration for the spectrometer</td>
</tr>
<tr>
<td>GetDefaultUnits</td>
<td>Retrieve the length unit currently used by the spectrometer</td>
</tr>
<tr>
<td>MovetoWavelength</td>
<td>Instruct the grating to turn until the desired wavelength is reached</td>
</tr>
<tr>
<td>GetCurrentWavelength</td>
<td>Retrieve the current wavelength set by the grating</td>
</tr>
<tr>
<td>IsBusy</td>
<td>Return the dynamics reserve setting</td>
</tr>
</tbody>
</table>

Table A.1: Subroutines to control the spectrometer in LabVIEW program.

LIA commands

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Return the channel 1 output</td>
</tr>
<tr>
<td>G</td>
<td>Return the sensitivity setting</td>
</tr>
<tr>
<td>D</td>
<td>Return the dynamics reserve setting</td>
</tr>
<tr>
<td>T1, T2</td>
<td>Return the pre-filter and post filter setting</td>
</tr>
</tbody>
</table>

Table A.2: Major commands for the LIA control.

DC servo motor subVIs

Stepper motor commands
### APPENDIX A. SUBROUTINES FOR EQUIPMENT CONTROL

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCOpen/MCClose</td>
<td>Open/Close a controller handle</td>
</tr>
<tr>
<td>MCEnable Axis</td>
<td>Enable/Disable an axis</td>
</tr>
<tr>
<td>MCDLGSaveAxis</td>
<td>Save current axis setup to an INI file</td>
</tr>
<tr>
<td>MCDLGRestoreAxis</td>
<td>Restore the axis setting from INI file</td>
</tr>
<tr>
<td></td>
<td>(this file must have been saved with a previous call to MCDLGSaveAxis)</td>
</tr>
<tr>
<td>MCGetStatus</td>
<td>Obtain current status information from the selected axis</td>
</tr>
<tr>
<td>MCDecodeStatus</td>
<td>Decode status bits from status word</td>
</tr>
<tr>
<td>MCMoveRelative</td>
<td>Move an axis a relative distance</td>
</tr>
<tr>
<td>MCGGetPositionEx</td>
<td>Read current position of selected axis</td>
</tr>
</tbody>
</table>

Table A.3: Major subVIs to control the DC servo motor in LabVIEW programs.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>Enable online mode</td>
</tr>
<tr>
<td>Q</td>
<td>Quit online mode</td>
</tr>
<tr>
<td>ImMx</td>
<td>Index (or rotate) motor</td>
</tr>
<tr>
<td></td>
<td>( m = 1, 2, 3 ) but we only use motor 1</td>
</tr>
<tr>
<td></td>
<td>( x ) is number of steps to turn motor (positive for CW, negative for CCW)</td>
</tr>
<tr>
<td>ImM0</td>
<td>Index motor to absolute zero position</td>
</tr>
<tr>
<td>SmMx</td>
<td>Set speed ( x ) for motor ( m )</td>
</tr>
<tr>
<td>AmMx</td>
<td>Set acceleration/deceleration ( x ) for motor ( m )</td>
</tr>
<tr>
<td>Bx</td>
<td>Set backlash compensation ( (x = 1 \text{ On}, x = 0 \text{ Off}) )</td>
</tr>
<tr>
<td>N</td>
<td>Null Absolute Position Register</td>
</tr>
<tr>
<td>X</td>
<td>Send position of motor to host</td>
</tr>
<tr>
<td>V</td>
<td>Verify controller’s status</td>
</tr>
<tr>
<td></td>
<td>(&quot;B&quot; ( \rightarrow ) busy, &quot;R&quot; ( \rightarrow ) ready for command, &quot;( \wedge )&quot; ( \rightarrow ) program is finished.)</td>
</tr>
</tbody>
</table>

Table A.4: Major commands for the stepper motor control.
Appendix B

Unit Conversion of Experimental Parameters

B.1 Calculation of Excitation Intensity

From the pump power ($\mu$W) measured after lens L2 and before the glass window (refer to Figure 3.3 and Figure 3.5), we need to consider the following factors in order to estimate the excitation power $P$ on a SWCNT:

- Transmission (at 800nm) of lens L2 (if it is present to introduce a small spot size): 0.9
- Transmission (at 800nm) of the ND0.1 filter used as a window for rH-regulated housing: 0.61
- Reflectivity (at 800nm) of the glass window: 0.1
- Transmission (at 800nm) of the aspheric lens: 0.9
- Contributed factor by the reflectivity (at 800nm) from Si/SiO$_2$ substrate: 1.2
The excitation area $A$ calculated from spot diameter, $d$, is: $A = \pi(d \times 0.849)^2$

The average excitation intensity (W/cm$^2$) is given by: $I_{exc} = \frac{4 \times P}{A}$.

Note: Conversion factor from $\mu$W/$\mu$m$^2$ to W/cm$^2$ is 100

Excitation photon flux, or pump fluence, (photons/pulse/cm$^2$) is computed as: $\phi_{exc} = \frac{I_{exc} E_{\lambda}}{E_{\lambda} \times 76 MHz}$, where $E_{\lambda} = \frac{hc}{\lambda}$ is the photon energy (e.g. $2.48 \times 10^{-19}$ J for 800nm, $2.31 \times 10^{-19}$ J for 860nm)

### B.2 Collection of PL emitted from a SWCNT

To account for the total efficiency in collecting PL emitted from a SWCNT to the entrance slit of the spectrometer (refer to Figure 3.3 and Figure 3.5), we need to consider the following factors:

- Transmission (at 1400nm) of the aspheric lens: 0.9

- Assuming PL is emitted in $4\pi$ sterian, the collection efficiency of the aspheric lens when the SWCNT is at the focal plane of the aspheric lens (i.e. yielding optimal PL) is $\frac{\pi (d/4)^2}{4\pi f^2}$, where $d$ and $f$ are the diameter and focal length of the aspheric lens. With $d = 0.2$ mm and $f = 6.24$ mm (Thorlabs C110TM), the collection efficiency is 0.136

- Transmission (at 1400nm) of the glass window: 0.90

- Reflectivity (at 1400nm) of 3 gold mirrors: 0.93

- Transmission (at 1400nm) of lens L3: 0.95

- Transmission (at 1400nm) of the LWP filter: 0.8

Throughput of the system, including the spectrometer, the InGaAs detector and the LIA has been discussed in Section 3.5.3.
Appendix C

LabVIEW Block Diagrams

Figure C.1: Block diagram of the “Data Recording.vi” LabVIEW program.
Figure C.2: Block diagram of the “Sample Rapid Scan.vi” LabVIEW program.
Figure C.3: Block diagram of the “Sample Step Scan.vi” LabVIEW program.
Figure C.4: Block diagram of the “Spectral Scan.vi” LabVIEW program.
Figure C.5: Block diagram of the “Automated FEC Measurement.vi” LabVIEW program.