INVESTIGATIONS INTO THE OPTICAL PROPERTIES OF

INDIVIDUAL, AIR-SUSPENDED,

SINGLE-WALLED CARBON NANOTUBES

by

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Abstract

Single-walled carbon nanotubes are naturally-forming nanostructures that have attracted considerable recent research interest due to their unique opto-electronic properties and comparative ease of fabrication. Two-thirds of nanotube species are semiconductors due to symmetry conditions imposed by their pseudo-one-dimensional tubular structure, and exhibit band-gap photoluminescence when isolated from their environment. Despite their elegant structural simplicity, fundamental properties of carbon nanotubes, such as their intrinsic quantum efficiency, non-linear excitonic recombination mechanisms, and the role of environmental effects, continue to be disputed in the literature.

The design of an apparatus capable of observing nanotube photoluminescence is presented, along with conclusive proof of the observation of a single (9,8)-chirality nanotube in the form of spectral, spatial, and polarization-dependent measurements. The dependance of the excitation and emission spectra of a single nanotube on the excitation intensity is explored and the emission spectra found to be described by a Gaussian peak function, in contrast to previously-reported results.

The unexpected ability to cause redshifts in the emission spectrum via the ambient humidity is discovered, which has consequences on experimental best practices.

Photoluminescence quantum efficiencies are measured to be $4\pm2\%$ and $13\pm6\%$ for
two different nanotubes. This is at the high end of the range for comparable literature results, and supports the validity of a recent literature value for the effective atomic absorption coefficient for carbon, $A_C = 1.6 \times 10^{-3} \text{ nm}^2$, which is ten times greater than previous literature values.

Pulsed power dependence studies show that the PL emission undergoes ‘hard’ saturation at an excitation intensity of $0.5 \times 10^{12} \text{ photons/pulse/cm}^2$, which is at least 100 times lower than previous reports and provides insight into non-linear decay dynamics. A novel theoretical model is developed to explain this saturation process, which yields an absorption co-efficient of $A_C = 1.2 \pm 0.3 \times 10^{-3} \text{ nm}^2$ as a fit parameter.

Time-resolved photoluminescence dynamics are explored using femtosecond excitation correlation spectroscopy. Results suggest that the one-body decay processes are bi-exponential, with time constants of $\tau_1 = 31 \pm 4 \text{ ps}$ and $\tau_2 = 313 \pm 61 \text{ ps}$, but also highlight the limitations of this technique in observing the expected very rapid ($\approx 1 \text{ ps}$) two-body Auger recombination process.
Co-Authorship

The research effort described in this thesis was a truly collaborative effort between co-workers Tam Q. Nhan, Y.-F. (Elsa) Xiao, supervisor James M. Fraser, and the author. While every effort is made in the body of the text to distinguish contributions that are identifiably the work of either Elsa or Tam, this approach does poorly describe the constant discussion of experimental techniques, results, and interpretations that did much to shape the studies reported here. Consequently, while the following paragraphs outline notable sections of work that were undertaken exclusively or to a significant extent by the author, and those that were primarily the responsibility of others, it should be remembered that most of the significant experiments and analysis were performed jointly.

The author notes his principle role in several areas of the research. This began when he was presented by his supervisor with an exciting idea about a proposed field of research, and a submission deadline for a conference that was scant days away. Hence he performed much of the initial literature search and scoping of the experiment, as well as much of the initial opto-mechanical design and placement, notably the ‘periscope’, ‘delay line’, ‘initial’ and ‘intermediate’ optics. (See Section 3.5). The author notes with delight his discovery of the first confirmed nanotube (‘Charlie’), but that the initial alignment and characterization work was performed jointly with

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Elsa, Tam, and James.

The author was primarily responsible for designing and implementing the environmental control system, and performing the experiments to determine the effect of humidity and ‘aging’ (See Section 4.6). This was followed by general studies (emission spectra, excitation spectra, spatial profile, etc.) on ‘short’ nanotubes, i.e. nanotubes less than 3 µm in length, particularly involving attempts to create PPD curves (See Section 4.4) with well-understood background. This work led directly to his creation of the simple theoretical model described in Section 4.4.4. The author notes his primary role in determining the spectral bandpass characteristics of the spectrometer (Section 4.2.1), performing the ‘pulse stretching’ FEC measurements using dispersive glass (Section 4.5.3), as well as the experimentation and analysis performed to investigate the relationship between the emission spectrum, excitation spectrum, and excitation intensity (Section 4.3).

As mentioned in the first paragraph, the contributions of co-workers Elsa and Tam to the work reported here were many and varied; only the most distinctive are mentioned here in the interest of brevity. Tam had primary responsibility for designing and implementing all of the various computer-control and data acquisition programs necessary for the experiment, which she accomplished using LabVIEW. These programs made an absolutely essential contribution to the success of this work. Additionally, Tam performed much of middle-game data collection and experimental refinement that helped broaden our understanding; both of the nanotubes, and our ability to interrogate them. Of additional specific note were her efforts to extend the range of the pulse-stretching FEC technique using a 4-f grating pair, her work with Elsa in using the stochastic model of exciton dynamics proposed by Barzykin et
al. [5], and her experimental investigations of nanotubes of (10,8) chirality.

Elsa also contributed much to the experiment, taking a lead role in characterizing the spectrometer system, tirelessly searching for nanotubes manually before the advent of the automated scanning program, and building up much of the ‘baseline’ PPD and FEC data sets from extensive experimentation on many different nanotubes. Her considerable familiarity with the peculiarities of the apparatus garnered from this experience made her a highly-valued resource in the lab. Elsa also spearheaded the effort to perform the stochastic modeling mentioned above, generating the simulation code later used by Tam.

Finally, it should be stated that any work not specifically attributed to another experimenter was performed by the author alone, or the author in close collaboration with Elsa, Tam, or James.
Acknowledgments

To James Fraser, my supervisor, for providing me with the tools, motivation, and encouragement that helped me succeed, and the understanding and support that I needed in the interim. I truly appreciate all of the extra effort you have put in to make both this project, and my broader studentship, a success.

To the faculty and staff of the Physics Department, who have helped me in many ways large and small.

To Elsa and Tam, my co-workers, for all of the work that you have put into this project, and the help that you have always cheerfully offered when I needed it; this was truly a collaborative effort.

To Paul, Jeff, Aaron, Rob, Matt and other denizens of 511H past and present, for making the difference between a lowly-paid researcher and a graduate student so plainly evident.

To friends during my time here at Queen’s, and particularly fellow members of the Houses of Jun and !Xobile, for making this time in this place into a life.

To my family, for support, encouragement, and the occasionally-necessary early-morning nag,

and to a Jen, for everything, still.
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<td>FWHM</td>
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<td>Optical Parametric Oscillator</td>
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<td>Numerical Aperature</td>
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<tr>
<td>ND</td>
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<tr>
<td>NEP</td>
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<tr>
<td>NRC</td>
<td>National Research Council</td>
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<td>RBM</td>
<td>Radial Breathing Mode</td>
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<td>Relative Humidity</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>S/N</td>
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Chapter 1

Introduction

Carbon nanotubes are intriguing molecular nano-structures that have attracted a tremendous amount of research interest since their discovery was first widely reported in 1991 [49]. Their unique properties have led to their use in diverse fields of research. To the materials scientist, carbon nanotubes are composite fibres which have superlative tensile strength, axial stiffness, electric conductivity, and can be centimeters in length despite their nanometer-scale diameter [33, 6, 125, 3, 116, 63]. From the point of view of the condensed-matter theorist, carbon nanotubes are highly symmetric, mono-elemental, pseudo-one-dimensional structures that can be modeled at a fundamental level, providing insight into the physics of quantum confinement at low dimensionality [22, 23, 115, 95, 104]. To the experimental physicist, carbon nanotubes are easily-produced and experimentally robust nanostructures that have intriguing electronic, phononic and optical properties that can be probed at the single-molecule level [93, 24, 75, 41]. Finally, to the applications-driven engineer, carbon nanotubes are promising new materials that have been implemented as saturable optical absorbers [103], electrochemical bio-sensors [117], fluorescent tags for studies of
pharmacokinetics [12], and additionally show promise for use in applications ranging from nano-scale electrical interconnects [67] to single-photon emitters [41].

Fundamental research into the properties of carbon nanotubes has been greatly aided by advances in synthesis. Whereas carbon nanotubes were initially observed as tangled fibres in soot from arc-discharge evaporation experiments [49], it is now possible to produce samples containing individual single-walled nanotubes that are isolated from their environment, and can be studied over an extended period of time [37, 107, 42, 70]. Concurrently with advances in synthesis technology, optical techniques such as absorption [52], Raman [57], and photoluminescence spectroscopy [93] have furthered our understanding of the intrinsic behaviour of carbon nanotubes. For example, two-photon absorption experiments showed that the expected one-dimensional electronic structure of carbon nanotubes is substantially altered by Coulombic electron-hole interactions [112], and studies of nanotube photoluminescence have made it possible to experimentally determine the physical structure of a nanotube simply by mapping its absorption and emission spectra [4].

Despite these advances, key questions about the intrinsic behaviour of carbon nanotubes remain unanswered. The effect of different environmental isolation techniques, namely solution-based micelle-encapsulation [93] and physical suspension in air between microfabricated supports [75], on the intrinsic carrier dynamics is unclear. Literature reports of the exciton lifetime vary from 7–320 ps [111, 79, 35, 36, 59], and there is further debate as to the nature of the mechanism that results in the observed ‘saturation’ of photoluminescence emission at high excitation intensities. Additional uncertainty exists because much of the research reported in the literature has been performed with ensemble samples, where possibly significant tube-to-tube variation
in properties is masked by averaging. Lastly, there is a substantial range in the reported values for the quantum efficiency ($1.7 - 700 \times 10^{-4}$ [93, 53, 111, 70]) and optical absorption cross-section ($1.2 - 160 \times 10^{-5}$ nm$^2$/atom [11, 52, 70, 107]) of carbon nanotubes. Not only are the answers to these questions important in terms of furthering our understanding of the relevant basic physics, but also because they would enhance our ability to use carbon nanotubes in practical devices.

In summary, much work remains to be done on carbon nanotubes; they are so elegantly simple in form that there is every desire to fully understand their behaviour. The work reported in this thesis represents first steps towards this goal. A literature survey gives context and background to the proposed experiments (Chapter 2). The novel preparation method used to create the carbon nanotubes under study is discussed, as the individual, air-suspended nanotubes that are used were only recently developed and provide new insight into which nanotube properties are the result of environmental interactions and which are truly ‘intrinsic’. Further, the apparatus and experimental techniques developed to enable experimentation on individual carbon nanotubes are described in detail (Chapter 3). The results of necessary calibration and preliminary experiments are presented, along with a full discussion of the various characterization techniques, both novel and well-established, employed to study the excitonic properties of these single-walled carbon nanotubes by optical means. Particular emphasis is given to understanding the dynamics of the processes that create photoluminescence through theory and experiment (Chapter 4). Conclusions are drawn from the comparison of experimental results to theoretical models and the literature, and recommendations are made for future work (Chapter 5).
Chapter 2

Background

2.1 Summary

Carbon nanotubes are fascinating nano-scale structures, due both to their physical properties, and their relative ease of fabrication. This chapter summarizes the discovery of nanotubes, then briefly addresses their superlative mechanical and electronic properties. The electronic band structure of single-walled carbon nanotubes is introduced as a derivation from the simpler band structure of two-dimensional graphene, and the commonly-used chiral index notation is introduced. Nanotube synthesis is summarily addressed, with an emphasis on the chemical vapour deposition techniques that are of particular relevance to the work. A summary is given of the first published observation of photoluminescence from carbon nanotubes, along with the experimental and theoretical work that has led to the accepted conclusion that nanotube photo-physics arises from excitons, which are then defined and briefly explained. The distinction in nanotube photo-physics between micelle-encapsulated and air-suspended tubes is introduced, as are the relative merits of ensemble and
single-tube studies. A brief discussion on the evolving understanding of the quantum efficiency of the photoluminescent process leads into a section on the techniques of measuring the dynamic behaviour of carbon nanotubes, and a summary of the current understanding of the inherent microscopic processes. Some outstanding research questions relevant to the work are introduced.

2.2 Discovery

The identity of the first ‘discoverers’ of carbon nanotubes (CNT) is a matter of considerable debate, and this is a consequence of one of their key properties; their relative ease of fabrication. Vapour-grown carbon fibres, filaments, and related structures have been known to science since the 1880’s [48, 96], and it is likely that nanotubes have been produced as a byproduct of these growth techniques since at least this time, as nanotubes have been observed more recently to grow co-incidentally with the carbon fibres under very similar conditions [28]. However, imaging technology with sufficient resolution to observe the <10nm diameter tubes did not exist at the time.

With the advent of electron microscopy, it became possible to observe carbon nanotubes directly. The first images of ‘hollow’ nanometer-diameter carbon fibres were published by Radushkevich & Lukyanovich in the Soviet Journal of Physical Chemistry in 1952 [97]. Although some of these transmission electron microscopy (TEM) images are highly suggestive of nanotubes, the publication attracted little attention in the West primarily due to Cold War tensions [89]. Carbon nanotubes formed from pyrolytic vapour deposition were ‘re-discovered’ in 1976 by Oberlin, Endo and Koyama as high-strength ‘cores’ left intact when carbon fibres were strained to failure axially [92]. While in hindsight, it is trivial to identify a hollow, 5nm
‘carbon fibre’ as a nanotube, the realization was not made at the time as TEM images of sufficient sharpness to resolve the characteristically concentric walls were not produced [33].

From the perspective of the literature, the first definitive report of carbon nanotubes was made by Iijima in 1991 [49], when he observed multi-walled tube-like structures of pure carbon aggregating on the negatively-charged electrode of an arc discharge cell. (Hereafter referred to as a multi-walled carbon nanotube, or MWCNT) Critical to Iijima’s work was his successful application of high-resolution TEM (HRTEM), which allowed the clear viewing of the concentric walls of the nanotube. This paper spurred research in the field, as it brought nanotube research into the field of fundamental physics research from the domain of materials science, and occurred at a time when many of technical capabilities and theoretical tools had matured to permit true nano-scale science [89].

The original discovery of the aptly-named single-walled carbon nanotube (SWCNT) is substantially more straightforward to establish. This achievement was simultaneously reported by two articles in a 1993 edition of Nature, one by Iijima and Ichihashi [50], and the other by Bethune et al. [8]. Both reports resulted from ongoing efforts to produce MWCNT filled with transition metals.

Although Iijima’s discovery was a partially serendipitous consequence of ongoing work on C$_{60}^1$, the unique and often superlative physical properties of carbon nanotubes have caused them to be the subject of a considerable research effort in their own right. The magnitude of this effort is alluded to by a cursory topic search on the ISI Web of Science, which finds that 53,949 nanotube-related articles and letters

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$^1$C$_{60}$, also known as ‘buckminsterfullerene’ or ‘buckyballs’ was the first of the ‘fullerenes’ to be discovered. Consisting of 60 carbon atoms arranged in a spherical shell and sharing a mixture of $sp^2$- and $sp^3$-hybridized bonds, it was first reported by Kroto, Curl, and Smalley et al. in 1985. [68]
were published between 1991 and June, 2008, with topics spanning physics, materials science, engineering, chemistry, and molecular biology.

2.3 Physical Properties

The unique properties of carbon nanotubes are the direct consequence of their unusual structure. A carbon nanotube can be conveniently described as a graphene sheet ‘rolled up’ into a cylindrical shell along an arbitrary lattice vector, which may be capped at the ends by two hemispherical sections of the appropriately-sized spherical fullerene \[22, 101\]. The simplest form of the nanotube is the single-walled CNT, comprising a single cylinder of graphene. By contrast, multi-walled carbon nanotubes are made up of two to over a hundred concentric graphene cylinders \[33\], with the inter-layer distance of 0.34 nm closely matching the layer spacing in graphite \[49\].

The extreme length-to-diameter aspect ratio of carbon nanotubes creates the pseudo-one-dimensional geometry which defines many of their properties. Conceptually, carbon nanotubes could have diameters that are arbitrarily large, or as small as a three-atom triangle. However, most synthesis techniques produce nanotubes with a specific range of diameters. This is because extremely narrow nanotubes are energetically unfavourable due to the bending strain imparted to the graphene lattice \[20\], and very large-diameter\(^2\) tubes are unlikely to form due to defects and competition from bulk carbon forms. Available MWCNT have diameters which range from 1.4 nm to at least 100 nm \[6, 33\] and lengths that can reach 4.5 mm \[116\]. This implies an aspect ratio up to the order of \(10^6\). SWCNT have been prepared with diameters of

\(^2\)For example, tubes with macroscopic (cm) diameters are extremely unlikely to form due to the astounding perfection that would be required to keep such a structure from ‘devolving’ into a simple carbon fibre.
0.4 nm [3] to greater than 3 nm [6], and lengths of 4 cm [125], meaning that the aspect ratio of some SWCNT could exceed $10^8$.

The mechanical properties of SWCNT are MWCNT are quite similar; they are both extremely rigid and strong. Reported experimental values for Young’s Modulus of individual CNT of both types can exceed 1 TPa, while the tensile strength has been measured to be in excess of 10 GPa [33]. It should be noted that these values can vary significantly between tubes as a function of length, diameter, and as result of defects. Further, these figures are only for individual nanotubes, and are difficult to achieve on a macroscopic scale. This is because individual nanotubes readily bundle.

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3By way of comparison, this is roughly 19 times stiffer, and 56 times stronger per unit mass than structural steel [6]. Nanotubes are approximately five times less dense than steel.
to form rope-like structures due to a significant (500 eV per µm) Van der Waals deriving binding energy for parallel tubes in contact [93, 106, 32]. Consequently, the physical properties of nanotubes on a practical, macroscopic scale often derive from the comparatively weak inter-tube binding, as opposed to the superlative strength of intra-molecular bonds.

The intrinsic electronic properties of CNT result from symmetries in their structure. Here, the structural simplicity of SWCNT makes them more theoretically tractable than MWCNT. Envisioning a SWCNT as a ‘rolled up’ sheet of graphene immediately defines a chiral vector, $C_h$, which describes the azimuthal symmetry condition of the nanotube with respect to the intrinsic graphene lattice vectors (as shown in Figure 2.2). Nanotubes where this vector lies entirely along $a_1$ are termed ‘zigzag’, while those with a vector lying along $a_1 + a_2$ are called ‘armchair’ [22]. These chiral vectors are commonly described in shorthand by the notation $(m, n)$, which is equivalent to $ma_1 + na_2$ [101]. This convention will be used throughout this thesis. It is additionally noted that the magnitude of the vector is equal to the circumference of the tube, so that the diameter can be calculated given $m$ and $n$ via Equation 2.1.

$$D_{NT} = |C_h|/\pi = \sqrt{3}a_{C-C}\sqrt{m^2 + mn + n^2}/\pi; \quad (2.1)$$

Where $D_{NT}$ is the diameter of the tube, and $a_{C-C}$ is the nearest-neighbour distance in the graphene lattice. ($a_{C-C} \approx 1.44\text{ Å}$) [105].

A chiral angle, $\theta$, is defined as the angle between the chiral vector for the nanotube in question and the $a_1$ (or equivalently the zigzag) vector. It can be quickly calculated using Equation 2.2.

$$\theta = \arctan \left( \frac{\sqrt{3}m}{m + 2n} \right) \quad (2.2)$$

The chiral vector uniquely defines the electronic structure of SWCNT, provided it
is free of defects. For example, one-third of tube species, where $m - n = 3q (q \in \mathbb{Z})$\textsuperscript{4}, are metallic and have displayed ballistic conduction of electrons along their axis [99, 119, 120, 77], allowing them to carry high current densities with minimal heating [6].

The remaining species are semiconducting [101], with bandgaps that range from near-zero\textsuperscript{5} to at least 1.488eV [4]. Additionally, it is common to speak of two ‘families’ of

\textsuperscript{4}This was defined as $2m + n = 3q$ early work by Saito, Dresselhaus and Dresselhaus [101], but this equivalent definition has become more common (for example, [4]). Occasionally, finer distinctions are made, in that tubes with $m=n$ (i.e. zigzag) are truly metallic, whilst those with $m - n = 3q$ are ‘tiny-gap’ semiconductors due to effects resulting from the curvature of the tube, but behave as a metal or semi-metal at appreciable temperatures [78].

\textsuperscript{5}The process of experimentally finding the ‘smallest possible bandgap’ would be both challenging, due to the small energies involved, and of little consequence. For example, it has been predicted that a SWCNT 3nm in diameter would have a bandgap small enough to be comparable to $k_B T$ at room temperature [24]. Recall that the ‘limiting case’ for a large-diameter nanotube, viz. a graphene sheet, is a zero-bandgap semiconductor [87, 24].
semiconducting nanotubes, which consist of those SWCNT having \((m - n) \text{mod}(3) = 1\) and \((m - n) \text{mod}(3) = 2\) respectively [4]. These families are useful in establishing scaling relationships for carbon nanotubes.

An intuitive explanation of the origin and nature of the the 1D band-structure of any SWCNT starts with the known electronic structure of a perfect, infinite graphene sheet. As shown in Figure 2.3(b), the band structure of graphene has particularly interesting properties near the six K and K’-points which sit at the corners of the hexagonal Brillouin zone\(^6\) [23, 104]. Two items are of specific interest. Firstly, the bands near these points have energies which vary are nearly linearly with \(k\), which implies that the effective mass of both electrons and holes in graphene is negligibly small. As shown in Figure 2.3(c), the band structure near the K and K’ points is often approximated as a double cone. Secondly, the conduction and valence bands come into contact at these points, but have exactly zero density of states (DOS). The Fermi energy also passes through these points, so graphene can be described as a zero-bandgap semiconductor [23].

As described above, the act of ‘rolling up’ the graphene sheet to create a SWCNT defines both a chiral vector, and a perpendicular axial vector for the tube relative to the graphene lattice. Given that the electrons are quantum-mechanically confined to states with momentum vectors along the axis, all of the allowed states are given by a series of one-dimensional slices from the two-dimensional graphene band structure[101]. Critically, the orientation of these slicing planes depends on the orientation of the axial vector (or equivalently \(C_h\)) relative to the graphene lattice. Furthermore, as the quantization is enforced by the periodic boundary condition in

\(^6\)K and K’ denote two sets of three points each which differ only by the helicity of the Bloch vectors. They are energetically degenerate in the absence of a strong axial magnetic field [124].
Figure 2.3: (a) Schematic diagram of the formation of a SWCNT from a ‘rolled-up’ graphene sheet. (b) Constant energy surfaces of 2D graphene showing a linear dependence on $k$ near the $K$ point in the Brillouin zone. (c) A ‘close-up’ of the band structure near the $K$ point in graphene (such that the bands appear linear). The heavy ‘cutting’ lines that intersect the conical surfaces result from the restriction that only axially-propagating states are allowed states for SWCNT. The structure of these cutting lines is dependent on the chirality of the nanotube, and hence is related to the 1D density of states (In this case for a metallic SWCNT). Reprinted with permission from [23]. Original authors G.G. Samsonidze and R. Saito. Copyright 2006 by Elsevier B.V.
the circumferential direction, the spacing of this family of planes varies inversely with the diameter of the tube [23]. As a result, each type \((m,n)\) of nanotube has a different band structure, as the family of cutting planes with which it is associated has a unique orientation and spacing. The location of these cuts defines the properties of the nanotube. Tubes with a cutting plane passing through the K-point are metallic [23]. Tubes with no cutting planes passing through the K point are semiconducting, with band gaps that depend on the chiral vector, and generally increase in size as the tube diameter decreases.

The one-dimensional density of states provided as the right-hand side of Figure 2.3(c) is also instructive. Clearly evident are the ‘van Hove singularities’ (vHs); specific energies that have a very high DOS. Given that the transition strength is proportional to the DOS via Fermi’s Golden Rule, these features dominate both the absorption and emission spectra of SWCNT\(^7\) [4]. Due to the importance of the van Hove singularities in spectroscopic work, the experimentally-observed transitions between some singular levels are given labels. ‘\(E_{11}\)’ refers to the lowest-energy transition between the lowest-lying vHs in the conduction band and the highest vHs in the valence band, hence defining the band gap of the nanotube [100]. As carriers rapidly relax to the band edge, this transition is responsible for the overwhelming majority of PL emitted from the tube. Similarly, ‘\(E_{22}\)’ refers to the transition between the second lowest vHs in the conduction band and the second-highest vHs in the valence band. ‘\(E_{12}\)’ and ‘\(E_{21}\)’ transitions have been experimentally observed [71], but these are polarized preferentially perpendicular to the nanotube axis, and are markedly weaker.

\(^7\)This statement is only approximate. As will be discussed below in Section 2.5, it is in fact exciton states made up of these 1D states which dominate the spectra. However, this statement reflects the prevailing sentiment in much of the early spectroscopic literature, as, until shown otherwise, it was assumed that the excitonic effects were a minor correction, as is the case in bulk semiconductors [112].
than the ‘$E_{11}$’ and ‘$E_{22}$’ transitions due to the de-polarizing effect of the extreme confinement in the radial direction \[1\].

The electronic properties of even ‘perfect,’ defect-less MWCNT are notably more complex, due to the coupling between shells \[99\]. Although MWCNT are predicted to exhibit behaviours that are broadly similar to SWCNT, as the coupling between concentric layers is thought to be weak \[6\], this statement is not without debate in the literature \[99\], and experimental results have been inconclusive (For example \[18, 30, 120\]). Consequently, given their comparative structural simplicity, SWCNT have been the subject of much of the literature on the electronic properties of nanotubes. However, both SWCNT and MWCNT have been shown to allow the easy propagation of phonons \[6\], with some measured thermal conductivities above 3000$W/m \cdot K$, which is 50% greater than either diamond or in-plane graphite \[63\]. SWCNT also show interesting phonon structure, including a relatively low-frequency ‘radial breathing mode’ (RBM), which corresponds to the perfectly symmetric radial expansion and contraction, and is unique to nanotubes. For further information on phonons in SWCNT, see, for example, the review articles by M. Dresselhaus or J. Hone (\[23, 43\]).

\[2.4 \text{ Synthesis} \]

While Iijima demonstrated that carbon nanotubes could be produced on the negative terminal of a carbon electrode used in low-pressure (100 torr of Argon) direct-current arc-discharge evaporation \[49\], numerous other growth methods have been discovered in the ensuing years, the most significant of which are the broad categories of arc discharge, laser ablation/laser vapourization\[8\], and chemical vapour deposition (CVD).

\[8\]This hybrid nomenclature is used as both terms are used in the literature to describe this process
All of these techniques are pyrolytic in nature, in that they involve the conversion of a carbon-bearing feedstock under the action of heat [33]. However, they vary substantially in the method of applying heat, the type of carbon feedstock used, the presence or absence of a catalyst, and the type of nanotubes which result. A brief overview of the main points of the three techniques is presented. For further details it is recommended to consult any of several review articles existent on the subject of nanotube synthesis, for example [33, 3, 82, 105].

2.4.1 Carbon Arc Discharge

Carbon arc discharge was the first reported method of nanotube synthesis [49], and was soon developed into a technique that could produce CNT on a gram scale [25]. As the name would suggest, the technique uses a DC arc discharge between two graphite electrodes to form the nanotubes. The anode is consumed and deposits are formed on the cathode which include nanotubes, carbon fibres, and amorphous carbon [25]. With pure carbon electrodes, only MWCNT are produced. The addition of metal catalysts to the anode (e.g. Ni-Co, Ni-Y, Co-Y) allows SWCNT to be produced [55]. The ambient gas plays a role in the growth process; the replacement of the standard He with H$_2$ produces MWCNT with very small innermost diameters [3], and the use of H$_2$ in an inert gas mixture can create macroscopic (20 – 30 cm) webs of SWCNT [3]. Advantages of this process are the simplicity of its implementation, comparatively reduced cost [55], comparatively large-scale synthesis, and the high crystalline quality of the MWCNT [33]. Disadvantages of arc discharge methods are that significant quantities of carbon byproducts are produced along with the nanotubes, and the SWCNT that are produced are highly bundled and tangled [55, 33].
2.4.2 Laser Ablation / Laser Vapourization

Laser ablation / laser vapourization is a technique pioneered by the Smalley group in their studies on fullerenes [68], and then applied to carbon nanotubes, notably in early publications by Guo [34] and Thess [106]. The technique is performed both on graphite samples heated in a furnace, and at room temperature [19]. Laser ablation generally favours the growth of SWCNT, but in general is very similar in operation to carbon arc discharge, in that in both cases; CNT are formed from condensation after the vapourization of a carbon target, have similar physical properties, and are produced along with a quantity of amorphous carbon and other byproducts [33].

2.4.3 Chemical Vapour Deposition

Chemical vapour deposition, in particular the catalyzed decomposition of carbon-bearing gases, has been used to produce carbon fibres for over a hundred years [96]. Endo et al. first alluded to a capability to create nanotubes from carbon-bearing gas in publications almost concurrent with Iijima’s 1991 paper [26]⁹, and first formally published results in 1993 [27]. Current CVD techniques for CNT production depend on the use of a transition metal catalyst (e.g. Fe, Ni, Co) and a flow of a carbon-bearing gas at elevated temperatures, usually 300 – 800°C for MWCNT, and 600 – 1150°C for SWCNT [33]. In the case of thermal CVD, heating of the substrate (Cold-wall CVD), or the entire reaction vessel (Hot-wall CVD) acts to initiate the decomposition of the carbon-bearing gas, causing the pure carbon to be deposited. In plasma-enhanced CVD, a plasma is used to decompose the gas feedstock at the correct

⁹Note in particular M. Endo’s participation in the 18th Meeting of the Japanese Carbon Society (1991), which he references in [27].
location, which has the important effect of lowering operating temperatures [105].
CVD is viewed as the most versatile production method for CNT as it can produce both short and particularly long nanotubes [125], CNT with specific orientation to microstructures on the substrate [75, 70], and CNT that include dopants such as boron and nitrogen. (For more information, refer to the extensive references in [6].)

Although a variety of specific techniques are used, three of particular relevance to the work are CoMoCAT, HiPCO, and an as-yet unnamed cold-wall CVD process developed by Homma et al. and refined by researchers at the National Research Council (Canada). The first two processes have been implemented on a commercial scale and are used to produce most of the nanotubes that are currently used in spectroscopic studies, for example [4, 93, 112, 17]. CoMoCAT (COBalt MOlybdenum CATalyst) uses carbon monoxide gas flowing over bimetallic cobalt-molybdenum catalyst particles which rest on SiO$_3$ supports to preferentially generate SWCNT [65].

After synthesis, post-processing is required to remove the silica, catalysts, and amorphous carbon byproduct. HiPCO (High-Pressure carbon monoxide (CO)), is a homogenous floating-catalyst technique, in that the Fe catalyst is introduced in the gas phase (as Fe(CO)$_5$ and forms aerosol micro-particles in the reaction vessel that are the sites for SWCNT growth [9]. Post-processing is again required to purify the sample. The third process was used to grow the SWCNT for the work reported in this thesis, and is described in detail in Section 3.3.2. In brief, SWCNT are grown at low densities on lithographically-pattered structures using a cold-wall CVD technique with Fe catalysts particles, ethanol as the source of carbon, and an ambient Ar-H$_2$ atmosphere. Significantly, no post-processing is required as the nanotubes are well-separated and easily accessible by laser light [42, 75, 70, 29]. Additionally, the
SWCNT produced with cold-wall CVD have, on average, slightly larger diameters than either CoMoCAT or HiPCO; $\approx 1.1$ nm vs $\approx 0.9$ nm respectively [72, 17, 4].

2.5 Nanotube Photophysics

2.5.1 Photoluminescence

A major advance in the field of nanotube research came in 2002, when the research group of Weisman and Smalley published the first observations of photoluminescence (PL) from an ensemble of HiPCo-grown single-walled carbon nanotubes [93]. This observation of band-gap fluorescence was not only elegant, unambiguous proof of the predicted semiconducting character of SWCNT [101], but it also presented researchers with a powerful tool with which to investigate the band structure and carrier dynamics of a nanotube.

The key innovation in the work was a method of sample preparation which both effectively de-bundled the SWCNT and kept them isolated from their environment. This was accomplished by dispersing the as-grown nanotubes in an aqueous solution that included a surfactant, sodium dodecyl sulfate (SDS), using high-shear mixing, then vigourously ultra-sonicating the solution to physically separate the small tube bundles into individual, surfactant-wrapped tubes. As a final step, the solution was ultra-centrifuged in an effort to separate the relatively buoyant single surfactant-wrapped tubes from the denser tube bundles, metal catalyst particles, and other forms of carbon [93].

\footnote{This experimental confirmation had already been reported in several papers published in 1998 using the techniques of resonant Raman spectrscopy and low-temperature scanning probe and scanning tunneling microscopy. For further details, refer to the discussion in [23].}
The results were striking; not only were the experimenters able to more clearly resolve the absorption spectrum of the ensemble of the tubes significantly more clearly than in earlier work, but the tubes also emitted bright photoluminescence at their bandgap energy, that is at chirality-dependant wavelengths ranging from 800–1600 nm. It was hypothesized that the PL had previously been suppressed as coupling between bundled SWCNT (some of which could have been metallic) provided rapid non-radiative recombination pathways for the excited electron-hole pair [93]11

2.5.2 Photoluminescence Excitation Spectroscopy

The utility of PL spectroscopy as an experimental technique was greatly enhanced by work reported in a second paper from the Weisman group later that year [4]. In this paper, the researchers observed the emitted PL spectrum of an ensemble sample of surfactant-wrapped nanotubes as a function of the input wavelength. This generated a 3D data set that was plotted as a 2D contour map with intensity as a function of excitation and emission wavelength. This type of plot came to be known as a photoluminescence-excitation (PLE) map [74]. The signal from each chirality of tube appears on the plot as a peak at a well-resolved point in the excitation wavelength/emission wavelength space.

Theoretical simulations had predicted that the peaks from SWCNT of the same family and the same diameter should appear on arcs in this space due the effects of trigonal warping [100], with adjacent tubes on the arcs differing in chiral index by \((m + 2, n - 1)\) or \((m - 1, n + 2)\) [4]. These arcs were observed in the data, and

\[\text{[11]}\] The effect of tube bundling has been the subject of significant work in the literature more recently. Hertel’s group showed that these early micelle-encapsulated samples likely included an appreciable fraction of bundles [17], while the specific effects of bundling on PL emission have been probed by the Heinz group [114].
hence it was only necessary to fix the chirality of one of the tubes in each arc to allow for the determination of the chiralities of all. This was done by measuring the frequency of the radial breathing mode through Raman spectroscopy, which has a simple, monotonic dependence on the diameter of the nanotube, and is selectively enhanced when the light used is resonant with an optical transition, allowing it to be unambiguously related to the position of a SWCNT on the PLE map \cite{21}\. Taken together, this provided experimenters with the ability to quickly identify the chirality of an unknown tube by creating the appropriate PLE map.

### 2.5.3 Exciton Photophysics

From the Weisman group’s first reports of PL, questions have been raised as to whether excitonic effects played a significant role in the nature of the observed PL spectra. In particular, the experimentally measured ratio of the $E_{22} : E_{11}$ varied substantially between tubes of differing chiralities and had an average value of 1.7 \cite{93}. This effect was not predicted by any implementation of a one-electron model \cite{58}, which always predicted that this ratio between the first and second transition energies would be equal to 2.0 \cite{93}. Drawing upon earlier theoretical work by Ando \cite{2}, Weisman et al. postulated that the discrepancy could possibly be the result of excitonic effects.

An exciton is a composite particle created when there is appreciable Coulombic interaction between an excited electron and a hole, leading to the bound pair behaving as a single quasi-particle. Excitons are classified as Mott-Wannier or Frenkel based\footnote{This property is also used to identify the chirality of tubes. A plot of the possible resonant $E_{11}$ transition energies versus the nanotube diameter is called a Kataura plot, after the first author of the paper in which it was first published \cite{61, 23}.}.
on their size with respect to the host lattice. Whereas the Mott-Wannier excitons in bulk semiconductors are much larger than the lattice spacing, the excitons in CNT are roughly the same size as the graphene lattice [112], and hence are classed as Frenkel-type excitons [69]. This size is dictated by their binding energy, which is, in turn, dependant on the degree of screening provided by the host lattice. In comparison to a three-dimensional semiconductor, a carbon nanotube provides very little dielectric screening, due in large part to the relatively few atoms interacting with the electron-hole pair [23]. It is noted that in the case of an ideal 1D electron-hole system, the screening goes to zero and the binding energy diverges [2, 35]. It has been shown experimentally that the exciton binding energy in SWCNT is on the order of 500 meV [23, 112], which is an appreciable fraction of the remaining $\sim 1\text{eV}$ bandgap [4].

Some experiments conducted in the following few years suggested that the optical behaviour of SWCNT was due to excitonic effects. Three examples are the deviations from the predicted ‘arcs’ reported in the paper by Bachilo et al. [4], the very weak dependence of the lineshape on temperature as reported by Htoon et al. [44], and the observation of intensity-dependant decay dynamics by Ma et al. [80]. Despite the growing evidence, no experiment was seen as adequately conclusive to rule out the simpler picture involving only one-body one-dimensional van Hove singularities.

The ‘exciton picture’ was given a substantial boost by the two-photon PLE spectroscopy reported by the Heinz group in 2005 [112]. In this work, an ensemble sample of SWCNT was excited nonlinearly via a two-photon process and the resultant PL spectra recorded to form a two-photon PLE map. It was observed that in no case was

$^{13}$The absence of screening in nanotubes is often visualized by considering that the electric field lines extending from the electron to the hole pass largely through free space outside of the nanotube [114].
the excitation energy of the ‘$E_{11}$’\textsuperscript{14} transition the same as the energy of the resultant PL emission, which, in simple theory, came from the same $E_{11}$ level. Instead, PL was only observed when the two-photon excitation was markedly blue-shifted ($\sim 250\text{meV}$) with respect to the emission [112].

This observation was incompatible with a one-body picture, as both one- and two-photon transitions across the bandgap would be allowed. Instead, it supported the exciton picture, as the various exciton states were known to obey selection rules that resulted from their underlying symmetry. Specifically, optically active excitonic wavefunctions were of defined parity. Consequently, allowed one-photon transitions could only occur between states of opposite parity, and two-photon transitions could only occur between states of the same parity [112]. As the lowest-energy exciton states were not expected to be degenerate [2], the observation of a difference between the two-photon excitation and one-photon emission energies was strong proof that ‘the optical resonances in SWCNT arise from excitons.’\textsuperscript{15}

The marked difference between the optical activity of different exciton levels has led to the discussion of ‘bright’ and ‘dark’ excitons, which can result from other effects than simple parity selection rules [23, 104]. A first consideration arises from conservation of momentum. Given that photons carry negligible momentum compared to the exciton, a requirement for an optical transition is that the center-of-mass wavevector of the exciton be within a small range of values about zero [104]. With the exception

\textsuperscript{14}Despite the fact that this work showed that the simple van Hove picture and, hence, the idea of an $E_{11}$ energy level was incomplete, this term will still be used to refer to the lowest-lying exciton level. This has some non-rhetorical justification, as this exciton wavefunction is made up of states from the theoretical (unperturbed) $E_{11}$ level.

\textsuperscript{15}This is a reference to the title of the important paper describing the two-photon experiment by Feng Wang \textit{et al}.\textsuperscript{et al}.
of low-probability phonon-assisted processes, this effectively rules out optical transitions from excitons having non-zero quasi-momentum, which has ramifications on exciton dynamics as discussed below in Section 2.5.8. In addition, given that excitons are expected to relax to a thermal distribution rapidly after they are created [39, 35], and that $k_B T$ is relatively large compared to this optically-active ‘window’, it is likely that many excitons will be ‘dark’ due to simple momentum conservation during a majority of the time [104].

A further effect that makes many excitonic states dark is a result of the spin-physics of the quasi-particle. When the exciton is created by the absorption of a photon, the constituent electron and hole are required to have opposite spins, which requires that the resultant exciton be formed as a spin-0 singlet [23]. However, for every singlet state, there exist a triplet of states with total angular momentum of one. It is possible for the optically-excited exciton to transition to one of these states due to further interactions; for example with the lattice via phonons. In fact, in semiconducting nanotubes the lowest-energy state is predicted to be a triplet state [23]. These triplet states are not optically active under ambient conditions, as the ground state has zero angular momentum and the one-body annihilation process which creates the photon must conserve total angular momentum [23]. A final note should be made of the interesting work has been done using high magnetic fields to break the underlying symmetry of the exciton wavefunctions, which can ‘brighten’ exciton levels that are ‘dark’ due to parity selection rules, and hence allow more thorough study of the exciton levels via optical processes [124, 90].

In summary, excitons play a dominant role in the optical behaviour of SWCNT. They rob the majority of the oscillator strength from the expected one-body van Hove
singularities [85], and hence are the dominant cause of the major experimentally-observed spectral features [112]. Additionally, the significant probability for an exciton to relax to a ‘dark’ state results in a diminished probability of radiative decay. This has important ramifications for both the exciton dynamics of SWCNT, and the intrinsic quantum efficiency (QE) of any PL process [104]. Although the demonstrated fact that excitons dominate the optical behaviour of SWCNT has had the effect of complicating the theory necessary to nanotube behaviour, the richness of exciton photophysics in SWCNT, combined with the relative ease of experimentation, has made them an important experimental playground to study this emerging field [23].

2.5.4 Individual vs. Ensemble studies

Although the pioneering work on the optical properties of single-walled carbon nanotubes was done on ensemble samples, some researchers soon began to acknowledge the limitations of ensemble measurements and investigate the properties of individual SWCNT [37, 44, 35, 73, 10]. Although ensemble samples generate substantially more detectable signal, provide instant ‘statistical averages’ of nanotube properties, and may be more applicable to early bulk applications, a specific concern with ensemble work was that the finer details of the PL lineshapes might be obscured by the process of averaging light from many tubes, even if the SWCNT are of the same chirality. Early single-tube work was performed by taking dilute samples of surfactant-wrapped nanotubes and spin-coating them onto transparent substrates [37]. Atomic force microscopy (AFM) measurements were used to confirm that the ‘bumps’ appearing on

\textsuperscript{16}For a more complete description of exciton effects, consult, for example, the text and extensive references provided by the review article by M.S. Dresselhaus [23]
the surface were approximately the size of an individual nanotube, and physically isolated from one another.

The PL of individual nanotubes was then probed by confocal microscopy; this experiment produced interesting results. Firstly, it was observed that the PL of the nanotube was highly polarized along the tube axis [37, 71]. This result was simultaneously evidence that the observations were from an individual SWCNT on the surface, as well as strong experimental confirmation of the diminished oscillator strength in the radial direction due to the extreme quantum confinement [1], which complemented earlier work that showed a similar polarization dependance in absorption spectra [76].

Similar to other nano-scale light-emitting systems such as individual dye molecules and semiconducting quantum dots [84], it was expected that carbon nanotubes would exhibit PL intermittancy on the scale of minutes, which is often referred to as ‘blinking.’ Although there was disagreement in the early single-tube literature (for example [37, 44]), it has become clear that PL intermittancy is both rare\textsuperscript{17} and most likely an extrinsic effect that is likely due to the interaction of defects in the nanotube with the environment involving the creation of localized exciton ‘trap’ states [84, 10, 64]. The consensus is that, at room temperature, the majority of nanotubes that emit PL do so in a highly stable fashion on time scales from 20ms to hours, which markedly distinguishes them from almost all other known single-molecule emitters [84, 13, 10, 38].

Clearly evident from this single-molecule work is variation in properties between tubes, even between those of the same chirality. While most spectroscopic work done

\textsuperscript{17}The exception to this statement is at extremely low temperatures ($\approx 1.8$K), where blinking is more commonly observed ($\approx 50\%$ of micelle-encapsulated nanotubes) [38]. However, observations published by Kiowski et. al. 2007, suggest that the low-temperature blinking only occurs in micelle-encapsulated SWCNT, and it entirely absent from air-suspended nanotubes [64]. The distinction between the two types of nanotubes is described in Section 2.5.5, but this work further supports the hypothesis that nanotubes are intrinsically stable PL emitters, and that blinking behaviour results from interactions with their local environment.
on single tubes generally confirmed the main features of the ensemble work, such as the position of resonance peaks and general spectral lineshapes, most experimenters found that some fraction of tubes displayed markedly different properties than others of the same chirality. These included variations in PL intensity [37, 70, 13], spectral width [73, 37, 35], decay dynamics [36], and peak position [70, 36]. These differences were observed to exist not only between tubes of the same chirality, but also between different areas of the same tube [13, 70]. It is hypothesized that many of these effects are extrinsic and depend on the local environment of the tube. This has encouraged further efforts to improve sample preparation, to ensure that SWCNT are truly separated (‘individual’) and protected from their environment (‘isolated’) so as to determine the true, intrinsic optical properties of SWCNT.

### 2.5.5 Micelle-encapsulated vs. Air-suspended

A novel method of isolating individual nanotubes that is particularly relevant to this thesis was developed by Homma et al. and reported in a paper published in 2002 [42]. Instead of chemically isolating the tubes using a surfactant, the group used CVD to grow SWCNT that were physically suspended between pillars (100 nm in diameter, 360 nm in height, 500 nm spacing) that had been formed via synchrotron-radiation lithography [75]. For PL spectroscopy, which was done by collaborators at the National Research Council (Canada), the CVD growth method was fine-tuned to ensure a low density of nanotubes, which avoided much of the bundling observed with other growth techniques [29]. The observation of PL from such samples was first reported by the NRC group in 2003 [75]. This technique had the natural advantage of producing individual SWCNT that were fixed in position with respect to the substrate, allowing
repeated experimentation on a single tube. Additionally, the experimenters could control the environment around the nanotube by exposing it to ambient air, vacuum, an unreactive gas, etc. [72], which made the environmental effects easier to quantify than for a micelle-encapsulated SWCNT.

Results published using this type of sample showed general agreement with earlier work with micelle-encapsulated SWCNT, but highlighted several differences. The emission and absorption peaks of air-suspended nanotubes were blue-shifted by an average of 28 and 16 meV respectively relative to micelle-encapsulated nanotubes of the same chirality [74]. This was attributed to a reduction in the dielectric screening provided by the soap molecules. Additionally, the line-widths for air-suspended SWCNT were also narrower than those reported in earlier surfactant-wrapped single-tube work [75, 73, 93, 37]. Further, in work with a slightly different ‘trench-like’ sample geometry (described in detail below in Section 3.3), the NRC group reported a single-tube quantum efficiency of 7% [70], which was more than an order of magnitude above previous reports [93, 4, 111]. Although the story continues, as described below, it has become evident that air-suspended samples offer unique insight into the intrinsic properties of single-walled carbon nanotubes, and have been used in recent work done by groups other than the NRC collaboration (For example, [110, 114, 64]).

2.5.6 Quantum Efficiency

The NRC report that air-suspended SWCNT exhibited quantum efficiencies as large as 7% [70] played a part in spurring a re-examination of previous data, which led to the realization that the surfactant-based sample preparation techniques were not as

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\[\text{\footnotesize 18} \text{This is in contrast with earlier solution-based work, but notably not the spin-coated individual tube work.}\]
effective as had been hoped at individualizing and isolating the SWCNT. Whereas the early papers concerning PL emission from micelle-encapsulated SWCNT had suggested that the QE was on the order of $10^{-3}$, new papers from both the Hertel and Weisman groups were soon published that suggested that the QE of SWCNT was on the order of a few percent [17, 107]. These papers attributed the lower QE numbers previously reported to the presence of a significant fraction of bundled SWCNT remaining in the sonicated and centrifuged samples [17]. These small bundles were much closer in density to single micelle-encapsulated tubes than the larger bundles that were of primary concern in the early micelle-encapsulated PL work [93], and as such were not as efficiently separated by centrifugation. The contaminating bundles absorbed light efficiently, but had greatly enhanced non-radiative loss processes due to energy transfer to smaller-bandgap and metallic tubes. It was argued that this had the net effect of lowering the observed average QE [17].

A further concern raised by the new work was the need for more accurate values for the absorption co-efficient of carbon nanotubes. These values were of critical importance as any experiment measuring the QE of a SWCNT using PL intensity would, at some point, require the comparison of an incoming photon flux to an outgoing photon flux. As a result, the measured QE would, naturally, be the product of the absorption and intrinsic QE co-efficients [70]. The paper from the Weisman group cast doubt on the absorption co-efficient published by Islam et al. [52], which was derived from absorption work in ensembles, and had been used in the ‘7%’ NRC paper [70]. It was argued that the very broad absorption line-widths found in the Islam et al. paper are characteristic of impurities in the samples, and that these diminished the resonant
enhancement of absorption by approximately a factor of ten [107]. Theoretical calculations of this absorption parameter have been attempted, but are complicated by the need to accurately model the excitonic effects (For example [58, 70, 104, 95]). Accurate measurement of the absorption cross-section of a single SWCNT independent of its quantum efficiency remains an active field of research (See, in particular, [110]), as does the accurate establishment of the intrinsic quantum efficiency of PL in SWCNT and the mechanisms by which it results.

2.5.7 Time-Resolved Photoluminescence

The extension of PL measurements performed on SWCNT to include measurements of the dynamic behaviour of the system provides new insight into the optical properties of the nanotube. In addition to providing fundamental information on the specific excitonic processes that govern PL in nanotubes, studies of dynamics can also shed light on nominally ‘steady-state’ problems. For example, it would be possible to entirely determine the PL QE of a SWCNT if both the radiative and non-radiative lifetimes could be independently measured. Experimental investigations of PL dynamics have taken many forms including both one- and two-colour transient absorption spectroscopy [10, 38, 126, 79], direct measurement of PL dynamics [35, 36, 80, 111, 59], and indirect techniques [39, 13, 40], as well as various theoretical studies [95, 80, 104, 5]. This list is by no means exhaustive and is indicative of the quantity of ongoing work. Consequently, a full summary of all current techniques is considered beyond the scope of this thesis.

The process of time-resolved PL spectroscopy is particularly relevant to this thesis.
In this technique, the SWCNT is optically excited and the internal dynamics interpreted from the resulting transient behaviour of the PL. Experimental techniques to measure these dynamics are important, given the relative difficulty in observing PL dynamics, which occur on timescales ranging from tens of femtoseconds out to nanoseconds [10, 36, 95]. Although almost all techniques use some variation on confocal microscopy to optically excite the nanotube and collect the resultant photoluminescence, there are a variety of wildly differing schemes in use to time-resolve the PL data.

The most straightforward technique involves the use of a fast photodiode or photomultiplier setup. In these cases, the intrinsic time resolution of the detector is adequately fast to obtain sample dynamics directly from the light collected from the sample. Reported time resolutions for these types of techniques are on the order of 60 ps [36]. Attempts are often made to further improve accuracy by de-convolving the measured instrument response function from the data in post-processing [36, 59].

A slightly more complex scheme to time-resolve PL data involves the use of a streak camera. This device improves the temporal resolution of a single detector by converting a temporal pulse into a spatially-resolved profile in a controlled fashion. The resulting ‘streak’ is then measured using a detector array. In this way, experimenters have achieved time resolution below ten picoseconds on SWCNT [35, 41]. In both cases, the data can additionally be spectrally resolved using filters or a spectrometer.\(^{19}\)

Reported techniques to achieve sub-picosecond resolution of the PL from SWCNT rely on non-linear optical phenomenon. A common feature of all such techniques is

\(^{19}\)A notable point is that most properties of the detector improve if Silicon, rather than Indium-Gallium-Arsenide technology can be used, due to the substantially greater industrial development of silicon microelectronics. A disadvantage is that Silicon has diminished performance beyond the visible spectrum, which can restrict researchers to using small-diameter SWCNT.
that the temporal resolution is achieved in the optical domain, as opposed to at the photodetector or in the subsequent electronics. Additionally, it is usual to use an ultrafast pulsed laser to excite the SWCNT, so that the laser light does not obscure the subsequent PL. A specific technique successfully implemented by the Heinz group uses a Kerr-gating technique, which relies on the non-linear Kerr effect to produce intensity-dependent birefringence in a crystal. In this technique, the polarization of the PL signal from the sample is rotated such that it is maximally blocked by a linear polarizer. Temporal resolution is achieved by passing the weak PL signal through a crystal simultaneously with a strong, \(\approx 100\) fs long gate pulse. The gate pulse produces a transient birefringence that rotates the polarization of a temporal slice of the PL signal, allowing it to pass through the polarizer. The delay of the gating pulse relative to the signal is varied so that a PL ‘movie’ can be constructed from the many temporal slices. Reported temporal resolutions with this technique are on the order of 200 fs [111]. As is discussed below in Section 3, other non-linear techniques were considered in the course this work reported in this thesis.

A common disadvantage of these non-linear techniques is the very small resultant signal. As an illustration, consider the case where the sample under question is a single nanotube with a QE on the order of a few percent. Additionally, as discussed further below, most short nanotubes are unable to emit more than one photon per pulse. Most non-linear techniques require very high pulse energies, necessitating the use of regeneratively-amplified ultrafast lasers, which have a typical repetition rate of a few kHz to a few hundred kHz. With these parameters taken together, even assuming perfect collection and detection efficiency, the maximum possible signal is only a few tens to a few thousands of photons per second. A time-resolving technique
that requires discarding all but a slice of the signal worsens the situation. In this way, the signal to noise ratio of such time-slicing technique often varies inversely with the temporal resolution. As a result, although studies of PL dynamics have been done on ensembles, and time-resolved data taken for single tubes, this author knows of no published report of the PL dynamics of a single tube that achieves sub-picosecond time-resolution using non-linear optics. This is in spite of the recognized need to perform further single-tube experiments with finer temporal resolution in order to fully grasp the dynamic behaviour of SWCNT, specifically causes of the observed variability in picosecond-scale PL dynamics between tubes having the same index [36].

2.5.8 Exciton Dynamics

Substantial effort has been devoted to identifying the various steps that are involved in the process of emitting PL from a SWCNT. A schematic cartoon summarizing the main steps involved in the process as currently envisioned is presented as Figure 2.4 to guide the following discussion. In general, it is important to note the relative time scales of the main steps. The excitation to the $E_{22}$ exciton state and subsequent internal relaxation to the $E_{11}$ exciton state are very fast, occurin within $\approx 150$ fs [81, 66]. The non-radiative Auger process, explained in detail below, is thought to have a time constant of $\approx 2$ ps [113, 115, 10]. Both linear non-radiative and radiative decay processes operate on the remaining band-edge population. Observed time constants for the non-radiative decays range from 7 to 320 ps, [111, 79, 35, 36, 59], which are all significantly shorter than the expected $\approx 1$ ns radiative decay pathway [104, 111, 59]. As a result, it is stated that non-radiative processes dominate the dynamic behaviour.
Figure 2.4: This schematic diagram shows the various processes that create photoluminescence in an SWCNT. 1) The nanotube absorbs a photon, creating an $E_{22}$ exciton, which is energetically red-shifted from the one-body $E_{22}$ level expected from the 1D joint DOS (JDOS). 2) The exciton undergoes rapid phonon-mediated interband scattering [10, 81] to an excited $E_{11}$ state, and 3) then quickly relaxes via phonon-mediated intraband processes to a thermal distribution about the $K=0$ point in the lowest $E_{11}$ exciton band [81, 35]. If there are multiple excitons present, the exciton can undergo a 4) two-body Auger decay process, with one exciton recombining non-radiatively and the other promoted to a higher level [10, 113]. 5) At room temperatures, both the lowest (dark) and second-lowest (bright) $E_{11}$ exciton states are populated thermally. The exciton can recombine 6a) non-radiatively, or 6b) radiatively, emitting a band-gap energy photon. Adapted from a figure presented by T. Hertel at WONTON ’08.
The first step in the PL process is the absorption of a photon to create an exciton. The straightforward case shown in Figure 2.4 involves the creation of an $E_{22}$ exciton, which is the process familiar to PLE spectroscopy [4]. This scheme is commonly used [113, 40, 111, 36, 59] as the very strong background from the excitation laser can be easily spectrally filtered and the $E_{22}$ resonance provides for efficient absorption. Other schemes have also been developed. For example, in recent work published by Högele et al., excitation was achieved by targeting a phonon side-band that lay only 70 meV above $E_{11}$ [41]. Theoretically, excitation schemes could be adapted from techniques used in steady-state PL work including two-photon excitation [112], perpendicularly-polarized excitation [71], and pumping higher-indexed resonances (e.g. $E_{33}$) [81]. An important question that remains is how many excitons can be created in a single tube, which is essentially the same as knowing how the absorption scales with intensity.  

Once created, the exciton relaxes very quickly out of the $E_{22}$ level. Transient absorption measurements taken on ensembles indicate that this process is described by a time constant on the order of 40 fs [81, 10]. This is so rapid that it is expected that the underlying process is due to a Fano resonance between the initial $E_{22}$ level and a degenerate excited state lying within the continuum of the $E_{11}$ states [81]. Such a process might imply the creation of an exciton away from the K point, which is shown schematically on the diagram. From here, the exciton rapidly thermalizes through continued interactions with the lattice, quickly reaching a distribution about the bottom of the band [81, 35]. The collective time constant for these two processes has been measured to be 40 fs via through transient absorption measurements [81].

\footnote{Experiments of this kind are nontrivial because of the remarkable difficulty in directly measuring the absorption of a single tube [110]. Additionally the physical fragility of SWCNT under extreme optical bombardment complicates matters further [56].}
We consider several one-body\textsuperscript{21} processes that can occur involving an exciton near the K point of the \( E_{11} \) exciton level. Firstly, it is noted that there are at least two exciton states of relevance, given that the lowest-lying state is dark, and so optical transitions can only occur under ambient conditions between the bright second-lowest state and the ground state \([7, 124, 90, 23]\). Given the splitting between these two states is on the order of 3 meV \([7]\), both states should be populated at room temperature and there should be efficient and rapid phonon-mediated population exchange between them\textsuperscript{22}. From both states, the exciton can recombine non-radiatively; its energy transferred to lattice phonons. This process is expected to be the dominant relaxation channel for low excitation densities due to its relatively short time constant, which is on the order of tens of picoseconds \([36, 80, 111, 59]\). By contrast, radiative decay processes can only occur involving excitons in the bright state. Estimates range significantly, but these processes are theoretically predicted to have time constants on the order of nanoseconds \([104, 111]\). This difference in time constants, which relates directly to the low QE of PL in SWCNT, is due to several factors, among which is the fact that the exciton has high probability of being in a dark state. Spartaru \textit{et al.} speaks of a hundred-fold effective lifetime enhancement due to linear momentum conservation as much of the expected thermal distribution of center-of-mass exciton wavevectors have more momentum than can be taken up directly by a photon. This is in addition to a five-fold enhancement due to the probability of being in the lowest state, which is dark due to parity selection rules \([104]\).

\textsuperscript{21}This term is used to refer to processes that involve a single exciton, even though the exciton itself a composite particle. This is as opposed to many-body processes that involve two or more excitons.

\textsuperscript{22}This step must also occur within the measured 40 fs time constant described by Manzoni \textit{et al.} \([81]\) as the photobleaching measurement was necessarily taken between the bright \( E_{11} \) state and the ground state.
In addition to these linear decay processes, experimental evidence suggests that PL from SWCNT also have non-linear dynamics. In particular, it has been observed that under strong excitation, PL increases sub-linearly with increasing excitation intensity [93, 107, 80]. One non-linear process used to explain this phenomenon is Auger recombination, which is a non-radiative process that can occur if two or more excitons exist in the same level at the same time. Auger recombination in semiconducting SWCNT, similar to the familiar atomic process, involves the non-radiative decay of one exciton where the energy is not lost to phonons, but is instead transferred to a second exciton, which is promoted to a higher-energy state [10]. Given that Auger recombination is a two-body process, it is natural to expect that the rate of recombination would scale with the density of excitons in the nanotube. This has the net effect of decreasing the effective PL QE under higher excitation intensities, which would explain the saturation behaviour observed.

Further experimental evidence supports the Auger picture. For instance, several groups have observed PL dynamics that are more complicated than a simple mono-exponential decay [113, 40, 41, 80, 59]. Most interesting are observations of decay dynamics that are intensity-dependent, and have a fast ($\tau \approx 2$ ps) decay component that increases in relative strength as the excitation intensity is increased [113, 115] as would be expected from an intensity-dependent process. A stochastic theoretical model developed by Barzykin et al. to explain this behaviour emphasizes the discrete nature of the process, and also proposes the process of Auger ionization [5]. The major difference between this process and Auger recombination is that the excited electron is fully ejected from the carbon nanotube, making the net effect of the process a $2 \rightarrow 0$ rather than a $2 \rightarrow 1$ decay [5]. The discrete nature of the process has been
observed via transient absorption measurements in that under moderately high excitation, the observed decay dynamics of the photo-excited $E_{11}$ exciton state separates into three bands, which is suggestive of the different decay rates for the one-, two-, and three-exciton cases [47]. Another recent experimental report which lent support to the Auger picture showed that moderately-short ($\approx 500\text{nm}$), micelle-encapsulated SWCNT cooled below 25 K behaved as true single-photon emitters under pulsed excitation, indicating that efficient non-radiative pathways suppress photon emission from all but the last-remaining exciton [41].

An alternative explanation proposed to explain the observed saturation behaviour in nanotube PL is the concept of phase-space filling [40]. This describes a situation where the density of excitons is adequately high so that the constituent fermions experience Pauli repulsion. This can be readily visualized as a nanotube ‘full’ of excitons, which has a fair physical basis as phase-space filling becomes relevant as the product of the exciton radius and number approaches the size of the system in question [102]. The proposed hypothesis for the PL saturation behaviour in SWCNT was that the absorption of the SWCNT became saturated due to the effects of phase space filling [40, 66]. Although the results of transient absorption measurements certainly attest to the existence of this effect [66, 10], saturating behaviour in SWCNT has been observed at excitation intensities much lower than would be necessary for this phenomenon to occur [36]. Additionally, it does not explain the aforementioned intensity-dependent or discretized time-dynamics.

In summary, though much has been discovered about the PL dynamics in SWCNT, there remains much to learn. A critical opening is for time-resolved experiments to be done on air-suspended nanotubes to permit a better understanding of environmental
effects on the dynamic behaviour. Additionally, it would be beneficial to extend the
temporal resolution of single-tube work to the femtosecond regime. Taken together,
this would provide important insight into the microscopic processes that define the
opto-electronic properties of SWCNT.
Chapter 3

Experimental Design

3.1 Summary

This chapter describes the apparatus used to perform the experiments reported in this thesis. The aim is not only to illustrate the purpose of the components and techniques involved in the experiment, but also to explain the reasons why these particular devices or methods were chosen. The chapter begins with a brief overview of the experimental capabilities that are required from the apparatus. The air-suspended single-walled carbon nanotube samples are discussed next, along with the reasons for their selection and a summary of the procedure required for their growth. The advantages of the mode-locked Ti:sapphire laser source used in this work are outlined and the principles of its operation are presented in brief. The final implementation of the opto-mechanical apparatus is discussed in detail, as its substantial evolution and improvement during experimentation was a non-trivial part of this work. Brief mention is made of the computer-control and data acquisition systems, as they were
largely designed by co-worker Tam Q. Nhan [91]. Descriptions of experimental methods involving preliminary alignment and routine operations are included as these best practises are a part of the final setup. In contrast, the specific techniques used for each of the different experiments performed with this apparatus are omitted from this chapter. This is done because the descriptions of these smaller experiments are generally brief and fit more naturally alongside the discussion of their respective results as presented in Chapter 4.

3.2 Required Capabilities

The requirements placed on the apparatus by the desired course of experimentation are considerable. Consider the observation of photoluminescence (PL) from a single nanotube, which is the foundation of all of the experiments reported here. For this experiment to work, not only must nanotube samples be prepared that are capable of emitting PL, but the apparatus must also ensure the availability of highly tunable laser light with at least 100 mW of optical power, the capability to perform spectrally-resolved measurements on very weak (100 fW) infrared optical signals, and the means to simultaneously deliver a focussed excitation beam to the sample and efficiently collect the emitted PL while avoiding saturating the detector with the strong excitation beam. In addition, control of the position of the sample with accuracy on the order of the 1 µm spot size is required to allow nanotubes to be located on the sample, and their physical extent mapped. The apparatus must include a laser capable of producing ultrafast pulses at the desired wavelengths to allow for the full investigation of high-intensity saturation behaviours and intrinsic nanotube dynamics, and a variable delay line to permit the use of the Femtosecond Excitation Correlation technique.
Lastly, as discovered during experimentation, the apparatus also needs to control of the ambient environment of the nanotube, particularly the ambient relative humidity. Taken together, these requirements present a considerable experimental challenge which is surmounted by the apparatus described below.

3.3 Samples

3.3.1 Selection

The single-walled carbon nanotubes (SWCNT) used in the work reported in this thesis were grown by collaborators at the National Research Council (Canada)\(^1\) (NRC) using the cold-wall chemical vapour deposition (CVD) technique that they developed [42, 75, 29, 70] following original work by Homma \textit{et al.} The technical details of this growth process are described in brief in Section 2.4.3 and explained in detail in Section 3.3.2.

Nanotubes produced by this technique were chosen for this work as they appeared to offer several important advantages. The first and, at the time of selection,\(^2\) dominant reason for choosing the air-suspended SWCNT grown by this cold-wall CVD method was that they had been reported to possess a PL quantum efficiency (QE) of 7\% [70], which was over an order of magnitude greater than the PL QE values previously reported\(^3\) for micelle-encapsulated SWCNT [93, 4, 111]. Given the anticipated difficulties in gathering enough signal to be able to obtain time-resolved data from a single nanotube (See the brief discussion in Section 2.5.7.), the opportunity to

\(^1\)Jacques Lefebvre, Paul Finnie, and Kate Kaminska.

\(^2\)These decisions were made in January, 2007

\(^3\)At the time, the author was unaware that papers suggesting that it was possible to observe PL QE on the order of 1\% from micelle-encapsulated SWCNT would be published later that year [17, 107].
increase the potential PL signal more than ten-fold was a strong motivation to choose these SWCNT.

Two other considerations which also favoured the use of SWCNT grown by cold-wall CVD were that they were novel, in that the author knows of no published reports of PL dynamics from suspended nanotubes at the time of writing, and available, as the researchers at NRC indicated that they would be willing to contribute samples for investigations on single-nanotube dynamics. Further, as the simplification of experimental conditions is generally desirable, it was thought that air-suspended samples represented an attractive opportunity to study SWCNT in the ‘cleanest’ possible state, particularly if studies of nanotube dynamics could be done under vacuum and at low temperatures. Lastly, it should be acknowledged that these light-emitting air-suspended SWCNT, which naturally form bridges between electrical-contact-like pillars, would seem to offer a more straightforward route towards practical implementation than soap-covered SWCNT; a point that was regularly highlighted in air-suspended work [42, 56].

In summary, air-suspended SWCNT grown by cold-wall CVD were selected for use in this work due to their novelty, availability, promise to produce substantially more signal than micelle-encapsulated nanotubes, and potential insight into the intrinsic properties of SWCNT.

### 3.3.2 Growth Technique

While the SWCNT used in this work were grown by collaborators at NRC and the details of the growth methods used are described in detail in several publications [42, 75, 29, 70], a survey of the method used is presented for completeness.
As stated in Section 2.4.3, the particular technique used is described as a cold-wall CVD process. This is because only the growth substrate is heated, and is in contrast to commonly-used hot-wall CVD processes which involve the heating of the entire reaction vessel. This seemingly minor change has several practical implications [29], the most important of which stems directly from the significantly decreased thermal inertia in cold-wall CVD systems. As described in Section 2.4.3, SWCNT grow best at higher temperatures than multi-walled carbon nanotubes (MWCNT), 600 – 1150°C as opposed to 300 – 800°C [33]. Consequently, the preferential growth of SWCNT is usually achieved at growth temperatures of about 900°C [29]. In a hot-wall CVD system, the entire reaction vessel must be brought to this temperature; a process which can take several minutes. To avoid MWCNT growth, this heating must be done with an inert gas atmosphere. However, even with this precaution, the long heating process can still affect the metallic catalyst nano-particles that are required for SWCNT growth. These effects include melting, agglomeration, and even chemical change [29].

In contrast, the substrate used in the cold-wall process is usually a small (∼ 1 cm²) piece of silicon wafer, and can be brought to the optimal growth temperature in seconds by passing a direct current through the substrate and taking advantage of natural resistive heating. A corresponding advantage applies when stopping growth; instead of waiting for all carbon-bearing gas to be purged from the reactor, the substrate must only be brought below the ∼ 300°C threshold temperature for MWCNT growth. This can occur in a few seconds with this technique [29]. As some SWCNT are known to grow axially in excess of 7000 nm/s [57], the improved temporal control of growth conditions offered by this method is an important advantage [29].
A second advantage of the cold-wall CVD technique is that growth is confined to the desired substrate, instead of throughout the heated chamber. This both reduces the demand for carbon feedstock and permits real-time observation of the growth process as viewports do not become obscured by the errant growth of carbon structures [56, 57]. Other advantages of cold-wall CVD are economic; a cold-wall CVD system is less expensive to implement, and growth takes considerably less time [29]. The chief disadvantages of the cold-wall CVD technique compared to hot-wall CVD are that the yield is generally lower and the temperature distribution on the substrate is less uniform, which results in slightly varying growth conditions across the substrate [29].

Figure 3.1: Schematic drawing showing the ridge and trench substrate geometry. Cartoons of four nanotubes are added, one which completely bridges the trench, and three that are suspended between a ridge and the trench floor. Adapted from [70], used with permission. Copyright 2006 by ACS Publications.

Although much of the published reports from the NRC group concerned SWCNT suspended between lithographically-prepared nano-scale ‘pillars’ [29, 75], the nanotubes used in this work were grown using a different geometry which featured nano-scale ‘trenches’, as SWCNT grown on this substrate geometry had produced the 7% QE result referenced above [70]. The trenches, as shown schematically in Figure 3.1
and in images generated using atomic-force microscopy (AFM) in Figure 3.2, are created in the following manner.

The fabrication process starts with a roughly $1 \times 1$ cm piece of 500 $\mu$m thick silicon with an 800 nm thick thermal oxide coating. Photolithography is used to define an interdigitated pattern of 5 $\mu$m wide ridges, and a wet chemical etch creates 400 nm deep trenches in the unpatterned regions of the oxide layer\(^4\). Finally, arrays of catalyst particles with average diameters of several nm are created by selectively depositing 1 nm of cobalt onto the un-etched ridges by a process involving photolithography and e-beam evaporation [70, 29]. A sample was imaged using AFM by Ben Lucht and Jennifer Campbell using apparatus in Dr. Rob Knobel’s lab. This work confirmed that the ridges and trenches are 5 $\mu$m in width, but suggested that the trenches were slightly deeper than expected at about 600 nm. It is unknown whether this reflects variability in the fabrication process, or calibration errors in the AFM apparatus.

The result of this process is a substrate that encourages the growth of SWCNT on the ridges, which makes it possible for some of these nanotubes to become suspended over the trenches. With the knowledge that PL from SWCNT in contact with the surface is strongly quenched [75, 70], it is thought that this relatively shallow trench geometry partially selects for very straight nanotubes as those SWCNT that are bent due to defects are likely to come in contact with the trench floor [70]. In addition to avoiding potential complications to the excitonic band structure resulting from defects in the carbon lattice, experimentation on straight tubes has the additional advantage of simplifying the polarization of the resultant PL\(^5\).

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\(^4\)Although a 150 nm of platinum metal on a 5 nm adhesion layer of chromium is deposited in the trenches only by E-beam lithography and a lift-off process for the ‘trench’ samples used by the NRC group in [70], the sample provided for this research had only a simple Si/$\text{SiO}_2$ ‘floor’ to the trenches.

\(^5\)As mentioned above in Section 2.5.4, both absorption and PL emission from SWCNT is strongly
Figure 3.2: An image formed from atomic force microscopy data taken from a ‘trench’ substrate. This is a small section of the entire $\approx 1 \text{ cm}^2$ substrate, but the $5\mu\text{m}$ wide parallel ridges (light) and trenches (dark) are evident. The trenches in this sample are roughly $600 \text{ nm}$ deep, slightly deeper than the expected trench depth of $250 \text{ nm}$. Image taken by Ben Lucht and Jennifer Campbell. Used with permission.

Once the substrate is prepared, it is loaded into the 1 L stainless steel vacuum chamber with an optical window, that serves as the cold-wall CVD reactor. Electrical contact is made with the sample to allow direct resistive heating. The chamber is evacuated to $\approx 0.1 \text{ mPa} \ (10^{-6} \text{ torr})$ by a turbopump. A 200 V bias is applied across the sample to ensure good electrical contact through the insulating oxide. However, the current applied to the sample is kept low at this stage to prevent heating. The sample temperature is monitored continuously using an infrared pyrometer [29]. To provide a source of carbon, a gaseous mixture of 98% argon and 2% helium is bubbled through ethanol before being admitted to the chamber [88, 70]. Nanotube growth is polarized along the tube axis. Straight nanotubes have a unique axial vector, making both excitation and PL collection more straightforward.
started by increasing the current delivered to the substrate, which raises it to the
growth temperature ($\approx 900^\circ C$) in a few seconds. These conditions are maintained
for a duration ranging from one to several minutes depending, for example, on the
desired nanotube density. Growth is stopped by turning off the electrical current, as
the sample falls several hundred degrees in a few seconds. It has been experimentally
demonstrated that this temperature ramp is adequately rapid to avoid the growth of
significant quantities of MWCNT [29]. Ambient air is admitted to the reactor, and the
samples removed. It is important to note that the samples require no post-processing
to prepare them for PL experimentation.

Although *in situ* monitoring of nanotube growth and, hence, a full understanding
of the growth mechanism remains an ongoing topic of research [56, 57], it is thought
that the growth mechanism for carbon nanotubes is fundamentally similar to the
vapour-liquid-solid process first proposed to explain the growth of silicon whiskers [29,
108]. In brief, a vapour-liquid-solid process is one where a flux of carbon-bearing
gas is decomposed by the catalytic metallic particle. The elemental carbon (now in
liquid form), eventually saturates the surface and the bulk of the catalytic particle.
This saturated condition can result in the precipitation of a nanotube if the geometry,
temperature, and other conditions are suitable. Otherwise, other bulk forms of carbon
are produced [29].

It should be noted that alteration of growth parameters such as the sample tem-
perature, partial pressure of the ethanol vapour, and duration of the growth phase
can effect changes in the resultant distribution of nanotubes. Specific to this work,
two types of samples were used. The chief difference was the average density and
length of the nanotubes on the sample. Early work was done with samples with a
Figure 3.3: An SEM image of a sample similar to those used in the experiment. The stippled pattern on the central ridge which bisects the image results from the nano-scale metallic catalyst particles. Tangled, white, unsuspended nanotubes are visible on the ‘lower’ side of the ridge, while two suspended nanotubes are clearly visible in the upper-right corner. It is noted that these nanotubes do not extend across the trench, but are suspended between the ridge and a point on the floor of the trench. Image taken by Kate Kaminska and Paul Finnie, used with permission. (Unpublished)

greater average areal density of bright (photoluminescing) SWCNT, but in which the average tube length was shorter (≈ 2 µm). In these samples, as shown in Figure 3.3, many tubes extended only from the catalyst-covered ‘ridge’ to the floor of a trench. Later work was done with samples containing nanotubes with longer average lengths (≈ 6 µm) that generally entirely bridged a trench. However these samples had a decreased areal density of SWCNT (See Figure 4.2).
3.4 Laser Source

A Coherent® Mira® 900-F mode-locked (ML) Ti:Sapphire oscillator was the primary light source used in this work as it offers particularly advantageous capabilities. This laser can produce both continuous-wave (CW) laser radiation as well as ‘ultra-short’ (< 200 fs) pulses of light. In both cases, the center wavelength of the light is quasi-continuously tunable between 700 nm and 1000 nm [15]. Although the full details of this process can be found elsewhere (For example [60, 31]), a brief summary is presented for completeness.

In all modes of operation, the Mira® is pumped by a Coherent® Verdi® V18 low-noise single-mode 532 nm (green) pump laser. This light is generated in two steps. A bank of laser diodes is used to generate infra-red light at approximately 808 nm. This radiation is used to pump a Nd:YVO$_4$ (neodymium-doped yttrium vanadate) crystal which is housed in a resonant cavity and lases at 1064 nm. A frequency-doubling crystal is also present in this cavity and is used to produce light at 532 nm, which passes through the dichroic output coupler. Active feedback control is used to ensure low-noise operation and maximal conversion efficiency. Tuning parameters include the temperature of the doubling crystal, which alters the phase-matching condition for second-harmonic generation, and the precise wavelength produced by the laser diode bank, which affects the absorption of the pump light by the Nd:YVO$_4$ crystal [14, 16].

In CW mode, the operation of the Mira® is relatively straightforward to describe. The Ti:Sapphire (titanium-doped Sapphire (Al$_2$O$_3$)) crystal is pumped by the CW beam of 532 nm light from the Verdi. The crystal sits in a resonant cavity formed by broadband dielectric mirrors (Coherent® X-Wave®) and a slightly-transmissive
output coupler, allowing for the build-up of sufficient intensity for lasing. Wavelength selection and tuning is largely accomplished using a birefringent filter (BRF) [94]. The resultant beam is optimized to be primarily composed of the TEM$_{00}$ mode.

Three further components are required for mode-locked operation, though they are not generally removed or altered when the laser is used in CW mode. Firstly, a ‘starter’ is used to add time-dependent noise to the existent CW beam. This device is a glass block through which the beam passes that is mechanically shaken to vary the signal. Kerr-Lens mode-locking is then used to introduce selective loss to the CW beam relative to an ultrafast pulse. In essence, this process exploits the intensity-dependent self-focussing possible in a Kerr medium to spatially differentiate between the collinear CW and ML beams [60]. In the Mira®, the net result is that at a point near the output coupler, the CW beam has a larger diameter than the ML beam. As a result, a physical slit can introduce adequate selective loss to the CW beam such that the laser enters stable ML operation. Lastly, a prism pair provides the dispersion compensation generally required to achieve sub-picosecond pulse durations [15, 60]. Most optical elements are on user-adjustable mounts, which is necessary to initially achieve lasing, and allows for daily optimization and switching between CW and ML modes of operation.

For experimentation, priority was given to achieving stable ML operation as this condition is more demanding than stable CW operation. Given that it was desirable to switch between ML and CW operation with a minimum of intra-cavity adjustments, and hence beam deviation, this resulted in CW operation that was somewhat non-ideal. Specifically, the CW laser light used in this experiment had relatively broad linewidth (1 – 2 nm) resulting primarily from quasi-simultaneous lasing from more
than one mode. As demonstrated below in Section 4.2, this does not significantly affect the experimental results due to the comparatively broad (FWHM ≈ 20 nm) absorption linewidth of an air-suspended SWCNT. By contrast, ML light from the laser has bandwidths ranging from 6 – 8.5 nm, implying transform-limited pulse durations ranging from 155 – 110 fs. This is experimentally verified in Section 4.5.3.

This laser was ideal for the proposed experiment for several reasons. Firstly, it could produce light at a wide range of wavelengths that were appropriate for exciting numerous known SWCNT species [4, 74]. Further, the laser can be easily switched between CW (for maximal PL signal) or ML (to permit the examination of time dynamics) operation depending on the demands of the experiment. The laser also had adequate power for the experiment; optical powers greater than 1 W are achievable in both CW and ML modes. By way of reference, a maximum of ≈ 2 mW is incident on the sample, which necessitates no more than 200 mW of power at the laser head after accounting for necessary and parasitic losses along the beampath. Lastly, the repetition rate of this laser was high (76 MHz) when compared to amplified oscillator systems. The high repetition rate directly increases the detectable PL signal when operating in pulsed mode relative to pulsed laser systems with a slower repetition rate as the ‘experiment’ is effectively repeated seventy-six million times each second.

### 3.5 Opto-mechanical Setup

While it could be argued that the optical setup used in this work is not very complicated, the final setup that evolved to meet all experimental needs is composed of a number of relatively independent components, meaning that any explanation runs the risk of becoming disjointed. To aid in viewing the apparatus as a whole, a schematic
diagram is presented as Figure 3.4 on page 52 to give the reader a sense of the relative position of the major components. The following discussion briefly outlines the necessity for and role of each major component in the optical setup. References to labels on the figure are in bold type and generally enclosed by parentheses.

Figure 3.4: This schematic diagram shows a representation of the optical setup used for all experiments reported in this work as viewed from above. The exception is the inset figure, which is a view from the side. The beam from the laser (solid red arrows) enters the diagram from the bottom right, and the PL from the sample (dashed blue arrows) finally enters the spectrometer at the left. The apparatus is divided into segments (labeled in green) used to structure the discussion in the text. Although the diagram is not to scale, all significant components are included and labeled; M1–M10 are mirrors, L1–L4 are lenses, I1–I6 are alignment irises, BS1–BS3 are beamsplitters, and W1 is a window. Not shown is the apparatus used to control the ambient environment (See Section 3.5.7).
3.5.1 Initial Optics

The initial group of six optical elements serves to deliver the beam from the laser to the delay-line portion of the setup. The first element (BS1) is a low-loss 33:66 beamsplitter that passes a third of the total Mira power through to the apparatus\textsuperscript{6}, while reflecting the remaining two-thirds so that it can be used to operate an Optical Parametric Oscillator (OPO)\textsuperscript{7}. Two subsequent mirrors\textsuperscript{8} (M1, M2) provide full control of the beam position and angle while two irises (I1, I2) placed about 50 cm apart ensure consistent alignment of the beam. It is estimated that careful alignment to the irises is accurate to within 2 mrad. This portion of the setup is necessary as the alignment of the beam coming from the laser can be altered by events such as daily laser optimization, the process of switching from CW to ML operation, as well as variations in ambient conditions. Even small changes in the beam alignment at this point can have significant deleterious effects on the experiment, due to the long (2 m) remaining beamline, as well as the sensitive delay-line segment. Finally, an AR-coated plano-convex lens (L1) with a focal length of 1 m (Thorlabs LA1464) is placed in the beam to roughly collimate the beam, and avoid overfilling at the aspheric lens.

\textsuperscript{6}The inversion of the destination of the reflected and transmitted beams is reversed on the diagram to conserve space

\textsuperscript{7}The OPO was used directly for some calibration studies as it can emit light at the same infrared wavelengths as the nanotubes. These studies were performed by co-workers and are detailed in the Master’s theses of Tam Q. Nhan and Yee-Fang (Elsa) Xiao.

\textsuperscript{8}All mirrors in this setup are Thorlabs PF10-03-M01 protected gold mirrors. At experimental wavelengths, the beam experiences less than 4% loss. Mirrors are mounted on Thorlabs KM100 kinematic mounts, allowing two-axis control.
3.5.2 Delay Line

The delay line portion of the apparatus is necessary for the Femtosecond Excitation Correlation (FEC) studies which are described in detail below in Section 4.5. This part of the apparatus has the net effect of splitting the incident pulse into two pulses which are temporally separated by a user-variable delay. As shown schematically in Figure 3.4, the beam is first split using a 50:50 beamsplitter cube (BS2). The transmitted portion of the pulse goes into the (fixed arm), where it reflects off of two mirrors (M3,M4), permitting arbitrary alignment, and is directed to a second beamsplitter cube (BS3). The portion of the incident pulse reflected off of the first beamsplitter cube (BS1) is directed onto a retroreflector (Newport U-BBR 1-2I) that is mounted on a linear stage. This portion of the apparatus is called the delay arm. The retroreflector, comprised of three mirrors mounted precisely at right angles to each other forming the corner of a cube, is critical to the setup as it has the property that any incident beam is reflected back parallel to itself [86]. This largely removes the threat of significant deviations in the beam at the sample caused by slight alterations in the beam angle caused by imperfections in the movement of the linear stage.

The stage itself is a home-built 1 m long unit that was salvaged from the lab of Dr. Sayer. The stage is composed of a ‘sledge’ that is mounted on pad-type friction bearings that slide along guideways machined into the aluminum base. Motion is provided by a stepper motor driving a threaded rod that passes through a receiver on the bottom of the stage. As briefly described in Section 3.6, the motion is controlled by a custom program written in LabVIEW, that interfaces with the Velmex NF90 Series Stepping Motor Controller. While the motion in one direction is roughly accurate to a few µm, namely the 1 mm pitch of the threaded rod divided by the 400 motor
steps required for one revolution, there is greater positioning error (<200 µm) in the system upon changing directions due to backlash in the mating of the receiver to the threaded rod.

To counter the effects of backlash, data is generally taken using ‘sweeps’ in which the length of the delay line is incrementally increased from the zero-delay point (See below) up to its maximum value, and then incrementally decreased in the opposite direction. This avoids unnecessary changes of direction as well as providing data collected from bi-directional ‘sweeps’ that should indicate if there are significant hysteresis effects in position. It is noted that an uncertainty in delay distance of 100 µm corresponds to an uncertainty in the delay time of 667 fs. Although there were concerns as to the transverse accuracy of the stage as it moved along the track, as shown in Section 4.4, it was possible to align the stage such that the total systematic variation in the PL observed as the stage moved through its 35 cm useful range of motion was less than 5%.

The reflected beam from the retroreflector passes through the second beamsplitter (BS3), where it recombines with the light from the fixed arm. It is important to note that the four degrees of freedom provided by the two mirrors on the fixed arm combined with the four degrees of freedom offered by similar positioning control of the two beamsplitter cubes allows for both beams to be made collinear at range of directions that is primarily limited by beam clipping resulting from the limited physical size of the mirrors and beamsplitter cubes.

It is critical for the experiment to ensure that a proper ‘zero point’ is established where the retroreflector is positioned such that the fixed and delay arms are of equal

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9This measurement was taken with the SWCNT in the ‘linear regime’ of PL emission. The variation is even less apparent when operating the ‘saturated regime’. For explanations of these terms, refer to Section 4.4.
length. This alignment can be readily achieved to within about 42 $\mu$m, which is the physical length of the $\approx 140$ fs pulse, once the beams are aligned to achieve good spatial overlap and collinearity. This is done in the following manner. Both beams are sent into a scanning spectrometer (Wavescan Laserspectrometer by APE GmbH), which monitors their combined spectrum at a rate of six frames per second. The delay line is scanned until interference fringes appear in the spectra, which indicates that the length of the two arms is nearly matched. The length of the delay arm is further adjusted until the spectra shows only a single ‘fringe’, in that small variations in the relative length of the two arms cause all frequencies to simultaneously interfere either constructively or destructively. At this point, the two arms are of equal length to a precision of approximately the physical pulse length. Precise spatial alignment can be similarly checked by ensuring that there are no spatial interference fringes under these conditions.

### 3.5.3 Intermediate Optics

The intermediate optics segment of the apparatus connects the delay line segment with the sample-holding periscope segment. This segment is notably long (2 m) for two reasons. First, it is generally desirable to have the final two irises $I_4,I_5$ reasonably far apart to improve the resulting accuracy of the angular alignment of the beam on the sample ($\approx 2$ mrad). Second, given that the beam must be raised to satisfy design constraints imposed by the ‘periscope’ section, the long distance (1 m) between mirrors $M_5$ and $M_6$ serves to minimize the impact on the orientation of the polarization of the beam that occurs when it is reflected such that it leaves its initial horizontal plane (i.e. is incident on a reflective surface with a relative polarization
that is neither purely s-polarized nor purely p-polarized). The first element this
segment is an iris (I3), which is used to ensure the delay line is properly aligned. As
shown in Figure 3.4, three mirrors are used in this segment. The first mirror (M5)
is located close to the delay line setup and is oriented so as to raise the beam the
requisite distance (≈ 3 cm) over the 1 m distance to (M6). The other two mirrors
(M6,M7) are placed closer to the sample (1 m and 50 cm respectively), and used
in conjunction with two irises (I4,I5) to permit precise alignment of the beam as it
enters the periscope assembly.

Glass slides (pick-offs) are commonly inserted into the beamline in the long 1 m
section between (M5) and (M6) during experimentation to extract a portion of the
light so that the spectrum and pulse duration can be simultaneously monitored. The
aforementioned APE Wavescan Laserspectrometer and an APE Mini Autocorrelator
are used to measure these parameters, respectively. A neutral-density (ND) filter
wheel (ND filter) (Thorlabs NDC-100C-4M) is also placed in this section. It allows
the variation of incident laser power by four orders of magnitude without affecting the
operating condition of the laser source. In some experiments, for reasons described in
Section 3.5.6, a chopper wheel component of a Thorlabs MC1000A optical chopper
apparatus is placed in the beamline in this segment as well. Additionally, a lens mount
(L2) on a micrometer-actuated three-axis (XYZ) translation stage (not shown) is
placed in the beamline between the I4 and I5, about 20 cm from the sample. Although
this mount is left empty during alignment, a 175 mm focal length plano-convex lens
(L2) (Thorlabs LA1229) can be added to decrease the spot size on the sample, as
described below in Section 3.5.4. Lastly, adequate space is left to allow the insertion
of a power meter immediately before the periscope (Thorlabs PM130 Digital Optical
Power Meter with Slim Sensor S130A (Germanium) to allow for direct monitoring of the incident power.

### 3.5.4 Periscope

The (periscope) segment holds both the sample and the optics required to perform confocal scanning microscopy. The name is partially descriptive as the segment incorporates one regular periscope and the ‘periscope-like’ confocal microscopy setup. As is described more fully in Section 3.5.7, half of this segment, including the sample, aspheric lens, glass window, and M8, is enclosed with quality plastic sheeting, to allow for experimentation in a more controlled environment.

The beam enters this enclosure via a window (W1, Thorlabs ND01A) and is incident upon a 5 mm thick uncoated glass window tilted 45° from the vertical. As shown in Figure 3.4, a portion (9.4%) of the beam is reflected directly downward towards the sample from the front face of the glass window by Fresnel reflection. Not shown is the additional 8.5% of the initial beam that is reflected downwards off of the back surface of the window. Although this beam initially caused some experimental difficulties, as it produced ‘doubled’ PL images, it was realized that it is sufficiently physically displaced from the first beam such that it can be blocked. Alternatively, the easily-recognized and well-separated double image could be ignored. A wedge, the traditional remedy for such problems, was not used to avoid any deviation of the PL beam.

It is admitted that the uncoated glass window used in this setup uses the incoming beam extremely inefficiently compared to the dichroic window usually used in confocal microscopy, However, a simple glass window was selected despite this deficiency for
several reasons. Firstly, the reflectivity and transmissivity of a bare glass window are relatively independent of wavelength, with any corrections being well-understood. Additionally, as this window must also efficiently transmit the reflected PL, it is an advantage that, at this angle, the window is reasonably transmissive ($\approx 82\%$) at all relevant emission wavelengths. By contrast, it is very difficult to achieve a dichroic optic that efficiently reflects light over the entire range of the laser ($700$–$1000$ nm), and has a high transmissivity for widely varying PL wavelengths. It is especially difficult to produce an optic in which the reflectivity and transmissivity are ‘flat’ over these broad spectral ranges, which is necessary to avoid distortion of the observed spectra. However, the deciding argument was that, as mentioned before, very little laser power was required to excite the sample relative to the full potential output of the Mira®, so even the loss of 90% of the excitation beam is of little concern.

The light reflected from the 45° glass window is focussed onto the sample by an aspheric lens (Thorlabs C570TM-C, NA = 0.67 or C110TME, NA = 0.4), which was selected for qualities such as high numerical aperture, reasonable working distance, high transmissivity at 1380 nm ($\approx 99\%$), and cost. The lens is mounted on a two-way translation mount (Thorlabs LM1XY) to allow precise alignment. The layout was such that the laser beam could be focussed to a $\approx 15$ µm spot directly, or to a $\approx 2$ µm spot if the L2 lens was added to the mount as described in Section 3.5.3. This particular configuration was chosen because much of the fine alignment was only possible if there was a PL signal, particularly owing to the differing focal lengths of the aspheric lens for visible, 800 nm, and 1380 nm light, and it was naturally much easier to find signal with a larger spot size.

The sample itself rests on a custom-made aluminium jig mounted on a three-axis
translation stage (XYZ Stage, Newport ULTRAAlign 562 Series). Accurate vertical adjustment of the sample was important, as it was the main manner of focusing the beam. Consequently, a manual, high-precision, geared adjuster (Newport DS-4F Series) was used. Although this actuation was uncalibrated, this adjuster offered sub-micron precision with negligible backlash. Experimentation was carried out under two different focussing conditions; maximum PL, where the sample is close to the focal length at 1380 nm, or minimum spot size, where the sample is close to the focal length at 800 nm. The maximum PL condition is produced straightforwardly by tuning the height of the sample. The minimum spot size condition is achieved by iteratively raster scanning a SWCNT and adjusting the sample height accordingly until a near-diffraction-limited spot is achieved.

Horizontal motion of the sample was either performed manually using standard micrometers, or provided by two DC servo micrometers (Thorlabs Z625B) which give \( \approx 200 \text{ nm} \) precision (The step size is 40 nm, but the system does exhibit backlash). The computer-based control of these motors is described in Section 3.6. The periscope section is completed by three mirrors (M8, M9, M10), which collectively cause the initially-vertical PL beam passing through the glass window to become horizontal at the level of the spectrometer. The beam leaves the plastic enclosure between M8 and M9 via an open 25 mm port. This port was left open to allow well-mixed air to escape from the enclosure, as well as to avoid any further loss of PL signal.

A photograph of the Periscope and Final Optics segments of the apparatus is included as Figure 3.5 to provide a sense of scale. This photograph was taken before the quality plastic sheeting was added to the setup to enclose the Periscope segment.
3.5.5 Final Optics

As shown in Figure 3.4, this segment of the apparatus has only a few components. A mirror in a flip mount (Flip Mirror) is used so that the beam can be easily diverted to an imaging system. In most cases this was a modified USB-controlled microscope (Digital Blue QX4 & QX5), which was used in conjunction with a standard lens (L3) (Thorlabs LA1608-C) to form an image of the sample. The microscope has both visible and some near-IR capabilities, which allowed for viewing of the substrate itself under visible light, as well as the spot created by the 800 nm laser beam. With
the flip mirror out of the beamline, a lens (L4) (Thorlabs LA1509-C, f = 100 mm) is used to focus the light on the entrance slit of the spectrometer. It should be noted that this was done to maximize PL collection rather than to perform ‘true’ confocal microscopy\textsuperscript{10}, as the entrance slit of the spectrometer is relatively large (1 mm × 1 mm) compared to the usually 15 μm spot size on the sample.

In experiments on the polarization dependence of the PL emitted from a single SWCNT, a polarization analyzer, made up of a rotatable half-wave plate (Thorlabs AQWP05M-1430 unmounted achromatic half-wave plate mounted in a RSP05 rotatable mount) and a linear polarizer (Thorlabs LPNIR050), was also placed in the beamline. Lastly, a long-wave pass filter (LWP, Thorlabs FEL1200) was placed in the beam to prevent the relatively intense 800 nm beam back-reflected from the sample from entering the spectrometer. Even though the spectrometer should, ideally, have no problem separating the 1380 nm PL from the 800 nm excitation light, it was feared that even small stray light effects, which are on the order of ≈ 5 × 10\textsuperscript{−4}, from the 800 nm beam would overwhelm the small PL signal.

3.5.6 Spectrometer and Detection

A Horiba-Jobin-Yvon iHR320 Imaging Spectrometer mounting a grating (Jobin-Yvon 530 60) with 950 lines per millimeter with a 900 nm blaze wavelength is used to perform spectroscopic analysis of the PL emitted from the SWCNT under study. With this grating, it is possible to observe wavelengths from 700−1700 nm. The spectrometer was used with a single-element liquid nitrogen-cooled indium gallium

\textsuperscript{10}The phrase ‘true’ confocal microscopy is used to refer to setups where a perfect image of the sample is created on a plane featuring a pinhole, which allows through only light which originate from a very small focal volume. The size of this focal volume is limited, in theory, only by diffraction.
arsenide detector, also provided by Horiba-Jobin-Yvon. This detector was selected as it is sensitive to wavelengths of interest (800 – 1600 nm), has a low noise-equivalent power NEP (1 fW) and high optical-to-electronic gain \((2 \times 10^9 V/W)\), and works well in conjunction with a lock-in amplifier (See Section 3.6). The use of variable-width entrance and exit slits allowed the spectrometer to be optimized for spectral resolution or throughput. Although spectral resolutions as fine as 0.06 nm are possible, optimization for high PL throughput (See Section 3.7) resulted in an experimental spectral resolution of \(\approx 15\) nm (See Figure 4.1). The motion of the grating was computer-controlled, as described in Section 3.6.

### 3.5.7 Relative Humidity Apparatus

As is described in Section 4.6, it became evident over the course of experimentation that the relative humidity (RH) of the ambient environment of the nanotube can strongly affect the PL emitted by the SWCNT. As a result, additional capabilities were developed to allow for the control of the ambient RH. As described in Section 3.5.4, this was accomplished by enclosing a portion of the periscope segment in quality plastic sheeting and limiting air exchange between the enclosure and ambient lab air to a single open 25 mm port. Although the sample was the only particularly critical element to enclose, the aspheric lens, glass window, and mirror M8 were also included in the enclosure due to physical limitations of the design. The enclosure could be purged and subsequently held at a wide range of RH values using a home-built humidity-controlled gas supply borrowed from Dr. Sayer’s lab. This operation of this device is described below.

A standard cylinder of industrial-grade dry nitrogen gas supplied both the source
gas and the pressure required for adequate gas flow. Under experimental conditions, this was typically 6 cubic feet per hour as measured by an in-line flowmeter. The nitrogen could be fed into a mixing tank via two paths. In one path, the gas was bubbled through distilled water to become saturated with water vapour (RH = 100%). In the other, the gas was passed through a set of copper heat-exchange coils held in a freezer maintained at −30°C to remove any moisture. The ambient RH in the mixing tank was monitored by a RH-sensing microcontroller (Electro-tech Systems Inc. Model 514 Automatic Humidity Controller), which actuated a solenoid valve (MAC Inc. Model 35A-AAA-DAAJ-1KD) to switch the incoming gas flow between the two paths, thus maintaining the RH in the mixing tank near a given setpoint. The mixed gas was continually fed into the sample enclosure where the RH and temperature were independently monitored (Pinnacle Technology Inc. Datalogger ID/TRH). In this way, the sample could be maintained at a stable RH value ranging from 5 - 50%, and the RH could be varied within this range at a rate of roughly 12%/min when required. After adding this component to the apparatus, and for reasons described in detail in Section 4.6, virtually all experimentation was conducted with a purged enclosure set to ≈ 18% RH.

3.6 Computer-Control and Data Acquisition

Computerized control and data acquisition were used extensively in this apparatus, due to the many large data sets that were collected to locate SWCNT and explore their properties. The necessary control routines were written in National Instrument’s LabVIEW programming environment, which facilitated direct communication with the various experimental components through universal serial bus and general-purpose
instrument bus connections. As acknowledged, these programs were developed and refined by co-worker Tam Q. Nhan [91]. Presented here are brief summaries of program capabilities to allow for a better understanding of the experimental method.

From the outset, it was anticipated that the use of optical chopping and lock-in detection would substantially improve the signal-to-noise (S/N) ratio of this experiment. In this technique the desired signal is modulated at a frequency as far away as is feasible from 0 Hz, so as to take advantage of the generally-applicable $1/f$ frequency dependence of random noise. The lock-in amplifier (Stanford Research Systems SRS 530) used to detect such signals is synchronized with the frequency and phase of the modulation, and is designed to exclude non-modulated background. Preliminary experimentation conducted by co-worker Elsa Xiao [122], indicated that the configuration to achieve optimal S/N in single-tube experiments involved chopping the pump beam at 70Hz and using the ‘low gain’ setting on the detector. Chopping at higher frequencies was shown to be counter-productive due to the limited bandwidth of the detector.

A common task in experimentation was to raster scan the sample when searching for bright nanotubes. Given the low areal density of bright SWCNT (See Figure 4.2) and the very small focal area, this time consuming process was automated. In this way, large-scale ‘maps’ of the sample could be produced (See Figure 4.2), which identified the locations of all bright SWCNT of a desired chirality. The chirality in question was specified by choosing the excitation and emission wavelengths of interest by tuning the laser and spectrometer, respectively. It is important to note that, once found, SWCNT would often remain accessible for days or weeks of experimentation,
which demonstrates not only to their robustness, but also the ability of the positioning system to return to within the $\approx 15 \, \mu\text{m}$ spot size of the nanotube. In addition to coarse scans of the entire sample, this program was also readily adapted to produce two-dimensional plots of individual nanotubes, with areal resolutions limited primarily by the spot size.

Other programs were similarly designed to automate other common tasks. Examples include the acquisition of SWCNT emission spectra of varying breadth, resolution, and start wavelength, as well as taking data readings while moving the delay arm through a set range in both linearly- and logarithmically-spaced increments. Generally, automated data acquisition substantially sped up experimentation, which directly improved the S/N by overcoming random error through repeated measurements. In all cases, data was automatically read from the lock-in amplifier and exported to Microsoft® Excel worksheets.

### 3.7 Calculation of Total PL Collection Efficiency

It is important to have an estimate of the total collection efficiency ($\eta_T$) of the apparatus that takes into account the combined effects of all components that interact with the PL emitted from the nanotube. Specifically, this allows for the conversion of the magnitude of the detected signal into an emitted photon flux from the nanotube under observation, which is an important part of the calculation of the quantum efficiency of the SWCNT. Due to the large number of factors involved, as well as the few major assumptions that must be made, the uncertainty in the resultant value is large. As such, results calculated using this coefficient should be used as order-of-magnitude checks to ensure the physical reasonableness of experimentally-observed
phenomena, as opposed to precision calculations.

The most critical component of the calculation of $\eta_T$ is the collection efficiency of the aspheric lens ($\eta_{\text{coll}}$). Although this value can be easily calculated theoretically, as shown in Equation 3.1, the applicability of the theoretical value to the experiment is entirely dependant on the assumption that the alignment technique described in Section 4.2.2 causes the nanotube under excitation to be perfectly located in the focal volume of the lens. This condition can be difficult to achieve as SWCNT can be more than 10 $\mu$m long and the focal length of the lens varies between the 800 nm excitation light and the 1380 nm PL emission. To account for these reservations, the ideal value is used as the upper limit of the collection efficiency, and a significant uncertainty ($\pm 33\%$) is added to the calculated value.

The relevant manufacturer’s specification required for the calculation of the collection efficiency of a lens is its numerical aperture (NA). Assuming isotropic emission from a source located a the focal point, the problem reduces to finding the ratio between the area of a spherical cap ($A_{SC}$) bounded by the cone of light accepted by the lens and the total surface area the sphere ($A_S$). Defining $n$ as the refractive index of the surrounding medium (in this case $n=1.0$ for air), and $h$ as shown on Figure 3.6,
the ideal collection efficiency of a lens is determined as follows:

\[ \eta_T \equiv \frac{A_{SC}}{A_S} \]

\[ \therefore A_{SC} = 2\pi hr, \quad A_S = 4\pi r^2 \]

\[ \therefore \eta_T = \frac{h}{2r} \quad (3.1) \]

\[ \therefore \theta = \arcsin(NA), \quad \frac{r - h}{r} = \cos(\theta) \]

\[ h = r \cdot (1 - \cos(\arcsin(NA))) \]

\[ h = r \cdot \left(1 - \sqrt{1 - NA^2}\right) \]

\[ \therefore \eta_T = \frac{(1 - \sqrt{1 - NA^2})}{2} \quad (3.2) \]

Figure 3.6: Cross-section of a sphere with an inset cone creating a spherical cap. Labeled variables are used to calculate collection efficiency in Equation 3.1.
Given that the aspheric lens most commonly used experimentally has a numerical aperture of $NA = 0.4$, the ideal collection efficiency of the lens is 4.17%. As stated above, this can vary significantly under experimental conditions, so that the experimental collection efficiency of the lens is stated as $\eta_{\text{coll}} = 0.03 \pm 0.01$.

The remainder of the necessary factors are obtained either through measurement, or by consulting the appropriate component specifications. A further assumption is made that the reflection off of the surface of the substrate is incoherent, so that there are no interference effects between the incident and reflected beams for either the excitation light or the PL emission. All co-efficients necessary for the calculation of $\eta_T$ are listed in Table 3.7, and have been evaluated at 1380 nm (899 meV), the approximate emission wavelength of a (9,8) SWCNT. Phrases in bold face are references to the labels on Figure 3.4.

As stated in the table, the resultant total conversion factor between radiant power from the nanotube to signal displayed on the lock-in amplifier is $\eta_T = 4 \pm 2 \times 10^6$ V/W. The uncertainty in this measurement is estimated by summing the fractional errors for each co-efficient in quadrature, as the sources of error are considered to be independent. Inverting the factor gives the result that each $\mu$V of signal results from the emission of $1.7 \pm 0.9 \times 10^6$ photons per second on average from the nanotube, or equivalently $0.02 \pm 0.01$ photons per pulse of the ultrafast laser. These values are particularly useful in estimating the nanotube’s quantum efficiency (See Section 4.4.2).
Table 3.1: *Table of co-efficients necessary to calculate the total detection efficiency, including optical loss, opto-electronic conversion, and electronic gain. Co-efficients for the spectrometer provided by co-worker Tam Q. Nhan [91].*

<table>
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<tr>
<th>Throughput of <strong>Periscope &amp; Final optics</strong></th>
<th>Co-efficient</th>
<th>Uncertainty</th>
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<tr>
<td>‘Extra’ PL reflected from the substrate</td>
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<td>Collection efficiency of the <strong>aspheric lens</strong></td>
<td>0.03</td>
<td>0.01</td>
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<tr>
<td>Transmission of the C-coated <strong>aspheric lens</strong></td>
<td>0.98</td>
<td>0.01</td>
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<td>Transmission of the uncoated <strong>glass window</strong></td>
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<td>0.98</td>
<td>0.01</td>
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<td>Transmission of the <strong>LWP Filter</strong></td>
<td>0.84</td>
<td>0.05</td>
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<td>Loss due to clipping on lens &amp; input slit</td>
<td>Negligible</td>
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<tr>
<td><strong>Subtotal</strong></td>
<td>0.020</td>
<td>0.007</td>
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<td>Reflectivity of grating</td>
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<td>Reflectivity of focussing mirror</td>
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<td>Loss due to clipping at a 7 nm output slit</td>
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<td>Reflectivity of elliptical mirror</td>
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<tr>
<td><strong>Subtotal</strong></td>
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<td>0.044</td>
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<td><strong>Detector</strong> quantum efficiency</td>
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<td>0.02</td>
</tr>
<tr>
<td>Pre-amplifier gain</td>
<td>$1.68 \times 10^9$</td>
<td>$0.01 \times 10^9$ V/W</td>
</tr>
<tr>
<td>Effective lock-in amplifier gain at 70 Hz</td>
<td>0.32</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>$4.94 \times 10^8$</td>
<td>$0.19 \times 10^8$ V/W</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$4 \times 10^6$</td>
<td>$2 \times 10^6$ V/W</td>
</tr>
</tbody>
</table>
Chapter 4

Method, Results and Analysis

4.1 Summary

Given the natural division of this work into multiple sub-experiments, this chapter presents the experimental methods, results, and analysis that relate to each experimental investigation in a self-contained manner. Preliminary calibration work of the spectrometer is reported, along with a summary of the iterative method used to find the ‘first’ photoluminescing single-walled carbon nanotube. The results of ‘high-resolution’ studies of the spatial distribution of the photoluminescence are presented, as well as an outline of the polarization dependence of the light emitted by the nanotube. A more thorough treatment is given the work done to clarify the relationship between the emission spectra, excitation spectra, and excitation intensity, including a discussion of the appropriate functional dependence of the peak. So-called ‘Pulsed Power Dependence’ studies are second major topic, as the strongly non-linear relationship between the excitation and emission intensities give insight
into the underlying dynamics. The experimental technique of ‘Femtosecond Excitation Correlation Spectroscopy’ is introduced, and its use to obtain time-resolved data on the photoluminescent process is described. Finally, a brief description is given of the experimentally-observed ‘aging’ phenomenon, whereby the photoluminescent signal from a nanotube would be abruptly and irreversibly quenched or diminished, which is accompanied by a discussion of the novel observation that exposure to elevated relative humidity can redshift the peak of the emission spectrum.

4.2 Preliminary Results and Calibration

4.2.1 Spectrometer Bandpass Calibration

An important preliminary step required for experimentation is the determination of the spectral band-pass characteristics of the spectrometer as a function of the width of its input and output slits. This is accomplished using a mercury-argon lamp, which emits light at a well-known series of narrow emission peaks, the energies of which are defined by atomic transitions. Although it would be preferable to conduct this study at the expected photoluminescence (PL) wavelength (1380 nm or 899 meV), this is not possible due to the high density of spectral lines in this region [98]. An isolated mercury line at 1128 nm (1099 meV) is significantly more convenient for experimentation.

While the input and output slits of the spectrometer can be varied from 0.1 mm to 7.0 mm, experimental concerns limited the utility of some of this range; particularly with regards to the input slit. As described in Section 3.5.5, the PL from the sample is focussed onto the slit of the spectrometer in an effort to maximize the amount of
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PL collected. Consequently, the spot size of the PL defines a width beyond which increases in the input slit size have no effect on the PL signal\(^1\)

However, as described in Section 4.2.2, it is difficult to ensure that the beam of PL collected by the aspheric lens is perfectly collimated. This has the effect of making it difficult to achieve a very small focus at the input slit, particularly given the small signal levels involved. It was assumed that the spot size could be reduced below 1 mm without significant difficulty, so the input slit was fixed at this width to determine the effect of variations of the output slit width on the performance of the spectrometer \(^2\). Lastly, it should be noted that the lamp was placed at a distance of 50 cm from the spectrometer, as the increased distance improves the collinearity of the light at the spectrometer entrance and thus better simulates the focused beam of PL from the SWCNT.

As shown in Figure 4.1, with the input slit fixed at 1 mm, the spectral resolution of the spectrometer varies quite linearly from 2.9 meV to 15.1 meV as the output slit is opened from 1 mm to 7 mm. Assuming a slit small enough that a linear approximation can be used to convert between the energy and wavelength scales\(^3\), the relationship between the output slit width in mm \((W_{\text{slit}})\) and the experimentally-observed spectral bandpass characteristics in units of either energy in eV \((\Delta E_{\text{eV}})\) or wavelength in nm \((\Delta \lambda)\) for a given center wavelength, \(\lambda_0\), and a 1 mm wide input slit

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\(^1\)Naturally, such further increases do have an effect on the magnitude of the background signal from ambient conditions.

\(^2\)Although subsequent experimentation with nanotubes showed that this spot size could be reduced below 500 µm, the difference in spectral resolution between the two cases is not significant when compared to the broad intrinsic emission lineshape of the nanotube. Compare Figures 4.1 and 4.6

\(^3\)This approximation is good to better than 1% for experimental wavelengths
Figure 4.1: Dependence of the experimental spectral resolution on the width of the output slit of the spectrometer. The data set was taken using a narrow, isolated line from a mercury-argon gas lamp. The single-ended black arrows indicate the increasing width of the expected ‘top-hat’ spectral bandpass function as the output slit it opened. The 2.9 meV lower-limit of the resolution derives from the input slit, which is fixed at 1 mm due to experimental considerations described in Section 4.2.1. The features outside the range from 1.09 meV to 1.11 meV result from other emission lines from the source. Lines on the plot are added to guide the eye. Uncertainty in the x direction is negligible. Although error bars on the y axis are not included for visual clarity, a good estimate for the uncertainty in the y-direction is the scatter in the points in the flat, ‘top-hat’ region.
is:

\[ \Delta \lambda = 3 + 2 \cdot (W_{Slit} - 1) \quad (4.1) \]

\[ \therefore E_{eV} = \frac{h \cdot c}{e} \cdot \frac{1}{\lambda} \]

\[ \therefore \Delta E_{eV} \approx \frac{h \cdot c}{e} \cdot \frac{1}{\lambda_0^2} \cdot \Delta \lambda \]

\[ \therefore \Delta E_{eV} \approx \frac{1240}{\lambda_0^2} \cdot (3 + 2 \cdot (W_{Slit} - 1)) \quad (4.2) \]

The ‘top-hat’ shape of the resulting spectrum can be understood as the convolution of the narrow, delta-function-like spectrum from the mercury lamp with the top hat created by the output slit. The slightly angled sides of the top-hat result from the further convolution of this result with a top-hat function resulting from the input slit. As expected, additional experimentation showed that the slope of the sides of the feature decreased as the input slit was opened, until the spectrum became triangular\(^4\).

With this knowledge, experimentation on nanotubes was generally performed with a 0.5–1.0 mm-wide input slit, as this did not affect the PL while excluding some stray background. As the majority of experiments did not specifically investigate the shape of the emission spectrum, they were performed with a 7 mm output slit so as to capture a maximal amount of signal. In cases where the emission spectrum was specifically under investigation (See Section 4.3), the concern with spectral broadening as a result of instrument response was either addressed experimentally by taking data using narrowed output slit, or accounted for mathematically during analysis.

\(^4\)This data set was not explicitly included in this thesis as it only has bearing on experimentation with the unfocussed beam from the lamp, and does not apply in the case of a PL beam focussed onto the input slit.
4.2.2 Instrument Alignment and Sample Map

A critical step towards successful experimentation on single-walled carbon nanotubes (SWCNT) is the alignment of the apparatus to effectively collect the photoluminescence (PL) emitted by a nanotube. This is non-trivial as it is a fundamentally coupled problem; it is difficult to properly align the apparatus without a nanotube, and it is unlikely to find a nanotube without a properly aligned system. Several methods are used to circumvent this apparent difficulty. Firstly, visible white light is shone onto the substrate, and the sample height (hence the focusing properties of the aspheric lens) is adjusted until the image of the substrate appears in focus on the microscope imaging system. This process is repeated with illumination from the laser at 800 nm, as this wavelength is closer to the expected infrared PL wavelengths.

One particularly useful method for preliminary alignment involves the use of an ensemble sample of quantum dots grown on a substrate with similar dimensions to the substrate of the nanotube samples, and which possesses comparable absorption and emission lines. Such a sample was furnished along with the SWCNT samples by collaborators at the National Research Council (Canada) (NRC) for this purpose. The emitted signal from the quantum dots sample was very intense, which facilitated the alignment of the PL beam through the focusing lens (L4 in Figure 3.4) and into the spectrometer. At this point, the sample height could be tuned to maximize the signal observed on the lock-in amplifier.

With this phase of alignment accomplished, the quantum dots sample was removed and a sample containing SWCNT was put in its place. A decision was made to search for SWCNT with (9,8) chirality as they had given the strongest signal in previous work using ensembles of nanotubes grown using a similar technique [72]. Further alignment
was aided by a faint background at the PL wavelength of interest produced by the silicon substrate under strong excitation; in this case, 1380 nm (1.55 ev) for a (9,8) nanotube. The sample height was tuned further to maximize this signal.

Further alignment required a nanotube to be found. At first, this was attempted by scanning the sample manually using micrometer actuators for the sample stage. However, it soon became evident that the density of bright tubes was too low for this to be effective. Accordingly, the automated scanning program described in Section 3.6 was employed to search a large sample area. A spot size of about 15 µm was used for this scan as it provided a balance between the faster scan rate possible with a larger spot size, and the increased PL collection offered by the improved focussing concomitant with a smaller spot size.

The results of this work are presented in Figure 4.2. An inspection of the figure shows that there is only one ‘bright’ (9,8) SWCNT on average per 1 mm$^2$ of surface area. This value is typical for the samples used in this work. Note that this implies that there is only one nanotube for every $\approx 6500$ ‘spot sizes’, confirming the utility of the automated scan. It took 2–3 hours to complete a scan of an area of the size shown in Figure 4.2. Scans of the sample done by co-worker Tam Q. Nhan in search of nanotubes of (10,8) chirality produced similar results [91].

Figure 4.2 shows a number of bright (9,8) SWCNT, each of which appears as a horizontal series of points of elevated PL intensity. It is important to note that the horizontal ‘streak’ is not indicative of the orientation of the nanotube; further experimentation (See Section 4.2.3) shows that the nanotubes observed are generally oriented vertically (i.e. along the y-axis). This orientation is preferred because the

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In this case, ‘bright’ means a nanotube that shows a signal-to-noise ratio of better than 2:1, or in this experiment an observed PL intensity value greater than 10 in the units used in this experiment. See the discussion in this section on the meaning of these units.
Figure 4.2: Map showing the relative position of PL-emitting (9,8) SWCNT on a sample, created by raster scanning the sample while exciting with 800 nm laser light and viewing the emission at 1380 nm. The resolution is limited by the step size of the raster scan (4 µm in x and 20 µm in y). The very low areal density of SWCNT should be noted, especially compared to the ≈ 15 µm beam diameter. Each cluster of points represents a single tube that is oriented vertically with respect to the diagram. Additional points in the horizontal direction are artifacts of the measurement. Some nanotubes that have undergone experimentation are named.
nanotubes are most likely to become suspended when grown perpendicular to the trenches, which are aligned parallel to the x-axis in this sample.

The horizontal orientation of the ‘streak’ of points is, rather, an artifact of the measurement that results from two factors. First, a peculiarity of the scanning program is that the raster scanning is done in discrete steps in y, but a continuous sweep in x. This is done to increase the rate at which the sample is scanned. During this process, the lock-in amplifier is periodically queried to obtain the currently-observed intensity, which is recorded along with the corresponding sample position. The result is that data points are taken in $\approx 4 \mu m$ steps along the x axis. However, as the spot size of the laser is 15 $\mu m$, even an infinitely narrow nanotube would appear as a series of several points. Secondly, the signal from a single nanotube is further ‘smeared’ along the x-axis as the lock-in amplifier is queried rapidly enough that several data points are taken within the set integration time. As a result, several points of above-background PL will be recorded after passing a bright SWCNT while the signal reported by the lock-in settles back down to the background level. It is important to note that this ‘problem’, i.e. the ‘smearing’ of the signal from the nanotube, is easily overcome by the method described in Section 4.2.3 whenever it is necessary to more accurately determine the position and orientation of the nanotube. However, this ‘streaky’ scanning method is preferentially used to create the large-scale maps of the sample because it greatly speeds up the process of locating bright SWCNT.

As is evident in Figure 4.2, the SWCNT observed on this sample vary considerably in their observed brightness. What is not apparent is the degree to which they stand out from the background light emitted by the sample. For reference, the background signal in this image has an average value of 3.2 and has a standard deviation of 1.8 in
the plot units. In comparison, the brightest nanotube, ‘Herbie’, has a brightness of 51. Although these values reported in ‘plot units’ are related to the amount of light at 1380 nm detected, they are presented in the form of arbitrary units because of their dependence on many factors other than the intrinsic brightness of the nanotube, such as the rise-time of the lock-in amplifier, the rate of raster scanning, the relative location of the nanotube in the scanning spot\textsuperscript{6}, and the local height of the sample\textsuperscript{7}. Consequently, it is unhelpful to attempt to draw conclusions from this data beyond the location of some bright tubes. Experimentally, the values obtained in this way were taken only as an indication of the location and as a rough guide of the brightness of the nanotube in question; further experimentation was always done on an individual tube to establish its particular properties more clearly.

4.2.3 High-Resolution Two-Dimensional Scan

Once a number of potential nanotubes have been located by the large-scale sample scan described in Section 4.2.2, the next step is to determine their positions and orientations more accurately. The following procedure is used for a nanotube selected from the sample map (Figure 4.2). Firstly, a second raster scan of the immediate area around the desired nanotube is performed to determine its exact location. This scan uses a variant of the automated scanning program that gathers data in discrete steps in both the x and y directions. This improves both the positioning accuracy, due to the inherent feedback control in the servo motors, as well as the measurement\textsuperscript{6}.

\textsuperscript{6}For example, two otherwise-identical SWCNT would display a markedly differing apparent brightness if one were located in the center of the spot, and the other towards the edge.

\textsuperscript{7}Although this varies locally, depending on the location of the nanotube with respect to the ridge and trench structure, the greater concern is a global variation in sample height caused by the substrate being not perfectly horizontal.
accuracy, due to increased time allotted for the output of the lock-in amplifier to settle at a given location. Although this type of scan results in a slower scan rate than the semi-continuous scanning described in Section 4.2.2, the marked improvement in the accuracy of the positioning justifies the reduced scanning speed over this relatively small area.

Once the tube has been roughly located, it is used as a reference emission source to aid in the reduction of the spot size. Firstly, an additional lens ($L_2$ on Figure 3.4) is inserted into the laser beampath to allow the excitation beam to be more tightly focussed. The spot size was minimized by iteratively adjusting the height of the sample, and then performing a small areal raster scan around the nanotube. The current spot size can be easily determined by finding the apparent width of the nanotube perpendicular to its axis. This is because the 1 nm-wide SWCNT is effectively a spatial delta-function, so the apparent width of the nanotube directly reflects the profile of the spot. This procedure must be followed for each SWCNT studied as the spot size is particularly sensitive to the vertical height of the sample under these conditions, as would be expected for a tightly-focussed beam, and the height of the substrate is non-uniform as it is not necessarily perfectly horizontal.

Once the spot size had been minimized, which usually results in a beam diameter on the sample of about 2 µm, a ‘final’ two-dimensional scan can be taken. This scan provides information on the length and orientation of the tube as well as highlighting any major variations in emission intensity along the tube. Results for a ‘long’ SWCNT that is 6.7 µm in length and a ‘short’ SWCNT that is only 2 µm in length are presented in Figures 4.3 and 4.4, respectively. It was usual to find SWCNT of various lengths on a single sample, these particular tubes are selected to serve as contrasting examples.
Figure 4.3: Spatial distribution of PL from a single ‘long’ carbon nanotube, along with two line profiles taken along orthogonal axes. The 2 µm-wide (FWHM) horizontal profile indicates the spot size. Consequently, the 7 µm-long vertical profile suggests that the ‘bright’ segment of the SWCNT is 6.7 µm long; the entire tube could be longer than this as only PL-emitting regions are observed. Although the observed PL emission is roughly uniform along the tube, inhomogeneities on a scale smaller than the spot size would not be resolved. Data taken by co-worker Y.-F. (Elsa) Xiao [122]
The ‘long’ nanotube shown in Figure 4.3 is typical of the nanotubes used for much of the experimentation in this work. These nanotubes were assumed to be suspended entirely across a trench, as SWCNT that appear vertical in the two-dimensional PL map are perpendicular to the 5 \( \mu \text{m} \)-wide trenches on the sample. In fact, some nanotubes were observed that exhibited more than one light-emitting segment, as they were long enough to bridge more than one trench in succession. The observation of these spatial emission patterns is strong evidence that the PL is coming from a nanostructure, which is, in this case, a nanotube. Although it might appear that the nanotube is a few \( \mu \text{m} \) wide, this is due to the finite spot size of the excitation laser. Briefly the observed 2 \( \mu \text{m} \) (FWHM) line profile taken perpendicular to the tube is the result of the spatial convolution of the 2 \( \mu \text{m} \)-diameter laser spot and the delta-function-like 1 nm-diameter nanotube. Extending this discussion to the line profile taken in the axial direction, the dependence of the observed length \( L_{\text{observed}} \) on the intrinsic length \( L_{\text{intrinsic}} \) and the spot size \( w_{\text{spot}} \) is given approximately by \[118\]:

\[
L_{\text{intrinsic}} = \sqrt{L_{\text{observed}}^2 - w_{\text{spot}}^2} \tag{4.3}
\]

Following Equation 4.3, the 7 \( \mu \text{m} \)-long (FWHM) vertical profile suggests a ‘bright’ segment of an SWCNT that is about 6.7 \( \mu \text{m} \) long. It is important to note that PL-emitting nanotubes of this length, while typical samples grown using the cold-wall chemical vapour deposition (CVD) method described in Section 3.3.2, are roughly ten times longer than PL-emitting SWCNT prepared using sonication and a surfactant (For example, see [93]). Further, nanotubes that are suspended over multiple trenches can approach and exceed 100 \( \mu \text{m} \) in total length, as reported by co-worker Tam Q. Nhan [91] as well as by collaborators at NRC [70]. The results are significant in light of the fact that PL is quenched by the ends of a SWCNT [13], so longer tubes
should present a more idealized experimental environment. Lastly, Figure 4.3 shows that the nanotube emits PL at a roughly uniform (±10%) intensity along its axis. Although this is expected from a SWCNT without defects, it is acknowledged that this procedure would not effectively resolve variations in PL intensity on a scale smaller than the spot size.

The ‘short’ SWCNT shown in Figure 4.4 is atypical of the nanotubes used in this experiment. It was found on a sample that consisted of SWCNT with a shorter average length that likely resulting from particularities of the growth conditions. These short tubes were used in experimentation in an effort to ascertain whether there was any clear length dependence on nanotube properties. As with the ‘long’ nanotube, the horizontal (radial) line profile is taken to indicate that the spot size is 2 µm in diameter. However, the vertical line profile has a FWHM of only 3 µm, which suggests that the nanotube is about 2 µm long. There is considerable uncertainty in this stated intrinsic length, given the 0.5 µm resolution of the spatial scan and the large variation in intrinsic tube length with respect to the observed tube length when the nanotube length is similar to the spot size.

4.2.4 Polarization Dependence of Photoluminescence

With some nanotubes, extra studies were performed to investigate the polarization dependence of the emitted PL. This was accomplished by inserting a polarization analyzer as shown in Figure 3.4 and described in Section 3.5.5. For this and all subsequent studies, the extra focusing lens (L2 in Figure 3.4) is removed so that the spot size of the excitation laser is large enough to excite the entire nanotube. Typical

\[\text{These results are discussed in the sections relevant to the particular experiment below}\]
Figure 4.4: Spatial distribution of PL from a single ‘short’ carbon nanotube (‘Pebbles’), along with two line profiles taken along orthogonal axes. The 2 µm-wide (FWHM) horizontal profile is taken as the spot size, so that the 3 µm-long vertical profile would result from a ‘bright’ segment of a SWCNT that is about 2 µm long. The appearance that the vertical line profile does not pass through the center of the nanotube is an artifact of the gridding process.
spot sizes with this setup range from 12–20 µm. The sample position is tuned in the x, y, and z directions to maximize the PL signal. The polarization analyzer is then rotated and the intensity of the PL signal is recorded at a number of different orientations. The resulting data set is presented in Figure 4.5.

A general note on graphs with vertical scales labeled as ‘PL Signal (µV)’: data plotted on this axis is in units of µV of signal detected by the lock-in amplifier. This scale is chosen for plots where the absolute value of the PL intensity emitted from the SWCNT is not important. Although it is possible to convert these values to a total rate of photon emissions from the nanotube (See Section 4.4), this process necessitates several assumptions about the nanotube properties and the experimental setup that contribute substantial systematic uncertainty (≈ 60%) to the measurement. By contrast, the chosen scale requires no such assumptions and is linear with the emitted PL intensity to first order, allowing the relevant physical process to be discussed without unnecessary complications.

The polarization data presented in Figure 4.5 is fitted with a function of the form \( A \cdot \sin^2(\theta - \phi) + B \), where \( A \), \( B \), and \( \phi \) are fitting parameters. This form is chosen as it describes a light field that is perfectly linear polarized, and contains additional parameters to account for unimportant experimental considerations; the angular offset, \( \phi \), is largely determined by the orientation of the optic axis of the half-wave plate with respect to the rotating mount; the major contribution to the vertical offset, \( B \), is unpolarized background from the silicon substrate; and the vertical scaling, \( A \), is a function of the PL intensity as well as factors such as the collection efficiency, noise level, and detection efficiency.
Figure 4.5: Polarization dependence of the PL emitted from a single tube. A function of the form $A \cdot \sin^2(\theta + \phi) + B$ is fitted to the data set, where $A$, $B$ and $\phi$ are parameters. The vertical scale is linear with PL intensity. Although similar studies were performed by the author, the data presented in the plot was taken by co-worker Y.-F. (Elsa) Xiao [122].

As such, the important conclusion to be drawn from the data presented as Figure 4.5 is that the emission from a single nanotube is well-described by the fitted function, indicating that the observed PL is strongly linearly polarized. Comparing the data with the known orientation of the nanotube on the sample (See Section 4.2.3), it is evident that the maxima in the plot correspond to PL emission parallel to the nanotube axis and the minima correspond to emission perpendicular to the axis. These observations, in agreement with expectations as discussed in Section 2.5.4 and reported elsewhere [37, 71, 76], provide further confirmation that the object under
observation is a single nanotube. Additionally, this observation validates the experimental orientation of the sample relative to the laser and the glass window, as SWCNT are most efficiently excited when the polarization of the excitation beam is aligned with the nanotube axis [1].

Brief mention should be made of the possible artifacts that could confound this measurement. Firstly, it is noted that the considerable polarization dependance of the spectrometer does not factor into this experiment, as it is the half-wave plate, not the final linear polarizer, that is rotated, so that the PL always enters the spectrometer with the same polarization orientation. One possible effect that could conceivably produce an artificially-polarized measurement is the fact that the PL passes through the glass window near to Brewster’s angle. Although the reflection off of this optic is strongly polarized, the polarization of the transmitted beam is altered much less significantly. Even in the worst case scenario where the window is precisely orientated at Brewster’s angle, the transmitted component of the beam with s-polarization would only be attenuated by about 17.1% relative to the unattenuated (p-polarized) signal. This effect is clearly insufficient to explain the strongly polarized signal, implying that the polarization dependance of the observed signal results from the nanotube, not the apparatus.

\footnote{In fact, the window likely results in a slight de-polarization of the observed PL signal as it preferentially (if slightly, as mentioned) reflects the s-polarized PL beam. As a note, none of the other optics in the relevant section of the beam path exhibit significant polarization dependence, and so are omitted from the discussion.}
4.3 Spectral Analysis

4.3.1 Photoluminescence Emission Spectrum

With a nanotube accurately located and fully mapped, it is possible to record its emission spectrum. This measurement is performed with the extra focussing lens (L2 in Figure 3.4) removed so that the spot size of the excitation laser is larger than the nanotube, providing more uniform excitation. Additionally, the position of the sample is tuned in three dimensions and the excitation laser is operated in continuous-wave (CW) mode to maximize the PL signal. The data are generally taken using a moderate excitation irradiance (≈100 W/cm²) to avoid complicating the excitation spectrum with saturation effects (See Section 4.4).

A typical emission spectrum from a single, air-suspended suspended (9,8) SWCNT (‘Pebbles’) is presented as Figure 4.6. In this case, the data set is taken using CW excitation at 800.0 ± 1.5 nm. The 729 ± 7 µW excitation beam is focussed to a spot 20 ± 3 µm in diameter, resulting in a Gaussian spot with peak power of 161 ± 14 W/cm². Two data sets are taken, one to obtain the PL as described in the preceding paragraph, and a second under identical conditions except with the sample displaced by a distance (in this case, 98 ± 1 µm) to remove the SWCNT from the excitation beam and allow for the experimental characterization of the background from the substrate. Each data set consists of a number (in this case, 4) of identical spectral sweeps taken sequentially to mitigate random error. Data points collected at the same wavelength are averaged, and the uncertainty in the data estimated by the standard error of the mean.

The analysis required to produce Figures 4.6 and 4.8 from the raw PL spectrum
Figure 4.6: Emission spectrum of a single (9,8) nanotube. Uncertainty in the PL signal is represented by error bars, most of which are hidden by the data markers. The data set is fitted to both Lorentzian and Gaussian peak functions. The residuals of this fit are presented as Figure 4.7. This data set is additionally plotted against a logarithmic scale in Figure 4.8.

is made up of several steps. In the first step, the measured background is subtracted from the measured PL signal\(^\text{10}\). Next, to facilitate plotting against the quantum mechanical energy of the photons as opposed to wavelength, the data set is then scaled by a factor of \(1/\lambda^2\). This factor addresses the concern that the spectral ‘bins’ formed by the combination of the grating and the output slit are constant in size only with respect to wavelength, and need to be scaled to avoid distortion when the data set is plotted against the photon energy. Following this scaling, the data set is normalized to the peak value.

\(^{10}\)For reference, the signal-to-background ratio for this data set is about 6:1 at the peak, 1:4 at the high-energy extreme, and 1:3 at the low-energy extreme.
As expected, Figure 4.6 shows that the PL emission forms a strong spectral peak. Two different peak functions, a Lorentzian and a Gaussian, are fitted to the data to aid analysis. The vertical offset term is fixed at zero for both fitting functions, to reflect the fact that the background has already been subtracted. The Gaussian function has the form:

\[ y = \frac{A_G}{w_G\sqrt{\pi/2}} \cdot \exp\left(-2 \cdot \left(\frac{x_G - x_{0G}}{w_G}\right)^2\right) \]  

(4.4)

The Lorentzian function has the form:

\[ y = \frac{2A_L}{\pi} \cdot \frac{w_L}{4(x_L - x_{0L})^2 + w_L^2} \]  

(4.5)

The \( A_G \) and \( A_L \) parameters are the vertical scaling of the Gaussian and Lorentzian peaks, respectively. The \( x_{0G} \) and \( x_{0L} \) are the respective peak locations, and the \( w_G \) and \( w_L \) parameters are the width parameters. Given the use of normalized data
and the easily established location of the peak, the width parameters are the most important for the subsequent analysis.

Of the two fitted functions appearing on Figure 4.6, the Gaussian fits the data points more closely, and only notably deviates from the data to underestimate the three highest-energy points in the spectrum. In contrast, the Lorentzian function nearly uniformly a poorer fit to the data. It simultaneously over-estimates the peak value and far shoulders of the spectrum while underestimating the near shoulders of the data. These observations are quickly verified by an inspection of the residuals of the two fits, which are presented in Figure 4.7. It should be additionally noted that these fits are fairly robust, in that the Origin 8.0 non-linear curve-fitting routine converged to similar values for the fit parameters in repeated fitting sessions. The superiority of the Gaussian fit extends to data taken for other nanotubes by the author as well as co-worker Y.-F. (Elsa) Xiao [122].

The only range where the Lorentzian function performs comparably to the Gaussian is over the three highest-energy data points. However, this discrepancy in the Gaussian fit (i.e. the underestimation of the high-energy points) was observed for PL spectra taken for the majority of nanotubes, and may be physical in origin. In early work reported in the literature, this asymmetry was attributed to the presence of van Hove singularities (vHs) in the one-dimensional joint density of states (JDOS) [73]. However, this rationale has been superseded by the confirmation of the exciton picture [112]. A possible explanation compatible with the exciton picture could involve emission from a phonon sideband related to the radial breathing mode (RBM) located about 35 meV above the peak in (9,8) nanotubes [45]. Further temperature-dependent experimentation would be necessary to evaluate this hypothesis.
It is significant that the SWCNT emission spectra observed here are best described by a Gaussian function as this contradicts a number of published results ([53, 37, 73, 51]) in which Lorentzian or other peak functions are fitted to the data. However, it should not be seen as a direct contradiction with some of these studies for several reasons. For instance, the studies reported by Jones et al. [53] were performed using ensemble samples which produced a cluttered emission spectrum, to which the researchers fitted several Voigt profiles in an attempt to define the position of spectral peaks.

Similarly, direct comparison to the single-tube work done by Hartschuh et al. [37] should also be made with caution due to the significant discrepancy in the observed emission linewidth of the nanotubes. Specifically, the group studied micelle-encapsulated nanotubes with a reported emission linewidth of 23 meV, which is similar to values reported in other studies of micelle-encapsulated SWCNT dispersed by long periods of sonication (For example, [53, 93]). However, this value is roughly two times larger than either the $13.2 \pm 0.2$ meV FWHM$^{11}$ linewidth that is obtained from the Gaussian fit to the data from air-suspended SWCNT reported in Figure 4.6, or the 10-15 meV range of room-temperature linewidths reported for suspended nanotubes by Lefebvre et al. in [73] and Kanemitsu et al. [51, 83]. Interestingly, similarly narrow lines are reported for long, micelle-encapsulated SWCNT prepared using a particularly brief sonication step reportedly performed to avoid unnecessarily ‘cutting’ the SWCNT [107]. This pattern suggests that some homogenous (i.e. Lorentzian) broadening may occur in short ($< 1 \mu m$) nanotubes. Given that it has been reported

$^{11}$The data used to arrive at this number was taken with a 7 mm output slit to boost the observed PL signal. Consequently, as described in Section 4.2.1, the reported value is likely an over-estimate of the intrinsic linewidth of the SWCNT. A set of data with a narrower (2 mm) slit was taken. The signal-to-noise is poorer under these conditions, so the plot is not displayed, the FWHM is only reduced to 10.8 meV. Further decreases in the slit width have little effect.
that the dominant broadening mechanism of the emission peak is from interactions between excitons and low-energy phonons [83], a possible explanation could involve highly de-localized excitons interacting with defects at the end caps of the nanotube. However, the strong Gaussian character of this data set does conflict more directly with two published results by the NRC and Kanemistu groups [73, 51]. In both cases, experiments are performed on air-suspended tubes which show room-temperature linewidths in the 10-15 meV range that are fitted using Lorentzian curves. A potentially relevant point is that the specific fitting of the Lorentzian to the data set is only a minor part of both publications, and in both cases the fit does exhibit a small
over-estimation of the low-energy portion of the curve, similar to the observations reported here. Additionally, in neither case are the plots displayed on a logarithmic scale, which emphasizes the large fractional deviations between the model and signal that occur far out into the shoulders of the peak (Compare Figure 4.6 and 4.8.). Also significant, the NRC group has not commented on the nature of the lineshape of the emitted PL spectra in their most recent papers [70, 71] despite presenting emission spectra for many tubes.

Given that Gaussian functions more closely fit the majority of SWCNT PL spectra measured as part of this work, even correcting for such factors as the background from the substrate and the spectral convolution with the output slit of the spectrometer, this discrepancy clearly requires further investigation. It is entirely possible, even likely, that both homogeneous and inhomogenous broadening processes are manifest in SWCNT, creating emission spectra that have both Lorentzian and Gaussian aspects. In this case, it is important to establish which experimental parameters affect the relative strength of these two processes, especially given the relevance of this discussion to an understanding of the role of environmental effects in this theoretically pristine system. The ideal experiment would clearly be to be able to compare SWCNT prepared using different methods using the same apparatus.

Less controversial than the identity of the peak function is the position of the peak of the spectrum. The peak of the Gaussian function fitted to this data set lies at 898.4 ± 0.1 meV; this compares well with the 877 meV peak reported for micelle-encapsulated (9,8) SWCNT [4] and the 904 meV peak reported for (9,8) SWCNT grown by our collaborators between pillars [74]. As discussed in Section 2.5.5, the relatively mild redshift observed in micelle samples is attributed to changes in the
dielectric environment of the nanotube. Given that some variation ($\approx 10$ meV) in the peak energy of air-suspended SWCNT with the same chirality has been reported by Inoue et al. [51], and observed experimentally by the author, the value for the peak of the emission spectrum reported here is in agreement with expectations. Taken in addition to the spatial profile and polarization data, the agreement of the location of the spectral peak with literature work removes any reasonable doubt that the object under study is a SWCNT.

4.3.2 Intensity-Dependence of Photoluminescence Emission Spectrum

Only a single spectrum was taken for most nanotubes, simply in order to verify that they exhibited the expected spectral peak and, hence, were of the desired chirality (See Section 2.5.2). However, a full set of data describing PL emission intensity as a function of emission wavelength, excitation wavelength, and excitation intensity was taken for a typical nanotube (‘June’ in Figure 4.2). A cut through this data set taken at the peak of the excitation spectrum is presented in Figure 4.9 to show the dependence of the emission spectrum on the excitation intensity. The two spectra taken at 75 W/cm of excitation intensity were taken at the start and end of experimentation, to ensure that the signal from the nanotube had not been affected by an ‘aging’ process (See Section 4.6).

The data presented in Figure 4.9 was re-scaled into units of energy using the procedure outlined in Section 4.3.1. However, subtraction of an experimentally-measured background was not performed as the collection of background scans for each value of excitation wavelength and intensity was not possible in the allotted available time.
Figure 4.9: Emission spectrum of a single (9,8) carbon nanotube recorded for different excitation intensities. The data set is presented without background subtraction as discussed in the text. Each spectrum is fitted to the sum of a Gaussian and a linear function. Uncertainty in the PL signal is estimated by the standard error of the mean and presented as error bars. All data points are normalized to the global maximum. This same data set is plotted on a linear scale with each spectrum normalized to its own peak value in Figure 4.10 to highlight the constant FWHM.
Consequently, the data points shown on the figure are each the sum of the PL emission from the nanotube and the background at the relevant wavelength. To account for this in performing the Gaussian fit, it was noted that the background from the substrate in this region of the spectrum could be modeled by a simple linear function of energy of the form: \( B_k = A \cdot E + B \). As a result, linear and offset terms were added to the Gaussian fitting function. Although it is acknowledged that this is not as satisfying as subtracting an experimentally-observed background collected from the substrate, it is emphasized that data taken in this way is intended to show the trends that appear in the emission spectrum as the excitation intensity is changed, as opposed to being a conclusive study of the emission lineshape (As in Section 4.3.1).

Immediately evident from Figure 4.9 is the lack of any significant dependance of the peak location or the peak width on the excitation intensity. This is more strikingly demonstrated both in Figure 4.10, which shows the remarkable overlap that results if each spectra normalized to its own peak value, and the inset graph, which shows the near-constant FWHM of Gaussian fits to the spectra taken at different intensities. The outlying point on the inset plot is not considered representative as it results from the spectrum taken at the lowest available excitation intensity where the PL signal is close to the detection limit. The uncertainty in the data imparted by these conditions is indicated by the large error bars shown for the corresponding spectra in the main figure. The demonstration that the emission spectrum is generally invariant to the excitation intensity is a useful experimental result because it shows that the emission spectrum is not modified by heating effects under experimentally-relevant excitation intensities.

\textsuperscript{12}This assumption stems from broad spectral scans of the background that were performed experimentally, but are not shown in this thesis. They collectively show that there are no significant peaks in the spectral vicinity of the PL emission.
Figure 4.10: Emission spectrum of a single (9,8) carbon nanotube recorded for different excitation intensities. Each spectrum is normalized to its peak value. The data set is presented without background subtraction as discussed in the text. Uncertainty in the PL signal is estimated by the standard error of the mean, and presented as error bars. This same data set is plotted on a logarithmic scale with each data point normalized to the global maximum in Figure 4.9 to highlight the accuracy of the Gaussian fit.

A second point to be drawn from Figure 4.9 is the validity of the summed Gaussian and Linear fit. The resulting function fits the data well for all excitation intensities, suggesting that linear fit could be used to rapidly account for the background contribution to the signal in post-processing in cases where high accuracy is not required. This is particularly useful given the need to experiment on many individual SWCNT to build up adequate statistics to provide strongly conclusive results [51].
4.3.3 Photoluminescence Excitation Spectrum

In addition to measuring the emission spectrum of a nanotube, it is also of interest to investigate its ‘excitation spectrum’. This phrase is used in preference to ‘absorption spectrum’ as the method used to make this measurement is indirect and unavoidably produces a result that depends on both the absorption and emission spectra of the nanotube. While it is assumed that the microscopic processes that dictate the emission spectra from the E_{11} exciton level do not significantly depend on the initial energy of the E_{22} exciton (See Section 2.5.8), experimental evidence is presented in Section 4.4 that suggests that strong ‘saturation’ mechanisms that occurring in the E_{11} level result in a non-linear relationship between the number of photons absorbed and the number emitted, so that the ‘excitation’ and ‘absorption’ spectra of SWCNT are not generally identical, and would only be the same under very low excitation intensities.

After a nanotube is located as explained in Section 4.2.2, the first step in measuring its excitation spectrum is to take emission spectra for a range of excitation wavelengths in the manner described in Section 4.3.1. To determine the intensity-dependence of the excitation spectrum, additional sets of emission spectra are taken at a variety of excitation intensities for each excitation wavelength. Care is taken when changing the emitted wavelength of the laser to ensure that the laser beam continues to be properly aligned through the setup to avoid introducing artifacts into the measurement. The wavelength of the excitation beam is continuously monitored by directing a fraction of the incident power into the APE Wavescan Laserspectrometer (See Section 3.5.3).

Each measured emission spectrum is plotted to ensure that the location of the
peak value does not change during experimentation. Although no significant shift in the emission spectrum attributable to changes in the excitation wavelength has been observed in the author’s experiments, this step is important to avoid artifacts from occasionally-observed ‘aging’ processes (See Section 4.6). After the measurement has been performed, a cut through the data set at the peak emission wavelength is taken to create a set of excitation spectra at various excitation intensities. Such a set of spectra, generated from a data set taken from the same nanotube (‘June’) used in Section 4.3.2, is presented in Figure 4.11. Following its implementation in Section 4.3.1, background subtraction is performed on each emission spectrum using a fitted linear function before the peak values are extracted to form the excitation spectra. As opposed to plots of emission spectra, it is not necessary to re-scale the data values when plotting excitation spectra to account for the unequal spectral bin sizes in wavelength and frequency because all data sets are taken with the spectrometer at the same position.

Immediately apparent from Figure 4.11 is that the excitation spectrum of SWCNT shows a distinctive peak. As with PL emission spectra (Section 4.3.1), both Lorentzian and Gaussian peak functions are fitted to the data. In contrast to the observations for the emission spectra, a Lorentzian function fits this data closely while the Gaussian function underestimates the peak and overestimates the shoulders of the curve. The difference between the two functions is clearly demonstrated in Figure 4.12, which shows the residuals resulting from both fits to each of the five data sets with the highest excitation intensity. For reference, the four data sets taken at lower excitation intensities exhibit a similar trend to those presented and were only removed to reduce visual clutter near the axis.
Figure 4.11: Excitation spectra of a single (9,8) SWCNT (‘June’) under a variety of excitation intensities. Background has been subtracted from the data as described in the text. The peaks are fitted with both Lorentzian and Gaussian functions with zero vertical offset. The residuals from these fits are presented in Figure 4.12. Error bars are not included as they are universally smaller than the data markers.

The Lorentzian fit to the data set is in agreement with previous work [72], and reveals that the excitation spectrum of a SWCNT is substantially broader than its emission spectrum, roughly $45 \pm 10$ meV compared to $13.2 \pm 0.2$ meV, respectively. This comparatively broad lineshape is attributed to the very short (20–50 fs) lifetime of excitons in the $E_{22}$ level due to phonon-mediated relaxation processes [47, 10, 81].

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133The very large stated uncertainty for the width of the excitation spectrum can be misleading as the majority of this range is the result of the intensity-dependence of the lineshape of the excitation spectra, as shown in Figure 4.13.
Figure 4.12: Residuals resulting from Lorentzian and Gaussian functions fitted to the PL excitation spectrum presented as Figure 4.6. Residuals resulting from the same type of peak function are identically coloured for simplicity. As the absolute value of the residuals generally scale with the size of the signal, residuals from the four spectra taken at the lowest intensities are not included to avoid clutter.

This attribution is also consistent with the fitted Lorentzian lineshape, as such a lifetime-dependent process would result in homogeneous broadening. A minor experimental consideration in determining the shape of the curve is the small amount of artificial broadening that results from the $\approx 3$ nm (6 meV) linewidth of the laser when operated under these conditions (See Section 3.4). However, this is relatively negligible compared to the size of the feature.

It is evident from a comparison of excitation spectra collected at different excitation intensities that the location of the peak does not depend on the excitation intensity $^{14}$ However, Figure 4.13 shows that the linewidth of the excitation spectra,

$^{14}$For reference, a blue-shift of this value with increasing intensity would suggest a phase-space filling effect [46].
Figure 4.13: Dependence of the linewidth of the peak of the excitation spectrum on the excitation energy. The linewidth is taken to be the FWHM of the fitted Lorentzian curve. The data set is plotted versus the excitation intensity on a logarithmic scale to show the simple logarithmic dependence. The fitted function is of the form $W_L = A + B \cdot \ln(I)$.

taken as the FWHM of the fitted Lorentzian curve, does appear to depend on the irradiance. This dependence is modeled well by a two-parameter logarithmic function of the form $W_L = A + B \cdot \ln(I)$. The coefficients resulting from this fit are $A = 30.4 \pm 0.07$ meV and $B = 4.4 \pm 0.2$ meV.

It is very likely that the dependence of the excitation linewidth on the excitation intensity results in large part from the intensity-dependent saturation effects that occur in $E_{11}$ that are discussed in detail in Section 4.4. In brief, the relatively large number of excitons created when the nanotube is excited resonantly are each less likely to emit PL as the presence of more than one exciton creates new two-body
non-radiative decay channels. In contrast, the shoulders of the excitation spectra are less strongly affected by these processes, as the comparatively inefficient absorption of light away from the peak leads to a reduced average exciton density. This has the net effect of flattening the curve and, hence, increasing the apparent linewidth of the peak.

Although it is possible in hindsight to cast the investigation of SWCNT excitation spectra as largely a confirmation of literature results, their importance lay with the fact that they provided important confirmation of the capabilities of the apparatus and the assumptions made about nanotube behaviour under excitation, which was highly necessary given that the Gaussian emission spectra observed experimentally differed from the Lorentzian fits used in literature results. In addition the observation of saturation effects in the PL behaviour of carbon nanotubes is intricately linked to the fundamental dynamic processes, and is at the center of the further experimentation reported in subsequent sections.

4.3.4 PLE Map

For the purposes of comparison, a PLE map is generated from the emission and excitation spectra recorded for the nanotube ‘June’ and presented as Figure 4.14. The data set is collected and analyzed as described in Section 4.3.2, and normalized to the maximum value. To avoid distorting the observed spectrum with non-linear effects, a low excitation intensity \((22 \pm 1 \text{ W/cm}^2)\) is used.

For comparison, a PLE map of a comparable (air-suspended) ensemble sample is taken from the literature and presented as Figure 4.15. Note the significantly differing
horizontal and vertical scales. The salient point is that the significant degree of isolation of the peaks in the ensemble PLE map permits the unambiguous determination of the chirality of the nanotube from the peaks of its emission and excitation spectra.

4.4 Saturation Studies

4.4.1 Motivation

The preliminary observations of saturation behaviour in the air-suspended SWCNT used in this work were taken as an invitation to examine this interesting behaviour more closely. As described in Section 2.5.8, non-linear PL behaviour had been reported in the literature prior to the start of these experimentations. However, all
of these studies had been performed using micelle-encapsulated nanotubes and most had only considered ensemble samples. In the light of the then-recent publication that SWCNT grown over trenches displayed quantum efficiencies (QE) more than an order of magnitude greater than observed in previous reports (See Section 2.5.6), and given the close relationship between PL saturation and the existence of efficient non-radiative loss channels, it was natural to explore PL saturation with the available samples. Further, as described in Section 4.5, the observed saturation behaviour became a tool with which to probe the intrinsic dynamics of the nanotube.
4.4.2 PL Saturation with CW Excitation: Estimation of QE

Initial studies on the saturation behaviour of PL emission from carbon nanotubes are performed on SWCNT that have been located and mapped as described in Sections 4.2.2 and 4.2.3. Before intensity-dependent experiments are performed, the excitation and emission spectra were measured in the manner reported in Section 4.3. All saturation studies are performed with the excitation wavelength tuned to the peak of the excitation spectrum (≈ 800 nm or 1.55 meV for a (9,8) SWCNT) and the spectrometer set to record the peak of the emission spectrum (≈ 1380 nm or 899 meV for a (9,8) SWCNT). This CW work was primarily completed by co-workers Tam Q. Nhan and Y.-F. (Elsa) Xiao, and is reported in their respective theses [91, 122]. As a result, the discussion here is limited to a brief summary of important findings and a discussion of the method of calculating PL quantum efficiency.

As shown in Figure 4.16, the dependence of PL emission on the excitation intensity becomes non-linear as the CW power is increased. This is in agreement with published reports (For example, [93, 107, 80]). However, as in literature reports, the PL vs. intensity curve exhibits ‘soft’\(^{15}\) saturation behaviour, in that the curve varies roughly with the square root of the excitation intensity. This point is illustrated by the inclusion of a fitted function of the form \(I_{PL} = A \cdot \sqrt{I_{CW}}\) in Figure 4.16. To be clear, it is not argued that this function entirely describes the observed trend, it is simply included to provide an estimate of the ‘strength’ of the saturation effect at these CW intensities\(^{16}\). The origin of this ‘soft’ saturation behaviour, particularly with respect to the differences between observations made on individual and ensemble samples is

\(^{15}\)The implicit comparison made here is to the ‘hard’ saturation effects seen when using ultrashort pulses, which are discussed in Section 4.4.3.

\(^{16}\)For reference, the value of the parameter, ‘A’, resulting from this fit is 22 ± 2.
Figure 4.16: Non-linear dependence of the intensity of the PL emission on the intensity of continuous-wave excitation for a single (9,8) SWCNT. A linear function of the form \( I_{PL} = A \cdot I_{CW} \) is fitted to the first seven data points to determine the slope of the low-intensity regime. An additional function of the form \( I_{PL} = A \cdot \sqrt{I_{CW}} \) is fitted to the entire data set for comparison. Error bars representing uncertainty from the standard error of the mean are not included as they are universally smaller than the data markers. Data collected by co-worker Tam Q. Nhan [91].

discussed in greater detail by co-worker Tam Q. Nhan in her thesis [91].

Additional information can be gleaned from a zero-offset linear function of the form \( I_{PL} = m \cdot I_{CW} \) fitted to the first seven data points. This range is selected as it only includes those data points for which the PL does not deviate noticeably from linear dependance on the excitation intensity. For this data set, this ‘linear’ regime is deemed to end at a peak intensity of the Gaussian spot of 50 W/cm\(^2\). This threshold value can vary by a factor of two between observations made on different nanotubes. The linear fit to this data set produces a value of \( m = 2.99 \pm 0.07 \) \( \mu \)V/(W/cm\(^2\)).
This fit parameter, which directly relates the excitation irradiance and the emitted intensity can be used to estimate the PL quantum efficiency, which is defined the ratio of photons absorbed to photons emitted:

\[ \eta_{QE} \equiv \frac{\Phi_{emitted}}{\Phi_{absorbed}} \]  \hspace{1cm} (4.6)

Several other factors and assumptions are required to complete this calculation, which follows the method developed by collaborators at NRC [70]. First, it is necessary to convert from the detected PL signal (in \( \mu \)V) to the total power radiated by the nanotube. As calculated in Section 3.7, the value of this co-efficient is \( \eta_T = 4 \pm 2 \times 10^6 \) V/W. The radiant power can be easily converted to a rate of photon emission via the quantum mechanical energy of the emitted PL (899 meV). An effective\(^{17}\) optical cross section for carbon atoms (\( A_C = 1.6 \times 10^{-3} \) nm\(^2\)) is taken from the literature \([107]\)\(^{18}\). The absorption cross-section of the nanotube is modeled using \( A_C \) and calculating the number of constituent atoms in the SWCNT from the areal density of carbon atoms in the graphene lattice (\( \sigma_{graphene} = 37 \) atoms/nm\(^2\)) and the physical surface area of the nanotube derived from its measured length (\( L_{NT} \)) and calculated diameter (\( D_{NT} \), See Section 2.3). Symbolically:

\[ A_{NT} = A_C \cdot \sigma_{graphene} \cdot \pi \cdot D_{NT} \cdot L_{NT} \]  \hspace{1cm} (4.7)

\(^{17}\)An experimentally-measured ‘effective’ cross-section is used in preference to the established theoretical atomic cross section due to the strong modification of the optical properties of the SWCNT by excitonic effects, which are difficult to model theoretically (See Section 2.5.3).

\(^{18}\)As discussed in Section 2.5.8, this value is considerably contentious. A much lower value (\( A_C = 1.6 \times 10^{-4} \) nm\(^2\)), reported by Islam et al. [52], was used (with qualifications) in the important paper published by collaborators Lefebvre et al. at NRC that reported a QE of 7% for SWCNT grown over trenches. Tsyboulski et al. [107] noted that the absorption linewidth of the ensemble sample used by Islam et al. to make the measurement was very broad and suggested that isolated SWCNT, which have absorption linewidths that are roughly ten times more narrow, would have absorption cross-sections that are enhanced by a factor of 10 on resonance. To the knowledge of the author, the consensus among researchers is that the larger number is more plausible, but that the ultimate resolution of this question is pending.
The length of the nanotube in question (Named ‘8591’) is measured as $L_{NT} = 10 \pm 1 \, \mu m$ using the technique described in Section 4.2.3. From its identified (9,8) chirality, its diameter is calculated to be $D_{NT} = 1.17 \, nm$ using Equation 2.1. Combining these values gives an absorption cross-section for the ‘8591’ nanotube of $A_{NT} = 2.2 \pm 0.4 \times 10^3 \, nm^2$.

Two assumptions must be made to use the $A_{NT}$ co-efficient to calculate the rate of photon absorption in the nanotube. Firstly, it is assumed that the the reflection of the incident light from the sample is incoherent. As a result, the effects of reflection are modeled by a scaling factor of $\alpha = 1 + R = 1.2$ to the incident intensity, given that reflectivity, $R$, of the Si/SiO$_2$ sample at 800 nm is 0.2 [91]. Secondly, the effect of variation in intensity across the Gaussian spot is modeled by including a factor, $G_{int}$, that relates the average intensity over a circular section with a diameter equal to the tube length to the calculated peak intensity. This relation is defined by Equation 4.8.

$$I_{avg} = \frac{2\pi \int_0^{L_{NT}/2} dr \int_0^{2\pi} rd\theta \, e^{-\frac{4 \ln(2) r^2}{FWHM^2}}}{\pi \cdot L_{NT}/2}$$  \hspace{1cm} (4.8)

For a 10 $\mu m$-long SWCNT located in the center of an 18 $\mu m$ Gaussian spot, the value of this parameter is calculated to be $I_{avg} = 0.9$. The uncertainty in this value is substantial, as it strongly depends on the ability to align the SWCNT in the focal volume. However, for the purposes of rough estimation, it is assumed that this uncertainty is accounted for in the stated 33% error for the collection efficiency parameter, $\eta_{coll}$ (See Section 3.7). The final factor necessary to determine the rate of photon absorption is the energy of the incident photons, which is 1.54 eV.

These myriad terms are combined to give an expression for the PL QE of a
SWCNT in terms of the fitted slope, $A$:

$$\eta_{QE} = A \cdot \frac{(1/\eta_T)}{(I_{avg} \cdot \alpha \cdot A_{NT})} \cdot \frac{1.54eV}{0.899eV} \cdot 1.54eV$$ (4.9)

Substituting the calculated values into Equation 4.9 shows that tube ‘8591’ exhibited a quantum efficiency of $\eta_{QE} = 4 \pm 2\%$. Performing the same calculation on the data set collected from the nanotube ‘June’ gives a result of $\eta_{QE} = 13 \pm 6\%$. Although these values would seem to provide straightforward confirmation of the 7\% quantum efficiency reported by our collaborators at NRC [70], the significant (10\times) difference between the absorption co-efficients used in the two calculations makes the appropriate conclusions more subtle. The first important comment is that, had the ten times smaller value for $A_C$ as reported by Islam et al. [52] and used by Lefebvre et al. [70] be used in these calculations, the result would be quantum efficiencies of 40\% and 130\% for this nanotube. Aside from the legitimate concern about the non-physicality of efficiencies greater than 100\%, these result would also be in disagreement with the expected quantum efficiency that can be obtained by comparing the observed $\approx 70$ ps non-radiative, and calculated $\approx 1$ ns radiative lifetimes. The consequence of all this is to support the growing consensus among the community that the value reported for $A_C$ by Islam et al. is too small, and that the appropriate absorption co-efficient should be on the order of $A_C = 1.6 \times 10^{-4}$.

The second conclusion to be drawn is that the nanotubes observed in this work exhibited significantly greater quantum efficiencies than the ‘7\%’ reported by our collaborators at NRC [70], even though the samples were highly similar. Correspondence with the authors indicates that the assumptions used to generate value reported were intentionally conservative. It is additionally useful to put the quantum efficiency
values observed here in context with the most recent reports of studies of micelle-encapsulated nanotubes, which have suggested quantum efficiencies of “greater than 1%” \cite{17} and “\(\approx 8\%\) for the brightest species” \cite{107}. Finally, it is useful to note the agreement between these results and the calculation of the number of photons collected per pulse in the ‘saturation regime’, which is described in Section 4.4.4.

Even accounting for the large uncertainty in the measurement as well as the considerable experimentally-observed tube-to-tube variation, the general agreement of this result with the most recent literature is considered a broad confirmation of the design of the apparatus and of the assumptions made during calculation. Further, it appears that the air-suspended samples may exhibit greater quantum efficiencies than micelle-encapsulated nanotubes. However, the current experimental method is clearly unsuitable for making precise measurements of the PL QE of carbon nanotubes. Simply put, there are too many experimental parameters involved, each of which contributes a fractional error. Methods to minimize these effects, such as measuring relative quantum efficiencies and comparing to a standard with calibrated absorption and emission characteristics would greatly increase the utility of the results. Nevertheless, given that the necessary calibration work to determine the various co-efficients has been done, this measurement is relatively straightforward to perform and provides a useful tool to help characterize single nanotubes.

4.4.3 Pulsed Power Dependence

Intensity-dependant studies conducted with ultrashort pulsed light have two substantial advantages over those performed using CW excitation. Experimentally, ultrashort pulses allow the SWCNT to be exposed to very high intensity light while markedly
reducing the risk of damage due to heating effects. This allows the investigation of regimes where intensity-dependant saturation effects more clearly apparent. Theoretically, the use of a well-spaced train of sub-picosecond pulses creates the situation analogous to an impulse response; SWCNT are rapidly excited and then allowed to evolve in time without the presence of an EM field. This provides an opportunity to observe dynamic processes that would be masked in steady-state studies.

The nanotubes used in these ‘pulsed power dependance’ (PPD) studies are located and characterized using the method described in Section 4.4.2. Only nanotubes with strong PL emission under CW excitation (> 200 µV of signal) are considered, as the signal produced under pulsed excitation is considerably smaller. (For reasons discussed below) Once the position of the nanotube is optimized for maximum PL signal under CW excitation, the sample is blocked and the laser is switched to mode-locked operation. Care is taken to ensure consistent beam alignment. The excitation intensity is reduced to a minimum value using the ND filter wheel (See Figure 3.4) before the beam is unblocked. The PL signal is measured repeatedly while the excitation beam is held at a constant intensity using an automated program (See Section 3.6). For a typical data point, the signal from the lock-in amplifier would be recorded every 100-300 ms (set by the RC time constant) for 2-6 seconds, resulting in 10-20 data points. The first few points are discarded to ensure that the signal has settled, and the remaining points averaged to obtain the measured PL signal.

Following a set of measurements, the beam is blocked, the filter wheel rotated to change the excitation intensity, and the process is repeated. Data is taken with both increasing and decreasing steps in intensity to ensure that any hysteresis effects do not corrupt the data set. In most cases, the intensity is ‘swept’ up and down more than
once. The major concern is ‘aging’, which appears to occur most frequently under pulsed excitation at high intensities, and can irreversibly diminish the observed PL signal (See Section 4.6). Following the collection of PL data, the sample position is changed to move the nanotube out of the excitation spot, and the process repeated to collect the background from the sample. The results from this procedure applied to a typical nanotube (‘June’) are presented in Figure 4.17. It should be noted that the data points are plotted against the excitation fluence, i.e. the number density of photons interacting with the SWCNT every pulse, instead of the irradiance (radiant power per unit area) used for CW work.

Several important observations can be made from Figure 4.17. The most significant is the very ‘hard’ saturation of the PL signal; once the background is subtracted from the signal (Shown in Figure 4.18), the PL emitted from the tube does not increase at all as the excitation fluence is increased from $0.5 \times 10^{12}$ to beyond $16 \times 10^{12}$ photons/pulse/cm$^2$. This is a substantially different result from the ‘soft’ saturation resulting from the CW work discussed in Section 4.4.2, or reported in previous literature using CW excitation on ensembles [93], CW excitation on single nanotubes [107], or pulsed excitation on ensembles [80]. In a very recent publication made since our preliminary reports of these observations [121], Högele et al. [41] have reported similar ‘hard’ saturation results for individual nanotubes under pulsed excitation.

The second significant observation is the very low fluence at which the PL emission saturates. To put the observed value of $0.5 \times 10^{12}$ photons/pulse/cm$^2$ into perspective, consider a 6 μm-long (9,8) tube with the maximum effective atomic absorption co-efficient reported in the literature ($A_C = 1.6 \times 10^{-3}$), and calculate the rate of
Figure 4.17: Raw data taken to create a Pulsed Power Dependance Curve for a single (9,8) nanotube (‘June’). Data was taken while increasing and decreasing the excitation fluence four times to verify repeatability. Data on the background light emitted from the sample is also included. No error bars are included, as the standard error for each point is small. Instead, the scatter in the data points is taken as the uncertainty of the measurement.

photon absorption / exciton creation as described in Section 4.4.2. Under these conditions, the data set suggests that non-linear saturation processes entirely dominate the behaviour of the nanotube when there are, on average, only 5.5 excitons created per pulse. This result argues strongly against the proposed phase-space filling model for saturation behaviour (See Section 2.5.8, as five localized excitons with $\approx 1$ nm center-of-mass separation clearly could not ‘fill’ the 6 $\mu$m long SWCNT. It is noted that the ‘threshold’ value observed here is nearly two hundred times smaller than
the value reported for individual micelle-wrapped nanotubes by Högele et al. [41],
suggesting that the saturation mechanisms in these two systems could be strongly
affected by the environment.

One possible explanation that is postulated here without adequate foundation in
theory is that the spatially non-uniform perturbation of the exciton wave-functions
caused by the micelle-wrapping causes the excitons to become ‘localized’, viz. less
able to interact with other excitons due to reduced spatial overlap of the wave func-
tions. The notion of ‘localized’ excitons is advanced by Cognet et al. [13] when they
discuss a point-like exciton that moves via diffusion along the nanotube, and has an
average ‘excursion range’ during its lifetime of $\approx 90$ nm. By contrast, to explain the
apparent rapid interaction of excitons that can be separated by $\mu$m, it is proposed
that the air-suspended nanotube would have much reduced spatial non-uniformities,
so that the excitons could ‘see’ each other from a greater distance. This hypothesis
requires considerable testing; experimentally, it would be desirable to compare the
saturation thresholds of individual micelle-wrapped and air-suspended SWCNT re-
sulting from data taken on the same apparatus to rule out discrepancies resulting from
the calibration of the apparatus. Additionally, theoretical work could give consider-
able insight into the ‘localized’ or ‘delocalized’ nature of excitons in the system, and
perhaps clarify the role of interactions with molecules on the surface of the SWCNT.

The large range of values of excitation fluence over which the PL emission is
unchanged has additional significance when one considers the Auger Recombination
and Auger Ionization models that are proposed to explain the saturation behaviour.
In either case, the process is characterized by a decay rate that scales with the density
of excitons and can be interpreted as the average time for an Auger-type interaction
to occur. For the PL versus Excitation Fluence relation to appear flat over such a large range of value, the Auger process must be very fast compared to the already-observed 7 to 320 ps one-body decay channels (See Section 2.5.3). Although this is demonstrated in considerable detail by co-worker Y.-F. (Elsa) Xiao using a stochastic model of the exciton dynamics [122], the statement can be explained schematically by considering that if the Auger process had a comparable time constant to the one-body decay, the extra population excited by the laser would have a roughly equal chance of emitting PL, leading to observable scaling of the emitted PL with the excitation fluence. For the relationship to be truly ‘flat’, the excitons created beyond the saturation threshold must recombine fast enough such that the time-integrated PL observed from the system is unaffected. This situation is particularly interesting given the fact that our experimental observations show that the saturation effect is already strongly present at very low exciton densities.

A third observation is the considerably smaller PL signal that is produced by SWCNT under pulsed excitation. The comparison can be easily made as CW PL data taken from the same nanotube (‘June’) was presented in Figure 4.11. A crude estimate for the time taken for the PL to decay after pulsed excitation could be made by multiplying the period between the laser pulses (13 ns) by the ratio of the maximum PL emission under pulsed excitation to the maximum PL under CW excitation. The assumption would be that, under such conditions, the only difference between the two cases would be that the SWCNT excited using CW light would emit PL constantly, and the SWCNT excited using pulsed light would only emit PL from the time where it is excited until all of the excitons have recombined. Experimentally, the difficulty with this measurement is that the very large CW intensities assumedly required to
reach the regime of ‘hard’ saturation would likely damage the nanotube. Still, using the largest observed PL measurement in CW (400 µV) and the 6 µV saturated signal seen under pulsed excitation in this way gives a 195 ps estimate for the upper limit of the decay process, which is in the range of values reported in the literature.

A few experimental points can also be taken from Figure 4.17. For instance, the data taken from repeated ‘sweeps’ from low to high intensity and back is consistent, ruling out irreversible damage to the nanotube as the source of the observed saturation effect. As shown on the plot, the PL signal measured in his experiment is quite noisy. It is emphasized that the ±1.5 µV scatter in the ≈ 6 µV raw signal persists even given the averaging at each point over several seconds of data collection 19. Additionally, the background is comparatively large, particularly for elevated excitation intensities, meaning that its characterization and careful substraction, performed here by using a linear fit to the data, is critical to proper analysis. As shown on Figure 4.18, it is desirable to investigate numerous nanotubes to determine which properties are intrinsic to the nanotube, and which are the result of defects and other factors that are specific to a single nanotube. Taken together, these points confirm the importance of the background-minimiztion techniques and automated data collection utilities already implemented, and make a strong case for additional work to improve the S/N characteristics to facilitate future in-depth experimentation.

19This is, naturally, in addition to the chopping and lock-in detection, optical filtering, use of a stable and liquid nitrogen-cooled low-noise electronics, etc... that is employed to make this measurement possible as described in Chapter 3.
4.4.4 Theoretical Interpretation

To better understand the saturation process, PPD experiments were performed on a number of different nanotubes which ranged in measured length from 2.5–10 µm and were of either (9,8) or (10,8). The PPD curves resulting from these experiments were plotted versus the excitation fluence, and then normalized to the ‘threshold’ saturation value to account for experimental differences in PL collection efficiency and the relative ‘brightness’ of a particular nanotube. No other scaling was performed. The result is presented as Figure 4.18.

Immediately apparent from Figure 4.18 is how closely the PPD curves from the different nanotubes overlap; they are generally consistent to within the scatter of the data over the entire range of excitation fluences. This implies that the non-linear mechanisms that result in the observed saturation behaviour do not significantly depend on either the chirality or the length of the nanotube. This fits well with the proposed Auger model as it depends only on the density of excitons in the $E_{11}$ level, which is unrelated to the chirality, and also should not depend on the nanotube length due to the identical scaling of absorption with the length of the nanotube.

A simple theory describing the saturation process was developed from inspection of the data, and, as evidenced by a comparison of the theory curves to the data points, seems to accurately model the observed behaviour. The model is predicated on the strong assumption that the many-body non-linear decay processes are so much faster than the established one-body processes that, effectively, all of the PL is produced by the ‘last’ exciton. In other words, regardless of the number of excitons created via the absorption of photons, the population is ‘quickly’ reduced to one exciton per tube once the pulse has passed.
Figure 4.18: This image shows the Pulsed Power Dependance Curves for several nanotubes. Each curve had the measured background subtracted, and been scaled to the value at the threshold of saturation. Theoretical curves are generated as described in Section 4.4.4. Individual error bars are not included; the uncertainty is taken from the scatter of data points taken at similar excitation fluences. Data was taken by the author (2.5 μm (9,8) nanotube (‘Betty’)), Y.-F. (Elsa) Xiao (other (9,8) SWCNT), and Tam Q. Nhan ((10,8) nanotubes)^20
The consequence of this is that the nanotube can emit a maximum of one photon per pulse; the probability of this emission being governed by the ‘usual’ radiative and non-radiative one-body decay channels\textsuperscript{21}. Experimental support for this assumption is provided by the observation that for the nanotube under consideration, ‘Betty’, the detected signal at saturation can be interpreted using the calculated collection efficiency (See Section 3.7) as implying that an average of 0.07 photons are emitted per pulse, which agrees well with the calculated one-body quantum efficiency (See Section 4.4.2). To summarize; the ‘fast Auger’ assumption implies that the nanotube can be left in one of only two states following excitation; if \textit{any} excitons were created, the nanotube will have exactly one exciton; if no excitons were created, the nanotube will contain no excitons. Saturation, then, occurs when at least one exciton is created in the nanotube with every excitation pulse.

The second assumption is that the distribution of excitons created by an excitation pulse can be modeled by Poissonian statistics. This is considered a very safe assumption given the large number of ‘events’, i.e. the interaction of a single photon with the nanotube, that occur each pulse and the relatively small probability of ‘success’, i.e. absorption. Given that the several seconds of integration involve the observation of hundreds of millions of pulses, it is expected that the result will not be influenced by small deviations from the mean.

Taking these assumptions together, the theory predicts that the PL emitted from the nanotube should scale as the probability of absorbing \textit{any} photons at a given intensity. Calculations are much more straightforward if this is written as $1 - P_0(x)$, i.e. one minus the probability of creating zero excitons. The probability function is the

\textsuperscript{21}Note that the consequences of this effect, i.e. the relative scaling due to the quantum efficiency of the nanotube, are removed by the normalization of the data
Poissonian distribution with the number of photons interacting with the nanotube, \( \Phi \), as the number of events, and the total absorption co-efficient for the entire tube, \( A_{NT} \) as the chance of success. The significant simplifications of the representation of the Poissonian distribution for the case of zero successes allow this model to be concisely described by Equation 4.10

\[
PL = 1 - e^{-\left(\Phi \cdot A_{NT}\right)}
\]

To test the validity of this theory, simulated data sets were created with various absorption co-efficients, and compared to the data. The results of this one-parameter fit to the data are shown in Figure 4.18. As shown, the theoretical equation used with an atomic absorption co-efficient for carbon of \( 1.2 \pm 0.3 \times 10^{-3} \) nm\(^2\) gives a curve that closely follows the data points\(^{22}\). It is noted that the value for the absorption co-efficient compares well to the \( 1.6 \times 10^{-3} \) value suggested by Tsyboulski et al. as discussed in Section 4.4.2.

Although the model does not give information on what microscopic process results in the ‘hard’ saturation, it does provide the important insight that the mechanism causing saturation must be strong enough so that there is only one exciton available for radiative emission very quickly after excitation. This unexpected result, which was reported by the author [123], was strongly confirmed by the photon anti-bunching result published by Högele et al. [41] that showed that SWCNT behave as true one-photon emitters.

A final point is the generally-observed gentle\(^{23}\) decrease in PL observed experimentally as the excitation fluence is increased well beyond the saturation threshold,

\(^{22}\)The uncertainty value given here is taken from the other curves fitted to the ‘top’ and ‘bottom’ of the distributions
\(^{23}\)The PL signal appears to diminish by 5-10% over two orders of magnitude of excitation power
which cannot be described by the simple model presented here. This effect has proven hard to quantify, especially given the dominance of the contribution of the background to the measured signal at these intensities, and more experimentation is considered necessary to understand this effect.

### 4.5 Exciton Dynamics:

**Femtosecond Excitation Correlation**

#### 4.5.1 FEC Theory

The observation of the ‘hard’ saturation of the PL emitted as a function of input intensity suggested a novel method of investigating the dynamics of the system, proposed by supervisor James M. Fraser. The technique was initially referred to as ‘Pump-Pump’ spectroscopy, a name which is indicative of the way in which it is performed. However, it was later re-christened ‘Femtosecond Excitation Correlation’ Spectroscopy (FEC) following the discovery of a publication reporting its use on micelle-encapsulated ensemble samples by Hirori *et al.*[40].

The core of the technique is the splitting of the pulsed excitation beam into two pulses, each of which is of adequate intensity to lie in the saturated regime of the PPD plot. In the cases where the pulses arrived at the SWCNT at the same time, the total PL measured from the SWCNT would be the usual ‘saturated’ PL number, as doubling the excitation intensity has no effect on the amount of PL emitted according to the ‘flat’ PPD curve. However, if the pulses were to arrive at the sample separated by a wide interval, it is assumed that the sample will have totally relaxed back to its ground state so that the total PL signal will be twice the saturation value, as both
pulses will contribute.

The real interest comes when the delay is varied between these extremes as the total amount of PL detected should vary smoothly between the limiting cases in a fashion describing the rate of decay of the PL signal. The simple model discussed in Section 4.4.4 gives an intuitive way of thinking about the technique: The first pulse leaves the SWCNT with one exciton, as it is of adequate intensity to saturate the PL emission. As time passes, this exciton has some probability of recombining, either emitting a photon or not. The arrival of the second pulse truncates this process, and leaves the nanotube with exactly one exciton, regardless of its previous state. This exciton recombines radiatively or non-radiatively, but produces a constant signal on average as the recombination process is allowed to proceed fully. Hence, the only variation in the total observed signal as the delay between the pulses is the contribution of the first pulse. In this interpretation, the signal is the time-integral of the function describing the PL decay through time. A pictorial representation of this process used on a system with a simple, mono-exponential decay is presented as Figure 4.19 A useful observation is that if the intrinsic dynamics of the system are

![Diagram of Femtosecond Excitation Correlation (FEC) technique](image)

Figure 4.19: *Pictorial representation of Femtosecond Excitation Correlation (FEC) technique.*
monoexponential, the time constant of the decay can ideally be determined simply by fitting a function of the form $A \cdot (2 - e^{-t/\tau}) + B$ to the raw data plotted as a function of the delay time. A perfect 2:1 ratio between the saturated level and the zero-delay minimum proved hard to achieve experimentally, so the actual fitting function would be of the form $A + B \cdot e^{-t/\tau}$.

The fitting technique becomes more complex if the intrinsic dynamics are not monoexponential. Consider the bi-exponential decay function that is used to fit data in Section 4.5.2. The functional form of the true time-dependance of the PL emission is given by Equation 4.11:

$$PL(t) = A_1 \cdot e^{-t/\tau_1} + A_2 \cdot e^{-t/\tau_2}$$

(4.11)

The critical observation is that the strength of each decay component is scaled by its respective time constant. As a result, although the theoretical time resolution of the FEC technique is limited only by the pulse duration, signals from very fast decay processes are relatively disadvantaged, and hence more likely to be lost in the noise. The factor is significant to the interpretation of the results presented below\textsuperscript{24}.

In summary, the real strength of the FEC technique is that it allows fast time-dynamics to be culled from data taken with very long effective integration times. This is an enabling advantage given the small signal emitted by a single tube, and the total collection and detection efficiency of the current setup. Additionally, the theoretical time-resolution of the FEC technique is limited only by the pulse duration, although

\textsuperscript{24}This derivation is presented in greater detail by co-worker Tam Q. Nhan in [91]
the detection of fast signals is relatively more difficult.

4.5.2 FEC Results

To implement the FEC technique experimentally, a candidate nanotube is located, mapped, and spectrally characterized as described in Sections 4.2.2, 4.2.3, and 4.3. A PPD curve is created for the nanotube as detailed in Section 4.4.3 to establish the excitation fluence corresponding to the threshold for saturation. Particular care is taken in the alignment of the delay line (See Section 3.5.2), as misalignment that is dependant on the position of the retroreflector is difficult to distinguish from the FEC signal. This effect is further combatted by the use of a large (> 10 µm) spot, which is achieved by operating without the L2 lens (See Figure 3.4). It is also necessary to determine the zero-delay point, which is done as explained in Section 3.5.2. In some experiments, the chopper wheel (also on Figure 3.4) is moved to chop only the beam in the delay-arm of the delay line. This has the effect of automatically excluding the uninteresting signal from the fixed arm alone, so that the plotted data should range from ‘0’ to ‘1’, instead of from ‘1’ to ‘2’ (In units of the saturated PL emission).

An early concern with the measurement was the validity of the assumption that the excited SWCNT will have adequate time to relax back to the ground state, given the maximum period between pulses when performing FEC measurements is only 6.5 ns. Failure to fully relax back into the ground state would result in the build-up of a steady-state component to the signal, which would presumably interfere with the

\[ \text{The FEC studies reported here are all performed exciting the } E_{22} \text{ exciton level at 800 nm (1.54 eV) and detecting the emission from the } E_{11} \text{ level at 1380 nm (0.898 eV). Although the FEC technique could work via any process that adds population to the } E_{11} \text{ state, resonant excitation at the } E_{22} \text{ level is ideal as the very large backreflected signal from the laser can be spectrally separated from the relatively small FEC signal, and the processes that transfer population from } E_{22} \text{ to } E_{11} \text{ are very fast (≈ 40 fs [81, 10])} \]
proper functioning of the FEC technique. However, encouraged by the fact that the 6.5 ns value was twenty times larger than the largest decay constant reported in the literature, experimentation was commenced. As the data will show, any such effect is likely negligible under experimental conditions as the FEC signal is not compromised.

Using the automated program (See Section 3.6), data points are taken as the delay between the pulses is varied in a steps that are spaced according to a hybrid linear/logarithmic pattern. Data taken at shorter delays (less than 300 ps) is taken using logarithmic spacing to oversample the zero delay regime. The remainder of the points (300-1200ps) are linearly spaced, which has the effect of oversampling the tail of the FEC signal; improving the accuracy of the fit. Similarly to the method used to create a PPD Curve (See Section 4.4.3), multiple measurements are made at each delay position and averaged. At a minimum, data points are taken as the delay is stepped from the zero-delay point up to the desired maximum value, as well as while the delay is stepped back down to zero to guard against backlash or other hysteresis effects. In the results presented in Figure 4.20, this ‘up-and-down’ procedure is repeated four times with interlaced sets of step positions.

As shown in Figure 4.20, the FEC technique does produce a signal that varies with the delay between the pulses. Also noticeable is that the data has considerable scatter when compared to the stated error bars, indicating that there is a source of systematic error at each data point. It is suspected that this scatter results from small variations in the alignment of the retroreflector as it is traversed along the delay line. This hypothesis is supported by the observation that this scatter seems to average out over repeated scans. Hence, while the measurement exhibits systematic error at a single data point, the error will eventually average out as the stage is swept
Figure 4.20: Femtosecond Excitation Correlation (FEC) data collected from a single (9,8) nanotube (‘Son of Driver’). The four data sets reflect four different ‘sweeps’ of the delay arm. The inset figure shows the low-intensity portion of the same data set plotted against a logarithmic scale. The standard error of the mean is presented as error bars in the y-direction, but this is clearly an underestimate of the uncertainty, as discussed in the text. The fit curve is from a monoeponential function which gives $\tau_{\text{mono}} = 71 \pm 16$ ps.
repeatedly.

A mono-exponential decay function of the form \( F \text{EC} = A \cdot e^{-t/\tau} + B \) is fit to the data. The time constant resulting from this fit is \( \tau_{\text{mono}} = 71 \pm 16 \ \text{ps} \), which falls well within the 7–320 ps range of time constants reported in published literature [111, 79, 35, 36, 59]. Although this mono-exponential fit does give general agreement to the data, it is not possible to force the function to fit both the sharp rise feature for short delays, and the subsequent slow increase in the FEC signal observed as the delay time is increased beyond 250 ps. This is suggestive that another function could be a better fit, which is explored in Figure 4.21

Looking at the inset graph, we see that the FEC signal remains effectively constant for the first 10 ps. This would suggest that there are no dynamic processes that are active on these timescales. However, as discussed, the ability of the FEC technique to resolve such fast signals is compromised by the significant difference in the size of the two time constants. This is especially significant when attempting to explain the functional form of the fitted curves in terms of microscopic dynamic processes.

Despite these positive results, this plot additionally demonstrates some of the frailty inherent in the method. The data shown here was taken with the optical chopper placed along the ‘delay arm’ of the delay line setup to eliminate the background from the fixed arm. To envision the process, consider that when the pulses are overlapped in time (i.e. zero delay) the signal should be zero, as the nanotube is always saturated by the un-chopped pulse train from the fixed arm, so that there should be no component to the signal at the 70 Hz chopping frequency. As is evident from the plot (particularly the inset), near zero delay, the signal is just under 3 \( \mu \)V, which deviates from the expected value of zero by an amount greater than any of the standard
error of each data point, the apparent scatter in the data, or the already-subtracted background. While a conceivable explanation for the observed phenomenon is that the zero-delay position is not accurately aligned, it is highly unlikely that this calibration was off by the \( \approx 50 \text{ ps} \) or equivalently 7 mm that would be necessary create this factor-of-two discrepancy in the observed PL. The specific reason for this offset factor remains unknown.

Figure 4.21 shows an aggregated set of FEC curves resulting from experiments conducted on five different (9,8) nanotubes. In each case, a PPD curve was created, and the FEC data taken at the threshold saturation fluence\(^{26}\). Each curve is normalized to the PL signal obtained at the longest delay (1300 ps), which is also the maximum value for each data set due to the nature of the FEC signal. Both mono- and bi-exponential functions are fitted to the data. The fitted curves appear on the main plot, and the residuals are shown in the two sub-figures. Although the time constant of the mono-exponential decay (72±4 ps) is in agreement with published values, the residuals from the mono-exponential fit show clear trending for longer delays, indicating that the fit does not totally describe the data. By contrast, the residuals from the bi-exponential fit are distributed symmetrically and randomly about zero. This suggests that the intrinsic decay process in SWCNT could be bi-exponential, a claim which is also supported by some literature studies (See Section 2.5.8 and [79, 54]).

The specific form of the fitted bi-exponential function is:

\[
PL(t) = A_1 \cdot \tau_1 \cdot e^{-t/\tau_1} + A_2 \cdot \tau_2 \cdot e^{-t/\tau_2} + B
\]  

(4.13)

As expected, the fitted value of the ‘B’ parameter is 1.00 ± 0.01 as a result of the normalization. The time constants resulting from the fit are \( \tau_1 = 31 \pm 4 \text{ ps} \) and

\(^{26}\)This value is included as a label for each FEC curve on Figure 4.21, along with the measured length of the corresponding
Figure 4.21: Femtosecond Excitation Correlation (FEC) data collected from a number of (9,8) nanotubes, which are labeled by their measured length, and saturating fluence. Each curve is normalized to the value at the longest delay. Uncertainty in the y-axis is not explicitly presented, but can be estimated from the scatter in the data. Uncertainty in the x-axis is negligible. Two functions are fit to the data, a mono-exponential decay and a bi-exponential decay. The residuals from these fits are presented on the two labeled sub-figures that are presented on identical scales. Data collected by Tam Q. Nhan and Y.-F. (Elsa) Xiao [91, 122].
Figure 4.22: Schematic diagram of proposed mechanism for mono-exponential, bie excitonic decay. The ‘dark’ and ‘bright’ levels represent the two lowest-energy levels of the $E_{11}$ band.

$\tau_2 = 313 \pm 61$ ps. These fall within the range of values reported in the literature. The large uncertainty in the long time constant indicates the strong dependence of the fit parameter on the final level at which the FEC signal saturates. Given that only four periods equal to the long time constant have elapsed by the end of the delay range possible with the current apparatus, it is likely that the signal has not entirely settled to its maximum-possible value. A very interesting point is that neither of these time constants is nearly short enough to be the very rapid Auger process that would be required to explain the ‘hard’ saturation found in the PPD experiments 4.4. It is tempting to state that this result implies that there are no dynamics in the observed nanotubes that operate on scales faster than 31 ps. However, as stated above, this conclusion over-reaches the capabilities of the technique, as very fast processes are difficult to observe with FEC.

This result suggests that not only are there radiative and non-radiative mono-excitonic decay channels, but that there are two parallel non-radiative processes that result in the bi-exponential decay. The bi-exponential nature of the decay dynamics
suggests a possible mechanism for this process. This is because bi-exponential decay
dynamics often result when a system has two independent reservoirs of population
with different decay dynamics and the ability to exchange population (Scheme shown
pictorially in Figure 4.22). From what is known about exciton dynamics in SWCNT
(See Section 2.5.8), a natural guess at the identity of two such states would be the
lowest-lying dark and light exciton states in the in the $E_{11}$ band. The theoretical
underpinning of this model has been developed substantially by Y.Z. Ma et al. [79].
Further experimentation along with refinement of the technique chosen to observe
exciton dynamics would be necessary to explore this result further.

4.5.3 Pulse-Stretching Results

In an effort to more closely investigate the region of the FEC plot near zero-delay, a
variant on the FEC experiment was attempted using highly dispersive glass blocks to
‘stretch’ the excitation pulses. This technique, which had the additional advantage of
removing the uncertainty in the accuracy of the ‘zero-delay’ calibration of the delay
line, was performed as follows. First, a carbon nanotube is located, mapped, and
spectrally characterized as has been described elsewhere 4.5.2. Next, a PPD curve
is recorded as per usual (Section 4.4) to serve as a baseline. The duration of the
excitation pulse is measured using the autocorrelator (Section 3.5.3). Typical values
for the approximately transform-limited pulse from the Mira laser system range from
137–150 fs, depending on the available bandwidth.

A dispersive glass block is placed into the beamline to impart chirp to the pulse
and increase its duration. This element is inserted near Brewster’s angle to avoid
second reflections\textsuperscript{27}, and the appropriate mirrors tuned to re-align the beam to the irises (I4 & I5 on Figure 3.4). The ND filter is rotated so that the identical power is incident on the sample, and a second PPD curve is taken. This process is repeated with the addition of further blocks, leading to PPD curves taken with pulse lengths or $137 \pm 2$, $303 \pm 6$, $359 \pm 6$, and $414 \pm 7$ fs. Although, via the same logic as the FEC technique, it would be assumed that a system with fast decay components would emit more PL if excited by a longer pulse of lesser average intensity, this result was not observed. All curves taken using this technique were identical to within error, further indicating the experimental difficulty in using the FEC technique to observe very fast decay dynamics.

In short, although the FEC technique is relatively straightforward to explain in these simplified terms, many subtle effects can alter the observed signal. This problem has been attacked on several fronts. Co-worker Y.-F. (Elsa) Xiao has produced results from a simulation code [122] that employs the rate equations derived from the stochastic model for exciton dynamics suggested by Barzykin \textit{et al.} [5]. This model attempts to determine the intrinsic PL dynamics as a function of Auger and non-Auger decay rates, and then generates simulated FEC data for comparison with experiment. Although Elsa and co-worker Tam Q. Nhan [91] have enjoyed some successes, work is ongoing to be able to fully interpret observed saturation (PPD) and FEC data. From the experimental side, some attempts, like the one described in the previous paragraph, have been made to produce a ‘cleaner’ FEC signal. A fundamental problem remains that while the S/N ratio of the current FEC technique is adequate to indicate that ultrafast time-dynamics are occurring and draw general conclusions, the combination of noisy data and a multi-parameter bi-exponential fit

\textsuperscript{27}The artifact produced by such reflections was a confounding factor in early experimentation
leaves much to be desired when trying to accurately measure the time constants of PL decay.

4.6 Relative Humidity Studies

It was occasionally observed during experimentation that nanotubes under laser excitation could suddenly stop emitting PL, or have their maximum PL emission irreversibly decreased. This process, termed ‘aging’, occurred without discernable warning and could take anywhere from seconds to minutes to complete. Although aging was occasionally associated with a 5–20 nm redshift of the spectral peak, this was not consistently observed; some nanotubes remained spectrally stable while their net intensity diminished. Though establishing experimental causality relations was difficult, given that the nanotube in question often emitted PL for hours or days before suddenly aging, aging did seem to occur most often when the nanotube was subjected to high-intensity optical excitation.

Following published work by our collaborators at NRC [56], it was assumed that the dominant ‘aging’ mechanism involved nanotubes being ‘pushed’ or ‘pulled’ down to the surface. This effect had been confirmed by the NRC group using post-facto SEM imaging. Once in contact with the surface, the PL from the nanotube would be quenched via energy transfer to the substrate, or the creation of new non-radiative recombination pathways as a result of the perturbation of the nanotube’s electronic structure [70]. Of the several mechanisms proposed to explain this process, two were expected to dominate; dipole/dipole interactions with the surface (analogous to the effect of an image charge), or dipole interactions with the gradient of the optical-frequency electric field [56]. This interpretation was consistent with our anecdotal
finding that the samples upon which the nanotubes were suspended between a ridge and the trench floor aged more readily than nanotubes that were suspended between two ridges. The argument would be that a fully-suspended nanotube has to be ‘pushed’ harder before coming in contact with the surface.

However, this explanation was not entirely satisfying, as nanotubes were occasionally observed to ‘age’ at excitation intensities much lower than were used by the NRC group. As a result, other hypotheses were investigated, including the possibility that built-up static charge played a role, possibly resulting from the photo-excitation of electrons from the Si/SiO$_2$ substrate. The result of this experimentation performed to investigate this effect was null; grounding the sample had no apparent effect on the PL emitted from the nanotube, or the frequency of aging$^{28}$.

A clue was provided when it was noted that the frequency of ‘aging’ incidents seemed to increase with the change of seasons from summer to fall. This suggested that the seasonal variations in the ambient conditions in the lab, most notably the relative humidity (RH), might play a role in the aging process. At first, the working hypothesis was that the reduced moisture content in the ambient air would allow charge to build up on the nanotube, possibly attracting macroscopic dust particles that would cause physical damage to the nanotube.

To explore this hypothesis, apparatus was constructed to permit the investigation of the relationship between PL emission and relative humidity, as described in Section 3.5.7. PL-emitting nanotubes were located, mapped, and spectrally characterized as described in Sections 4.2.2, 4.2.3, and 4.3, respectively. The RH-control

$^{28}$It is noted that this experiment was not fully rigorous, in that grounding one part of the macroscopic poorly-conductive substrate might not necessarily avoid local accumulation of charge near the laser spot. However, it would be impractical to achieve this kind of local control of the charge distribution using the current setup, so this avenue of research was abandoned.
apparatus was used to purge the sample enclosure with nitrogen gas and bring the ambient RH up to $\approx 45\%$. This process usually took several minutes, during which enough humidified nitrogen was added to the enclosure to displace the lab ambient air several times.

With the nanotubes prepared in this manner, the automated spectral-scan program (See Section 3.6) was modified to record the emission spectrum of the nanotube every 10 seconds, and the nanotubes were exposed to high-intensity ($> 750 \text{ W/cm}^2$) CW illumination. The relative humidity inside the enclosure was gradually reduced to below 10% over a period of about 15 minutes. From this point onward, the experimental protocol varied considerably from tube to tube. This was because some nanotubes did not exhibit aging behaviour, even when exposed to high CW excitation intensities over extended periods of time at various values of relative humidity.

However, in two cases, (‘Fred’ & ‘Wilma’), ‘preliminary aging’ was observed which allowed further experimentation to proceed. In the first case, the PL emission spectra remained unchanged during three trials that were performed as described in the previous paragraph, but then sudden and uniformly (i.e. with no spectral shift) decreased to half of its initial value during 45 minutes of constant excitation at 675W/cm$^2$ and a relative humidity of about 32%. In the second case, ‘Wilma’ remained unchanged during 11 such ‘aging’ scans as well as a variety of other experiments (High-Resolution 2D scans, spectral scans, etc.) at a number of points in the excitation intensity-relative humidity parameter space over three days without any detectable change in the emission spectrum, before undergoing a similar irreversible reduction in the emitted PL intensity while under 1050W/cm$^2$ of excitation intensity and at 40% relative humidity.
Figure 4.23: This graph shows the red-shift that occurs as the ambient humidity is increased from 17% to 36% to 41%. The three spectra have been taken from the same tube under identical excitation and PL collection conditions. Uncertainty in the y axis is comparable to the size of the data markers. The connecting lines are added to the graph to guide the eye.
Though this was an interesting result, the most interesting effects occurred when further experimentation was performed on these two nanotubes after they had undergone ‘preliminary aging’. As shown on Figure 4.23, an increase in the ambient relative humidity beyond a 35–40% threshold caused the emission peak to redshift by 15 meV in less than a minute. It is notable that the redshift did not involve the continuous displacement of the emission peak, but, as suggested by the middle trace on the graph, the disappearance of the original peak and the simultaneous appearance of the redshifted peak in its place.

More interesting still was that this humidity-induced redshift could be reversed. As shown on Figure 4.24, the reduction in the ambient RH below a 30–35% threshold resulted in a recovery of the original peak position. Although the peak PL intensity occasionally returned to the value observed before exposure to moisture, the intensity more commonly declined, with the peak intensity only recovering to $\approx 70\%$ of the its previous value. This type of cycle is shown in Figure 4.24. The process of raising the humidity to cause a redshift, and reducing it to cause the peak to return to its initial location could be successfully repeated a few times. However, the commonly-observed $\approx 70\%$ loss in peak height as a result of the shift was partially cumulative, and neither nanotube continued to emit observable PL by the fourth cycle.

An explanation for the physical basis of this effect is suggested in a recent publication by Walsh et al. [109] which reported an experiment conducted using (13,2) and (12,4) SWCNT suspended across trenches. By employing resonant Raman spectroscopy, which can identify the energies of the major excitonic and phononic states even in nanotubes that are ‘quenched’ and unable to emit PL, Walsh et al. reported observing redshifts of $\approx 10$ meV when the nanotubes are exposed to nitrogen gas.
Figure 4.24: This graph shows the blue-shift that occurs as the ambient humidity is decreased from 41% to 15%. The three spectra in grey are identical to those presented in Figure 4.23, and are included for reference. Note that the spectral peak returns closely to its previous location, but is exhibits diminished intensity. All spectra were taken from the same tube under identical excitation and PL collection conditions. Uncertainty in the y axis is comparable to the size of the data markers. The connecting lines are added to the graph to guide the eye.
with 82% relative humidity, and $\approx 30$ meV when the nanotubes are exposed to liquid water. These relatively subtle shifts of the peak location are attributed to much larger ($\approx 300$ meV) changes to the exciton binding energy and to the size of the band gap (via band-gap renormalization) that result from the increased dielectric screening. The two effects are thought to largely offset each other, leading to the smaller observable redshift.

Given the similarities between this work and the results reported in this thesis, it is suggested that the humidity-induced redshift observed experimentally results from the adsorption of water molecules onto the surface of the nanotube, which change the ambient dielectric coefficient. To the author’s knowledge, no studies reporting this type of controllable change in the photoluminescent spectrum have been published.

It would certainly be very interesting to perform the rest of the suite of experiments described in this chapter on nanotubes before, during, and after this redshift. It is thought that PPD or FEC techniques might provide insight into the changes to the nanotube’s excitonic structure that occur during this process; something particular to be investigated would be the changes in the PL decay dynamics. However, with the current apparatus, the signal produced by a humidity-redshifted nanotube under pulsed excitation would be well below the detection threshold, making such experiments currently impossible. It is hoped that improved equipment, samples, and experimental techniques might allow the resumption of this line of investigation in the future.

Nevertheless, this experimentation did have practical impact on the techniques used to perform all of the other experiments described in this thesis. Notably, it became standard practice to purge the sample enclosure with clean nitrogen with a
moderate relative humidity (15-20%) for several minutes before exposing the nanotube to the laser and taking data. These conditions are maintained during experimentation. Anecdotally, this has substantially reduced the incidence of aging, which is attributed both to the avoidance of adsorbed water, and the generally cleaner ambient environment created by the system. Such an environmental control system is highly recommended for any future work.
Chapter 5

Conclusion

The work reported in this thesis was diverse in execution, but unified in purpose; to use optical techniques to improve our understanding of the basic physics of carbon nanotubes. Several successes, conclusions, challenges and insights gleaned from the work bear repeating here.

Firstly, an apparatus was constructed, and its capability to observe photoluminescence from an individual, air-suspended single-walled carbon nanotube was established beyond all reasonable doubt. The combined weight of evidence from the observed excitation and emission spectra, high-resolution 2D spatial profiles, polarization dependance, and saturation and dynamic processes overwhelmingly confirms that observations were made of the properties of individual nanotubes.

Additionally, the choice of the type of nanotube sample proved fruitful. An enduring strength of this experimental programme was the fact that a given nanotube
routinely survived days of repeated experimentation, allowing a more complete picture of its particular properties to be built up through the use of a range of experimental techniques. Although the experimentally-observed photoluminescence quantum efficiencies, $4 \pm 2\%$ and $13 \pm 6\%$, are numerically similar to the $7\%$ previously observed from similar samples [70], the implications are different. This is because the more recent absorption co-efficient used to calculate the values reported here ($A_C = 1.6 \times 10^{-3}$ nm$^2$ [107]) is ten times greater than the value used by Lefebvre et al., which implies that the nanotubes observed here are ‘brighter’, in that they emit more photons for a given incident photon flux, than those reported previously. This result also supports the validity of the newer, higher absorption co-efficient, as quantum efficiencies calculated with the earlier value would be non-physical.

Given the noted wide range of reported values for this absorption constant in the literature, the fact that a value of $A_C = 1.2 \pm 0.3 \times 10^{-3}$ nm$^2$ is derived from the simple theoretical model developed to explain the ‘hard’ saturation behaviour is seen as a very strong, novel result. Although this model is not expected to completely describe the dynamic processes, its accurate, one-parameter fit to the observed saturation dynamics argues strongly for its continued relevance. It is expected that, at a minimum, this functional form will be a limiting case of the ‘true’ PL dynamics of single-walled carbon nanotubes in the case of rapid Auger recombination.

The observation of strong saturation effects at very low excitation intensities is also a novel result of this work. Firstly, although saturation effects have been observed in carbon nanotubes by other researchers, the ‘hard’ saturation reported here, where the emitted PL does not increase at all while the excitation intensity is increased beyond the threshold value by orders of magnitude, has not been widely reported$^1$. In addition

$^1$The one report known to the author is a single suggestive point on a plot in the recent paper
to the fact that the results reported here were obtained using a single nanotube, as opposed to an ensemble sample, the observation of this result is speculatively attributed to the effects of isolation technique, specifically micelle-encapsulation, on exciton dynamics.

A related result of considerable interest is that the onset of this ‘hard’ saturation occurs at much lower excitation intensities ($0.5 \times 10^{12}$ photons/pulse/cm$^2$) than has been reported previously. For example, the threshold for saturation reported here is nearly 200 times smaller than the saturation value suggested by Högele et al. [41], and about 100 times lower than the value reported for the onset of non-linear behaviour by Huang et al. [47]. It is notable that both of these experiments involved short, micelle-encapsulated nanotubes. Using conservative estimates, the nanotubes used in this thesis were found to be entirely within the saturation regime when there were only 5.5 excitons created in the nanotube on average per pulse. This argues strongly against the proposed phase-space filling model for saturation behaviour, and suggests that excitons in air-suspended nanotubes must undergo Auger recombination over large distances\(^2\). The performance of comparative experimentation between micelle-encapsulated and air-suspended nanotube as well as nanotubes of varying lengths to address this question seen as the most promising direction for this work in the immediate future.

Another observed discrepancy between this work and the literature is the marked Gaussian (as opposed to Lorentzian) nature of the emission spectrum. The accurate measurement of this characteristic of light-emitting nanotubes does not seem to have been an emphasis of previous literature work, and the more careful identification by Högele et al. [41].

\(^2\)Whether this results from rapid center-of-mass movement, or interactions between diffuse spatial wavefunctions is beyond the scope of this work.
of the role of homogenous and inhomogeneous broadening processes in nanotubes of differing lengths and prepared with different environmental isolation techniques might shed light on the saturation controversy mentioned above.

The rest of the spectral work performed in this thesis agree well with the literature. The locations of the excitation and emission peaks of the (9,8) nanotubes under study agreed with literature values, and the general invariance of the emission and excitation spectra\(^3\) to different excitation intensities is consistent with results taken at similar temperatures and intensities.

The femtosecond excitation correlation technique is implemented to study ultra-fast photoluminescence dynamics, and produces interesting, if mixed, results. The observation is made that despite having a purported time resolution limited only by the pulse length [40], the FEC technique suffers from poor sensitivity to short-lived components of the decay. Consequently, the absence of a signature of the expected ‘fast’ (\(\approx 1\) ps) intensity-dependant Auger decay process is explained as a shortcoming of the measurement technique. However, FEC results do suggest that the remaining one-body decay channels exhibit a bi-exponential dependence, suggesting the explicit contribution of two independent internal states (possibly the dark and light exciton states) to the decay dynamics. This fact may be interesting for experimentation in the distant future the population in these two states can be coherently manipulated.

Finally, it was discovered that the peak of the emission lineshape could be reversibly red-shifted by exposure to a high-humidity environment. Although one literature report using Raman spectroscopy has observed a similar process, to the knowledge of the author the observation of this phenomenon using photoluminescence has

\(^3\)Excepting the noted logarithmic dependance of the excitation linewidth on intensity, which is attributable to saturation effects.
not yet been reported. This discovery led to improved techniques for controlling the ambient environment of the nanotube that reduced the impact of nanotube ‘aging’.

Despite these successes, limitations of the as-built apparatus also factored into the work. Although most experiments performed with continuous-wave excitation produced data with a robust signal-to-noise ratio, many studies performed with pulsed excitation would benefit from improved signal-to-noise. Among these, the accurate measurement of the photoluminescence quantum efficiency, the use of Femtosecond Excitation Correlation to produce more accurate estimates of the time constants that characterize photoluminescence decay, and the ability to investigate the dynamics of nanotubes that have experienced a humidity-dependant redshift stand out.

The most straightforward way to remedy these concerns would be to improve upon the aggregate $1.3 \pm 0.7\%$ optical collection efficiency of the current apparatus. Two major factors should be addressed. Firstly, the use of an aspheric lens with a higher numerical aperture could substantially improve the collection of PL emitted from the nanotube; even improving the NA to 0.65 would triple the observed PL signal. The second major source of optical loss is the spectrometer. Although the taking of spectra is a necessary feature, the net 41% transmittance is a major issue when detecting faint signals. As a result, a ‘bypass’ beam path, where spectral filtering can be done using high-transmissivity bandpass filters would be a very useful option when the complete spectral profile is not required.

Aside from the recommendations for the immediate future made in previous paragraphs, and the ongoing work by co-workers, the author believes that there could be significant value in ‘2nd generation’ studies. Three particular types of experiments are seen as particularly promising. First are those performed at low temperatures,
where the suppression of linewidth broadening by phonons makes interesting lifetime effects more clearly visible [83]. This would require the acquisition and installation of a cryostat, and the determination of appropriate experimental techniques to allow air-suspended nanotubes to be cooled without being quenched, but it is noted that these challenges have been overcome by others (e.g. [72, 83]). A second avenue of experimentation would be to build up the capacity to measure photoluminescence dynamics more directly, using a combination of fast detection technology and non-linear gating processes. Such an implementation would be challenging from a perspective of collecting adequate signal, but it is believed that significant improvements in this regard can be made given the experience with the current setup. Lastly, the accurate measurement of the absorption cross-section of a single tube using absorption spectroscopy techniques is a challenge that hovers on the borders of what is thought to be experimentally feasible. Although the work reported here does advance the state of knowledge regarding this important parameter, a robust and direct measurement would allow for the ‘untangling’ of some current coupled problems, most notably the intrinsic quantum efficiency.

When all is said and done, single-walled carbon nanotubes remain a fascinating experimental system, and should continue to pique the interest of the scientific community for a few years to come.
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Glossary

AFM  Atomic Force Microscopy is a scanning probe microscopy technique in which an atomically-sharp tip, set on the end of a cantilevered beam, is dragged over the surface in question. The beam is mechanically deflected by the contours of the surface. This deflection is measured, usually by optical means, giving an indication of the physical profile. A three-dimensional image can be built up via raster scanning. Page 24.

BRF  A BiRefringent Filter or birefringent tuner is a device used to produce tunable narrow-band radiation from a laser with a broad intrinsic gain curve. The simplest case is a single birefringent plate where linearly-polarized laser light is incident at or near Brewster’s angle (to minimize reflection losses). The crystal is orientated so that the optic axis is at approximately 45° to the incident polarization vector, so that laser light travelling through the crystal will experience a frequency-dependant polarization rotation. As the reflection loss from the second surface is polarization dependant, frequency-dependant loss has been introduced into the system. A stack of a few such crystals of varying thicknesses results in a frequency-space filter function that has sharp, well-separated peaks. The precise location
of these peaks in frequency space can be tuned by tilting the plate [94].

Page 50.

**CNT**  
A *Carbon NanoTube* is a naturally-forming cylindrical carbon nanostructure structurally similar to a graphene sheet ‘rolled up’ along a chiral vector. The ‘C’ is added to distinguish carbon nanotubes, which were the first discovered and currently predominant nanotube, from other more recent exemplars, such as boron, copper and bismuth nanotubes. *Page 5.*

**CVD**  
*Chemical Vapour Deposition* is a process used to fabricate solid structures from a gaseous precursor. The multitude of existent sub-techniques have in common the exposure of a substrate to a feed gas which is made to chemically decompose, depositing the desired material on the surface. Careful control of the reaction parameters can influence the structures ‘grown’ on the substrate. *Page 14.*

**CW**  
*Continuous-Wave* laser radiation is a theoretical electromagnetic waveform that has is purely monochromatic, i.e. has a frequency spectrum that can be described as a delta function. This condition directly implies that the wave is unvarying in amplitude and is of infinite duration. Practically, a ‘CW’ laser is one that produces narrow-linewidth laser light that has a relatively constant intensity over an appreciable period of time. *Page 49.*

**dichroic**  
The term *dichroic* has two different meanings, both relating to light. In the science of optics, a dichroic (or dichromatic) material is one that reflects one wavelength range of light while transmitting another, essentially
a specific implementation of an optical band-pass filter. Experimentally, this is usually achieved by exploiting multilayer interference effects. Optical dichroism is not to be confused with normal dispersion. The second definition, commonly used in geology and biology, refers to a material has optical properties which are polarization dependent. Thus a geologist would refer to a mineral as dichroic if it displayed two different colours under two different polarizations of light (pleochromism), or a biologist might speak of circular dichroism spectroscopy, where the relative absorption of right and left-circularly polarization by chiral molecules is investigated. Page 49.

**DOS** The *Density Of States* of a system describes the number of available states, usually with respect to energy. A DOS of zero implies that no state can exist at the specified energy. Page 11.

**FEC** *Femtosecond Excitation Correlation spectroscopy* is a technique that can be used to obtain information about PL dynamics in a system where the PL shows strong saturation behaviour. See Section 4.5. Page 54.

**graphene** *Graphene* is a two-dimensional sheet of $sp^2$-bonded carbon atoms. Naturally-occurring graphite is essentially a very large stack of graphene layers, and carbon nanotubes can be thought of as graphene sheets rolled into tubes. Graphene has unusual mechanical and electronic properties, as discussed in Section 2.3. Page 7.

**HRTEM** *High-Resolution Transmission Electron Microscopy* refers to the result of a suite of refinements to the standard TEM technique which collectively
improve resolution. Although specific methods differ, increased resolution is usually achieved by using phase-contrast imaging, where the usual absorption contrast is augmented by deconvolving the observed diffraction pattern using the known characteristics of the microscope to produce an image. Page 6.

**JDOS**  
The *Joint Density Of States* is a representation of the density of states available which explicitly shows the density of electron and hole states that are separated by a specific energy. As the probability of absorbing or emitting a photon of a given energy depends on both the electron and hole DOS, this is a convenient way of identifying resonances in a material’s absorption or emission spectrum.

**ML**  
A *Mode-Locked* or equivalently a phase-locked laser has the defining characteristic that there is a fixed phase relationship between the various longitudinal modes of the cavity. The term ‘modelocking’ refers to this phenomenon in general. The end result is that the many modes interfere to produce a temporal ‘pulse’, which can be very short (< 10 fs) if there are enough phase-locked modes. Mode-locked lasers are commonly referred to at ‘ultra-fast’ lasers which produce ‘ultra-short’ pulses of light. Page 49.

**MWCNT**  
A *Multi-Walled Carbon NanoTube* is a carbon nanotube having multiple cylindrical shell. These tubes are readily produced in all general synthesis techniques, and can have anywhere from two to over a hundred concentric graphene cylinders. The literature occasionally refers to ‘Double-Walled CNT’ as a separate category. Page 6.
NA The *Numerical Aperature* of a lens characterizes its ability to collect light. The numerical aperture is defined as $NA = n \sin(\theta)$, where $n$ is the refractive index of the medium outside the lens (e.g. 1 for a lens in air), and theta half of the interior angle of the cone of light rays that can be accepted by the lens after having passed through the focal point. Lenses with a high NA collect more of the light emitted isotropically from an object in the focal volume. *Page 67.*

ND A *Neutral Density* filter is an optical element that provides a frequency-independent (‘grey’) attenuation of the beam. ND filters are often identified by their ‘optical density’ (OD), which is defined as the negative of the base-ten logarithm of the ratio of the transmitted power to the incident power. *Page 57.*

NEP *Noise-Equivalent Power* is used as a measure of the sensitivity of an optical detector. Generally, it is defined as the intensity of optical signal required to produce a signal-to-noise ratio of one. Accordingly, a more sensitive detector has a lower NEP. The NEP of a detector is occasionally quoted in units of $W/\sqrt{\text{Hz}}$ to show the dependance of the detector noise on the bandwidth of the detected signal. *Page 63.*

NRC The *National Research Council (Canada)* is the Government of Canada’s national organization for scientific research and development. Of particular relevance to this work is the NRC’s Institute for Microstructural Sciences, at which the samples used in this work were grown. *Page 41.*
An Optical Parametric Oscillator is a device used to enhance the efficiency of the non-linear process of difference-frequency mixing, also known as parametric amplification, whereby an incident high-energy photon is converted into two different photons, whose energies sum to the original value. An OPO consists of an appropriate non-linear crystal set within a resonant cavity, which enhances the conversion efficiency. Practically, this device dramatically extends the wavelength range available from an ultrafast Ti:Sapphire laser into the infra-red without sacrificing repetition rate, as in common in systems that rely on amplification before the down-conversion step. Page 53.

**PhotoLuminescence** is a general term to describe processes where a material absorbs a photon (photo-excitation), and later emits a photon (luminescence). The phenomenon of photoluminescence is often sub-divided into three categories: resonant radiation, fluorescence, and phosphorescence. In resonant radiation, the material does not relax between excitation and emission, meaning that the outgoing photon is iso-energetic with the absorbed light. In fluorescence, the material absorbs a photon and enters an excited state. It rapidly undergoes internal relaxation processes bringing it to a meta-stable state, and then re-emits a photon with lesser energy, corresponding to the meta-stable state. Phosphorescence is similar to fluorescence, except that the re-emission is delayed due to the existence of an intermediate trapping state, which is usually spin-dependant. Page 18.

**PhotoLuminescence Excitation** spectroscopy is a technique where the intensity of the PL emitted from a nanotube is measured with respect to
the excitation and emission wavelength. This data set can be used to generate a PLE map, upon which nanotubes of a particular chirality appear as peaks. This technique allows for the determination of the chirality of an unknown tube via comparison with literature values. *Page 19.*

**PPD**

This acronym was created as a short-hand to refer to *Pulsed Power Dependence* studies, i.e. investigations of the intensity-dependence of the PL emission from a single SWCNT using ultrashort pulsed excitation. See Section 4.4. *Page 114.*

**QE**

The *Quantum Efficiency* of a photoluminescent process is defined as the percentage of absorbed photons which are re-emitted as PL. Used in this way, quantum efficiency is equivalent to ‘Fluorescence Quantum Yield’, a term more commonly used in chemistry journals. *Page 24.*

**RBM**

The *Radial Breathing Mode* is a relatively low-frequency phonon mode unique to SWCNT in which all of the carbon atoms symmetrically expand and contract radially about the axis. This mode has considerably experimental utility, as it is proportional to the inverse of the tube diameter, and can thus aid in the identification of the tube species. *Page 14.*

**RH**

*Relative Humidity* is defined as the ratio of the partial pressure of water vapour in a gaseous mixture at a certain temperature to the vapour pressure of water at the same temperature. The higher the RH value, the more moisture is in the air; high RH values are associated with condensation. *Page 63.*

**S/N**

The *Signal-to-Noise ratio* is defined as the ratio between the magnitude
of the desired signal and the average noise floor resulting from a measurement. Experiments with a high S/N are preferred as the relatively low noise will not obscure the looked-for effect. Experiments with low intrinsic S/N, and where the noise is predominantly random, can be improved by the taking of repeated measurements, and the use of appropriate statistics. Page 65.

**SWCNT** A *Single-Walled Carbon NanoTube* is a carbon nanotube having only a single cylindrical shell. These nanotubes have the simplest possible band structure, and are very sensitive to the environment as a consequence to having exclusively ‘surface’ atoms. Page 6.

**TEM** *Transmission Electron Microscopy* is a technique where an image is produced by analyzing the transmitted fraction of a beam of accelerated electrons onto a thin-film sample. The resolution of this type of microscopy can be significantly better than light microscopy, owing to the reduced diffraction limit granted by the comparatively short wavelength of the electrons. Page 5.

**vHs** *A van Hove singularity* is a region in the DOS of a system where the derivative, \( \frac{d\text{DOS}}{dE} \), is divergent. In a true 1D system, this also implies that the DOS itself becomes very large. Page 13.