Doctoral Thesis

The development of near-field optical antennas for the study of carbyne

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THE DEVELOPMENT OF NEAR-FIELD OPTICAL ANTENNAS FOR THE STUDY OF CARBYNE

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

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Abstract

As humans, optical imaging and spectroscopy serve to enhance our innate vision. These enhancements include spatial and spectral resolution, optical sensitivity, and optical response time. Traditional optics composed of lenses and mirrors are limited in spatial resolution due to the diffraction of light through apertures. Optical imaging techniques based on the application of an optical antenna, termed near-field optical microscopy, have demonstrated true optical imaging with a spatial resolution generally on the order of 10 nm. These methods, developed first in the 1980s, have been plagued by technical challenges that have greatly limited adopters to optical physicists. Correspondingly, the scientific output of near-field methods has also been limited.

In this thesis, a simple optical antenna based on a single gold nanoparticle is used to map the distribution of a membrane protein, complement receptor 1, in human erythrocytes. While much is learned regarding the cellular organization of the protein, challenges in antenna fabrication demonstrate that the antenna cannot be widely used by researchers and its limited resolution (∼60 nm) makes the antenna insufficient for some applications.

Further antennas are designed, fabricated, and characterized with both the fluorescence of individual dye molecules and the Raman scattering of carbon nanotubes. The first new antenna, termed the cascaded particle antenna, demonstrated an optical spatial resolution of <20 nm and confirmed existing optical antenna theory. Then a highly-reproducible mass-fabricated optical antenna, the
pyramid antenna, was developed. The pyramid antenna provided an optical imaging resolution of $< 20 \text{nm}$ with fluorescence enhancement rates of up to 200 and localized field enhancements of $\sim 10$. The pyramid antenna has solved many of the technical challenges associated with near-field microscopy and will help facilitate usable commercial turn-key near-field optical microscopes.

The applicability of the pyramid antenna, and in fact near-field methods in general, is demonstrated by the optical study of a novel sp hybridized carbon system, carbyne chains encased in double-walled carbon nanotubes. The carbyne chains, which have lengths of up to $\sim 1 \mu \text{m}$, have a strong resonant Raman mode with a frequency that softens with increasing chain length. Near-field microscopy has been applied to measure the length of individual chains and confirm the relationship between the Raman frequency and the chain length. No other method can non-destructively measure such long structures with such high spatial resolution. These measurements have been integral to develop new theory that may help explain experimental outliers, as well as validate that far-field measurements are, in fact, measuring individual, continuous, carbon chains. Finally, an experimental geometry is developed to facilitate the measurement of the optical coherence properties of materials on single wavelength length scales.
Zusammenfassung


In dieser Dissertation verwenden wir zunächst eine einfache optische Antenne, bestehend aus einem einzelnen Goldnanopartikel, um die räumliche Verteilung eines Membranproteins in menschlichen Erythrozyten abzubilden. Während die Anwendung der optischen Antenne wertvolle Einsichten in die zelluläre Organisation des Proteins ermöglicht, limitieren Herausforderungen in ihrer Herstellung ihre weitere Verbreitung in der Forschergemeinde. Zudem ist die begrenzte räumliche Auflösung der Antenne (∼60 nm) nicht ausreichend für zahlreiche Abbildungsanwendungen.

einer einzelnen Wellenlänge zu messen.
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Foreword

I have performed all of the work presented in this dissertation, with the following exceptions.

- The ‘zusammenfassung’ was translated by Martin Frimmer.
- The SEM image of the dimer antenna in figure 5.1 was made by Palash Bharadwaj.
- The calculations shown in 5.3 were performed by Lukas Novotny.
- The TEM image shown in figure 5.4 was made by Brian McIntyre.
- The fabrication of the Au pyramid shells were prepared by Timothy W. Johnson and Lisa Poulidakos.
- The calculations shown in 5.8 were performed by Sergio Rodrigo.
- The fabrication of the LLCCs@DWCNTs was done by Lei Shi and Philip Rohringer.
- The calculations for the LLCC-mode were performed by Angel Rubio’s group.
- The theoretical background for determining the degree of coherence from the two-pinhole experiments was done by Shawn Divitt.
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1 Introduction

Optical imaging and spectroscopy are perhaps the most fundamental means through which humans observe the world. We have eyes that, at least while we are young, have a resolution defined by the limitations of physics, and we can see a broad spectrum of colors. This innate ability inspired the development first of lenses and mirrors, followed by simple objectives, and even complex, spatially extended, telescopes. The goal of all of these devices has been very simple: as humans we wish to directly see and observe our world.

The resolution limit for a traditional optical system is caused by diffraction, making the smallest resolvable spot approximately half a wavelength of the light being used for imaging \([? \ ? \ ?]\). This resolution can be understood as the minimum separation between two physical objects such that they can each be resolved without \textit{a priori} knowledge or other statistical methods. This resolution corresponds to approximately 250 nm and therefore does not limit our vision in any appreciable manner, however, diffraction is not limited to visible light but to all electromagnetic radiation and, in fact, all waves.

It turns out that physical apertures are at the root of diffraction and that it is not a limitation of radiation itself. Electromagnetic radiation is readily confined to arbitrarily small volumes by using antennas (ex. cellular telephones, AM/FM
radios, etc.). Similarly, although less commonly, antennas can be used to control optical radiation on the sub-wavelength scale, by acting as a transducer that converts energy between far-field propagating radiation and near-field evanescent fields [? ] . The challenges associated with optical antennas are related to the short wavelength of light (400 – 700 nm), requiring antenna fabrication with a resolution on the order of 10 nm [? ]. Additionally, metals are poor conductors at optical frequencies, resulting in scaling and design considerations that differ from traditional antenna theory [? ].

Fundamentally, near-field scanning optical microscopy (NSOM) techniques utilize optical antennas to control and localize optical radiation on sub-wavelength scales and, simultaneously, enhance the interaction between light and matter. This effective circumvention of the diffraction limit typically achieves a true optical resolution of 10 – 20 nm [? ? ? ], although even sub-nanometer, sub-molecular resolution has been demonstrated [? ? ]. There are other far-field optical imaging methods that achieve similar diffraction-unlimited resolution, but they generally require a priori knowledge of the sample and create an image from statistics [? ? ? ? ], or require high laser intensities that can damage samples [? ]. Additionally, methods that are based solely on far-field optics do not provide any enhancement of the light-matter interaction and therefore have limited applications.

In this dissertation, I develop antennas for near-field microscopy by first experimentally confirming a theoretical understanding of optical antennas and then developing a highly-reproducible mass-fabricated optical antenna. I demonstrate, using the novel one-dimensional carbon allotrope carbyne, that the high spatial resolution and spectral sensitivity of near-field microscopy is necessary to fully understand the optoelectronic properties of single molecule systems. While much information can be gained from far-field optical microscopy and spectroscopy, near-field methods are still required to ensure that only single molecules are present and therefore validate the far-field findings.
1.1 Nanocarbons

Recent years have brought the so-called “carbon revolution”. While silicon has been the staple material used to develop electronics and optoelectronics, the demand for higher-performance devices has accelerated beyond the capabilities of traditional semiconductor electronics [? ? ]. Nanocarbon materials, such as carbon nanotubes and graphene, are being considered as a platform for the next-generation of integrated optoelectronics. These materials are fundamentally nanoscopic and, analogous to semiconductor devices, can have their electronic properties carefully engineered with dopants, structural modifications, and material interfaces.

Graphene, the two-dimensional realization of sp² hybridized carbon, is a promising material not only because of its physical dimensions, but its optoelectronic properties. It is a zero bandgap semiconductor with a linear dispersion [? ] that allows charge carriers to travel ballistically and, correspondingly, room-temperature electron mobilities of 200,000 cm²/(V·s) have been demonstrated [? ? ]. Amazingly, these properties are highly dependent on the conformation of graphene. Graphene can be rolled into carbon nanotubes that can be insulating, semiconducting, or metallic, or folded into fullerenes [? ]. Even the edge states in graphene can modify the material’s electric properties, as has been demonstrated in graphene ribbons [? ].

Thus far, near-field Raman microscopy, also known as tip-enhanced Raman microscopy (TERS), has been used to characterize nanocarbons [? ? ]. The optoelectronic properties of strain and point defects have been studied in carbon nanotubes [? ? ] and graphene [? ? ], along with the influence of the local environment [? ? ? ? ]. The use of the optical antenna in TERS has applications beyond direct imaging and has been used to study the phonon correlation lengths in graphene [? ].
Carbon can exist in many different allotropes, or chemical bond configurations, that give the material drastically different properties. Diamond, which exhibits sp$^3$ hybridized carbon, has a large band gap, and therefore insulating electrical properties. The sp$^2$ hybridized graphene has zero bandgap, exists in two-dimensions, and can readily be rolled into carbon nanotubes that exhibit yet different electrical properties. Less known and even less studied is sp hybridized carbon, termed carbyne, that will be explored in this dissertation.

1.2 Thesis overview

Chapter 2

The physics of optical antennas for applications in near-field imaging and spectroscopy are covered. The effects of antenna size and shape are explored with respect to the localized field enhancement and the potential to quench the optical emission of the sample, both in a near-field scanning optical microscope geometry. Chapter 5 utilizes this understanding to develop two types of improved optical antenna geometries.

Chapter 3

The physical and optical (far-field ensemble) properties of carbyne are discussed. This material system, which is comprised of both a linear carbon chain and a double-walled carbon nanotube, is currently incompletely understood. Even theoretically, the precise atomic structure of the system is not clearly defined due to the large number of possible host nanotubes. The current understanding of the fabrication process and the observed Raman modes are discussed. This understanding is essential to the work presented in chapter 6.
Chapter 4

In this chapter, the “particle antenna”, an early optical antenna, is utilized for biological imaging. Small clusters of a membrane protein are localized and quantified in human erythrocytes, but it is observed that the resolution and optical enhancement afforded by the particle antenna is generally insufficient for biological applications. This motivates the need for antennas with a higher enhancement-confinement ratio, developed in chapter 5.

Chapter 5

This chapter covers the development of the next generation of optical antennas for applications in imaging and spectroscopy. I start by explaining the development of the cascaded particle antenna. While this geometry is quite difficult to work with, it allowed for the fundamental physics of the antenna to be confirmed. This work was followed by the pyramid antenna, allowing for reproducible, high-resolution, near-field imaging and spectroscopy. The pyramid antenna is then used to study carbyne in chapter 6.

Chapter 6

The optical properties of carbyne are experimentally explored on a single molecule level. This work includes both far-field and near-field optical measurements. It is found that not all results agree with the current theory. The results, along with a possible theoretical understanding of the system, is discussed. This is the first work to study individualized linear carbon chains and is essential to understanding their physical properties both from a theoretical point of view as well as potentially using the linear carbon chains for optoelectronic applications.
Chapter 7

One possible intriguing property of the linear carbon chains is spatially coherent Raman scattering at room temperature. To this end, a novel two-pinhole interference experiment is designed and implemented to understand field correlations on the order of a single diffraction-limited spot. Coherence for the linear-chain is not yet observed but reference measurements of Rayleigh scattering and photoluminescence from gallium arsenide nanowires are made and simulations (appendix A) are performed.
2 Near-field microscopy and optical antennas

Near-field scanning optical microscopy (NSOM) techniques have allowed scientists to circumvent the diffraction limit, and achieve a true optical resolution of only a few nanometers, and even sub-nanometer, sub-molecular resolution. The concept was originally proposed by Edward Hutchinson Synge in 1928, both in a publication and letters to Albert Einstein. His ideas included the use of a small aperture held just a few nanometers from a sample surface to illuminate an area defined by the diameter of the aperture, today known as aperture-type NSOM or a-NSOM. Synge’s other idea, which was not as well received by Einstein, used a small scatterer to act as a nanometric scattering light source, termed scattering-type NSOM or s-NSOM. Synge’s ideas were far ahead of the technology available at the time and it would take several reinventions of his ideas and over 50 years for NSOM to be experimentally realized. A very nice history recounting the first decade of publications based on NSOM techniques has been written by Dieter Pohl.

The applications of NSOM are numerous: combining the spectroscopic information afforded by optical techniques with high spatial resolution and strong local electric fields has made NSOM valuable in many applications spanning both physics and biology. Considering the topographic image provided by NSOM (dis-
cussed below), no other single imaging technique can provide all of the information produced simultaneously by NSOM. Unfortunately, nearly all of the available NSOM methods have been plagued by technical challenges which has limited most adopters to optical physicists.

NSOM is conceptually done by combining a traditional confocal microscope with a scanning probe microscope (SPM). Beyond that, there are a seemingly endless number of unique experimental realizations. Fundamentally all of the methods can be divided into the two original proposals by Synge, namely aperture-type and scattering-type. Each of the methods has advantages, but all of the work done in this thesis was s-NSOM in transmission. a-NSOM will be briefly outlined for completeness.

2.1 Scattering-type near-field microscopy

All of the work done in this thesis is based on s-NSOM and, unless stated otherwise, all references to near-field microscopy are based on the geometry given in figure 2.1. There are several necessary key features that allow for near-field measurements. In the order of the optical path, first a radially polarized laser excitation is focused onto a transparent sample (from below) by a high-numerical aperture (NA) objective. Then, the optical antenna is positioned into the center of the optical focus (from above) and maintained a few nanometers above the sample surface by a sensitive dynamic normal mode atomic force microscopy (AFM) feedback system. Spectroscopic emission from the sample is collected by the same objective and sent to an optical detector for point spectroscopy. Images are formed by raster-scanning the sample and recording the optical emission at each point. A topographic image is recorded simultaneously with the optical image as the optical antenna maps the relative height changes of the sample surface. Fundamentally, this experimental setup is the combination of an inverted confocal
Figure 2.1 – Schematic diagram of the experimental setup used for NSOM. Here, a radially polarized laser excitation is focused onto the sample by a high-NA objective. Light is further localized by the optical antenna that is maintained above the sample surface by AFM feedback. Spectroscopic emission from the sample is collected by the same objective and sent to either a spectrometer or single photon detector. The sample is then raster-scanned between the optical antenna and the objective to form an image. Adapted from reference [? ].

microscope and a standard AFM outfitted with an optical antenna as the AFM probe.

The reasoning for such a geometry is easily understood. The confocal microscope allows for the greatest optical localization, for both the excitation and emission light, of any traditional microscopy technique. This is achieved by imaging a point source excitation onto the sample and spatially filtering the collected emission to ensure that only the emission corresponding to the excitation volume is collected. To further localize the optical excitation, near-field microscopy employs an optical antenna as described by Synge. The localized optical near-field extends ∼10 nm beyond the antenna apex and therefore it is necessary that the
antenna is kept very close to the surface. AFM is an ideal system for that dis-
tance control as it is very sensitive to maintaining a tip-sample separation of a
few nanometers on nearly any surface material.

Experimentally, this distance control is achieved by mounting the antenna on
an oscillating quartz tuning fork. The tuning fork is mechanically driven at its
free-space resonance frequency (∼32.7 kHz) and the actual oscillation frequency
is continuously measured with a phase-locked loop (PLL). When the antenna is
close enough to feel the sample (a few nanometers away), the oscillation frequency
of the tuning fork shifts slightly to higher frequencies. A frequency-shift set point
(~0.5 Hz) is set and a proportional-integral (PI) gain controller is used to maintain
the frequency-shift set point by adjusting a piezo controlled tip-sample separation.

The high-NA focusing of a radially polarized laser excitation is necessary to
optimally excite the optical antenna. This geometry generates a strong longitu-
dinal field component at the center of the optical focus [? ]. These fields in turn
excite oscillations along the tip axis that generate highly localized optical fields at
the tip apex. The rational for generating a longitudinal dipole is two-fold: (1) this
is the inherent geometry of many optical antennas and (2) quenching effects. The
quenching effects can be understood by considering the imaging dipole of the tip
in the sample. A longitudinal dipole adds constructively, while a transverse dipole
and its image will form a non-radiating electric quadrupole. Tightly focusing a
radially polarized mode is the optimum way to have strong longitudinal electric
fields at the optical focus.

2.1.1 The particle antenna

Theory

The physics of the optical antenna is dependent on its material, the optical wave-
length, and the type of spectroscopy being studied. As an illustrative example,
the first optical antenna described [? ], as well as the first used for s-NSOM [? ], was a simple metallic sphere, now referred to as the particle antenna. The metallic nanoparticle is suspended by a dielectric and functions as a broadband dipole transducer to localize an incident optical excitation, as well as scatter fields from the sample. Despite the non-optimized spherical geometry, the single gold particle antenna provides a fluorescence rate enhancement of \( \sim 10 \) [? ]. The reproducible colloidal synthesis of metallic nanoparticles makes the particle antenna attractive for NSOM. The well-defined spherical geometry is relatively easy to simulate and understand [? ], making it ideal for quantified electromagnetic measurements.

The most important parameters regarding a metallic nanosphere as an optical antenna are the particle’s scattering cross section,

\[
\sigma_{\text{scatt}} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha(\omega)|^2, \tag{2.1}
\]

and the particle’s absorption cross section,

\[
\sigma_{\text{abs}} = \frac{k}{\varepsilon_0} \Im \{\alpha(\omega)\}. \tag{2.2}
\]

Here, and in the following equation, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_1(\omega) \) is the material permittivity, \( \varepsilon_2 \) is the permittivity of the surrounding medium (generally air and therefore dispersion free), \( k = \sqrt{\varepsilon_2}w/c \) is the wave vector in the surrounding medium, \( \omega \) is the optical frequency, and \( \alpha(\omega) \) is the quasi-static polarizability of the particle, given by,

\[
\alpha(\omega) = 4\pi\varepsilon_0 a^3 \left[ \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2} \right]. \tag{2.3}
\]

Where, \( a \) is the particle radius and \( \Re \{\varepsilon_1(\omega)\} = -2\varepsilon_2 \) is the condition for a localized surface plasmon resonance for a gold nanosphere [? ]. Since \( \alpha(\omega) \propto a^3 \), for small particles it can be seen that the particle’s absorption cross section will be larger
than its scattering cross section. Therefore, small particles lead to strong absorption while large particles provide poor localization. In general, an 80 nm diameter gold particle provides the best compromise between fluorescence enhancement and localization for fluorescence imaging [? ].

Related to the ability of an antenna to localize optical radiation, it facilitates an enhancement of the localized light-matter interactions. This can be understood by considering an optically active single molecule. The single molecule, generally, can be modeled as a short dipole emitter with a length of 1 nm, having an optical cross section of \( \sim 1 \text{ nm}^2 \) (analogous to an optical photon having a “size” of \( \sim \lambda^2 \)). The antenna coupled single molecule represents a hybrid system where the antenna effectively increases the optical cross section of the molecule to the antenna’s scattering cross section. Correspondingly, the antenna mediates out-coupling energy from a single molecule by effectively increasing the size of the molecule. The power radiated by a short dipole is given by,

\[
P_{\text{rad}} = 30\pi^2 i^2 \left( \frac{l}{\lambda} \right)^2,
\]

where, \( i \sim e\omega/2\pi \) is the current in the dipole. It is clear that increasing the size of the dipole to the order of \( \lambda \) will increase the radiated power by four orders of magnitude. Just as the antenna assisted in the excitation of the molecule, it also, equally, enhances the molecule’s emission [? ].

Below saturation, the molecular fluorescence rate, \( \gamma_{\text{em}} \) can be expressed as [? ],

\[
\gamma_{\text{em}} = \gamma_{\text{exc}} \left[ \gamma_r/\gamma \right],
\]

where, \( \gamma_r \) is the radiative decay rate and \( \gamma_{\text{exc}} \) is the excitation rate which is proportional to \( |\mathbf{p} \cdot f_e \mathbf{E}_0|^2 \) where, \( f_e \) is the local field enhancement factor at the tip apex and \( \mathbf{E}_0(\mathbf{r}_m, \omega) \) is the input field. Fermi’s golden rule defines the total spontaneous
decay rate, $\gamma$, as (SI units),

$$\gamma = \frac{2\omega}{3\hbar\epsilon_0} |\mathbf{p}|^2 \rho(r_m, \omega). \quad (2.6)$$

Where, $\rho$ is the electromagnetic density of states. As developed analytically by Sun et al. [?], different optical scattering processes will behave differently when coupled to an optical antenna. Fundamentally, there are three processes that are simultaneously happening: (1) enhancement of the excitation field, (2) increase of the radiative decay rate, and (3) increase of the non-radiative decay rate. As described above, the gold particle acts as a broadband dipole transducer that locally enhances the excitation field. Additionally, the Purcell effect alters the lifetime of the molecule being studied, thereby increasing the radiative decay rate, $\gamma_{\text{rad}}$. However, the introduction of the particle in the vicinity of the molecule allows the molecule’s radiative decay to couple into higher-order, non-radiating, surface plasmon modes of the particle, termed quenching. Higher-order modes are increasingly more confined to the particle surface and therefore quenching varies inversely with the particle-molecule separation.

Experimentally, I work with high quantum-efficiency fluorescent molecules. This means that there can be minimal fluorescence enhancement due to the Purcell effect and, therefore, there is a competition between excitation enhancement and quenching. Shown in figure 2.2a, the fluorescence rate of a single molecule is recorded as the separation between an 80 nm gold particle tip (figure 2.2b) and a longitudinally oriented (along the optical axis) Nile blue dye molecule is varied. The emission rate is enhanced a maximum of $\sim$10-fold at the optimum particle-sample separation. As the particle is brought into contact with the molecule, a net decrease in the fluorescence rate is observed. This decrease is attributed to a transition to a relatively shorter non-radiative lifetime than radiative lifetime.

Raman scattering is a fundamentally different process than fluorescence and,
Figure 2.2 – The 80 nm particle antenna fluorescence enhancement. (a) An approach (red) and retraction (blue) curve showing the fluorescence rate enhancement of a single longitudinally oriented (along the optical axis) Nile blue molecule on cover glass as a function of the antenna-sample separation. (b) An electron micrograph of a representative particle antenna, showing an 80 nm gold sphere suspended by a glass pipette.

therefore, responds differently to the optical antenna. Shown in figure 3.3 Raman scattering can happen with or without utilizing an electronic resonance. For the non-resonant case, the quantum efficiency of the Raman process is so low (with a rate that is an order of magnitude less than the metal-loss rate), quenching can simply not be observed. For a resonant Raman process, the system can be modeled similar to a low quantum efficiency fluorescence process. In this case, if the resonance is narrow and the excitation energy is carefully tuned, it is possible to observe quenching [? ]. Despite the near-resonance Raman process studied in this thesis, Raman quenching has never been observed.

Fabrication

Fabrication of the particle tip antenna is a well-defined, bottom-up, process. First, a quartz pipette (OD/ID, 1.0/0.5 mm) is heated and pulled to a sharp point. At this stage, there are two pathways that can be followed: either the pipette can be pulled to tip diameter of \( \sim 100 \) nm that can be used as-is (figure 2.2b), or it can be pulled to a smaller diameter \( \sim 20 \) nm. If a small diameter tip is pulled, the tip can be imaged in the scanning electron microscope (SEM) and simultaneously controllably reshaped by local heating and charging do to the electron beam. By
this method, a ‘pocket’ can be created that the particle will later fit into.

Regardless of the above fabrication methods, the pipette tip is then oxygen plasma cleaned and chemically functionalized with APTMS (3-Aminopropyltrimethoxy-silane) in vapor phase by evacuating a desiccator filled with the clean pipettes and a small, open, container of APTMS. After 24 – 48 hours, a uniform monolayer of APTMS coats the pipette tip. In a dissection microscope, the pipette tip is cut from the rest of the pipette and glued with a two-part epoxy (UHU Schnellfest) to a quartz tuning fork to be used as an AFM probe.

A substrate (glass) coated with colloidally grown gold particles of the desired size is then prepared by spin casting 20 µL of 0.2 nM particles in water at 2,000 rpm. This creates a sample where there are generally 1 – 2 gold particles per 25 µm², all of which are only loosely adhered to the substrate. By scanning the sample with the functionalized pipette tip, individual gold particles can be localized and their height measured. Then, by centering the pipette tip over the gold particle and increasing the tip-sample interaction force, the gold particle will preferentially adhere to the chemically functionalized tip and be removed from the glass surface, becoming (nearly) permanently attached to the pipette.

### 2.2 Aperture-type near-field microscopy

Proposed by Synge [? ], it is also possible to circumvent the diffraction limit when illuminating a sample surface with a sub-wavelength aperture source. This is done by tapering an optical fiber such that it becomes a zero-mode waveguide. Optical radiation coupled-in at the unaltered end of the fiber then leaks out of the tapered end as an evanescent field that is localized to the diameter of the tip. In order to realize this experimental geometry to its full potential, the outside of the tapered portion of the fiber needs to be metallized and there needs to be a
large cone angle of the taper, explained below.

Following Novotny and Hecht [? ], the aperture probe behaves as a metal coated waveguide, where each transverse section in the tapered region is of a slightly smaller diameter than the previous. Starting with an HE$_{11}$ mode input, there is very little loss until the light reaches the tapered region where, at a certain diameter dependent on the wavelength of light and the material properties, only evanescent modes are supported. Approximately one-third of the power is reflected backwards into the fiber and most of the rest is absorbed by the metal coating. By accounting for a lossy waveguide mode and the progressively decreasing diameter of the tapered waveguide, we can obtain the power transmission through the aperture,

$$P(z) = P(z_0)e^{-\int_{z_0}^{z} \alpha_{11}(z) dz}.$$  

(2.7)

Here, $P(z)$ is the power exiting the aperture, $P(z_0)$ is the power at some region in the fiber a distance $z_0$ before the aperture, and $\alpha_{11}$ is the attenuation of the HE$_{11}$ mode. For a metallic coating of infinite thickness, the attenuation of the HE$_{11}$ mode is found to be,

$$\alpha_{11}(D) = \text{Im}\{n_{\text{coat}}\}k_0e^{-AD}.$$  

(2.8)

Here, $D$ is the fiber diameter at a given location, $n_{\text{coat}}$ is the index of refraction of the metal coating, $k_0$ is the free space propagation constant, and $A$ is a constant. From Eqs. (2.7) and (2.8), it is found that the two most important parameters for having a large power output at the tip of the aperture probe are the aperture diameter and the cone angle of the tapered region of the fiber. Increasing the aperture diameter and the cone angle will both yield increased power transmission, so it is important to optimize these parameters while maintaining sufficient spatial resolution.
While the aperture probe has some experimental advantages in that there is no confocal optical background, the tip diameter is very large for topography and the resolution is generally low due to the relationship between fiber aperture diameter and optical transmission. Researchers have tried to solve these challenges with a tip-on-aperture design [? ]. This design works well, however, the fabrication is quite challenging and the throughput of each tip needs to be carefully characterized.

Despite these challenges, the first ever near-field optical measurements were made on October 22, 1982 by Winfried Denk working with Dieter Pohl at IBM using an aperture probe [? ]. Dieter Pohl published his first near-field images in 1984 [? ]. The technique, termed “optical stethoscope”, a corollary to the medical stethoscope, achieved an optical resolution of $\lambda/20$ with a 488 nm excitation.
3 Carbyne fundamentals

Before we explore the experimental results of carbyne, it is important to understand the physical properties of the linear carbon chain (LCC). The system studied in this thesis, long LCCs inside of double-walled carbon nanotubes (LLCCs@DWCNTs, hereafter simply referred to as LLCCs), is quite new. This work represents the first measurements of individualized LLCCs and is the basis for ongoing theoretical studies. The topics in this chapter include the history of the discovery of LCCs, the fabrication of LLCCs, and ensemble far-field optical measurements of those same chains.

The nomenclature to discuss the different allotropic forms of carbon is complex given the large number of possible (including fractional) hybridizations. Here, I make the following definitions for clarity. An infinite linear chain of carbon atoms is termed carbyne. Carbyne can exist in the polyyne form, consisting of alternating single- and triple-bonds ($-\text{C}=-\text{C}=$)$_\infty$, or the cumulene form which is described by double-bonds ($=\text{C}=$)$_\infty$. These two forms have different optical and electrical properties. The symmetric cumulene form is Raman inactive due to symmetry and therefore is not studied in this thesis.

In practice, all LCCs are finite and terminated by an end-capping group, and referred to simply as polyynes or cumulenes. The often large end-capping groups
can alter the electronic properties of the chain. In this thesis, the LLCCs are sta-
bilized primarily by a host carbon nanotube and therefore the end-capping atom
or small molecule is considered to have a minimal influence on the optoelectronic
properties of the LLCC as compared to the host nanotube.

3.1 Carbyne history

The rich history of the progress towards carbyne synthesis has been discussed in
detail by Kudryavtsev [? ]. The name “carbyne” was coined in 1969 by Sladkov et
al. [? ], although the first attempts to fabricate LCCs were published by Adolf
Baeyer in 1885 [? ]. Unfortunately, Baeyer was unable to synthesis chains (even
with only four carbon atoms) using his oxidative coupling reaction and proposed
that such a synthesis was impossible [? ]. Given his reputation at the time,
continued research into the synthesis of LCCs was greatly slowed.

In the 1950s and 1960s there was a renewed interest in the synthesis of LCCs
that resulted in chains of up to 20 carbon atoms [? ? ]. At this point, much of
the progress in LCC synthesis happened in the USSR, including the first micro-
diffraction patterns and electron micrographs of carbyne, revealing two different
forms proposed to be polyyne and cumulene [? ]. Many more observations of
carbyne followed [? ? ? ], but due to its high reactivity it is not readily found in
nature nor easily synthesized in the lab, and therefore it generated much contro-
versy [? ? ]. To date, the largest rigorously studied polyynes fabricated include
44 contiguous carbon atoms [? ]. While this is a tremendous step forward since
the 1960s, such chains are still too short to be used in practical applications and
another fabrication method was needed. Longer chains, of up to an estimated
300 carbon atoms, were synthesized in 1995 using a laser ablation method [? ].
While the work is quite intriguing and elucidating with respect to the growth of
fullerenes and possible growth of carbyne, the samples were difficult to quantitively
understand and individual chains could not be extracted.

In 2003, it was demonstrated that LCCs could be grown inside of multi-walled carbon nanotubes (MWCNTs), originally termed “carbon nanowires” (CNWs) [?]. In this work, long chains consisting of over 100 carbon atoms were grown within MWCNTs. The new system, not strictly a polyyne alone, has paved the way for the realization of studying and utilizing LCCs. The fabrication methodology has since been significantly altered and optimized such that LLCCs, consisting of thousands of carbon atoms, are reproducibly grown inside of DWCNTs [?].

3.2 Structure of carbyne

The structure of LCCs is quite different from other carbon allotropes. The electron configuration of carbon ([He] 2s² 2p²) means that it has four valence electrons to form bonds with adjacent atoms, leading to different allowed hybridizations between the s- and p-orbitals. In carbyne, each carbon atom has only two adjacent atoms to bond with, meaning that a double-bond should be formed between each of the carbon atoms to both account for every valance electron as well as maintain the innate symmetry of the system. This is achieved by a hybridization between the 2s and the 2pₓ orbitals (z being the dimension along the chain) forming an sp orbital, while the 2pₓ and 2pᵧ will remain perpendicular to the linear chain. The sp orbital will form a σ-bond with each of the adjacent carbon atoms while the 2pₓ and 2pᵧ orbitals will form π-bonds with adjacent atoms, shown in figure 3.1. The σ-bond is at a lower energy than the π-bonds and therefore each carbon atom in the linear chain contributes two valence electrons, one into each of the πₓ- and πᵧ-bonds.

If such a system is at low temperature and under no external stresses, it will form a cumulene geometry such that all atoms are equally spaced, meaning that there is only a single atom in each unit cell. It is, however, possible that there is
Figure 3.1 – Diagram showing the electron configuration of sp hybridized carbons. The sp hybridization forms a $\sigma$-bond shown in black between adjacent carbon atoms. The $p_x$ (blue) and $p_y$ (red) orbitals will form $\pi$-bonds with adjacent atoms.

a Peierls transition that breaks the symmetry of the system by creating a small amount of dimerization of the carbon atoms. This transitions the chain from a metallic (cumulene) to a semiconducting (polyyne) state [? ]. This physical effect was discovered by accident by Rudolf Peierls while he was writing a textbook, Quantum Theory of Solids, in 1955 [? ] and can very simply be understood through the Kronig-Penney model, derived in Kittel [? ].

The Peierls transition is favorable as it reduces the electronic energy of the system at an elastic cost. For a symmetric chain, each carbon atom is bound to each neighboring atom by a double-bond, donating two electrons that are divided between the two orthogonal valence bands (the $\pi$-bonds). From the Kronig-Penney model, a single band can accommodate 2N electrons (where N is the number of unit cells). In the symmetric case, there are N carbon atoms and N unit cells, resulting in 2N electrons. But, the two bands (the two $\pi$-bonds) can accommodate a total of 4N electrons, whereby the orthogonal electronic bands are each half-full. If the atoms dimerize into an alternating single-/triple-bond configuration, there are N/2 unit cells for the same 2N electrons, resulting in filling of the two orthogonal bands. Chains with half-full bands are metallic while those with full bands are semiconducting. The band gap is a function of the amount of dimerization.
present.

The electronic properties described above allow carbyne to have very impressive mechanical properties, as shown by Liu et al. [? ]. Their calculations predict that carbyne has a specific stiffness that is twice that of graphene and carbon nanotubes, approaching $10^9 \text{(N}\cdot\text{m/kg)}$. Its specific strength has been estimated at $7.5 \times 10^7 \text{(N}\cdot\text{m/kg)}$, again stronger than any known material and corresponding to a breaking force of $\sim 10 \text{nN}$. Additionally, it has been calculated that carbyne has a persistence length of 14 nm despite being only a single atom thick (0.772 Å). These calculations conclude a Young’s Modulus of 32.71 TPa and a shear modulus of 11.8 TPa [? ].

### 3.3 Carbyne fabrication

The fabrication of the LLCCs used in this thesis is described in references [? ? ?]. In summary, single-walled carbon nanotubes (SWCNTs) are annealed in a high-temperature high-vacuum environment for several hours. Under these conditions, additional carbon structures can be grown inside of the host nanotube, utilizing the nanotube as a nanoreactor. This type of fabrication methodology has previously been implemented for the growth of fullerene filled carbon nanotubes [? ]. If the diameter of the host nanotube is carefully chosen, following the growth of an inner nanotube, there remains exactly the correct space inside of the inner nanotube to support the growth of an LCC (shown schematically in figure 3.2). Specifically, the nanotube that directly encases the LCC should have an optimal diameter of $\sim 0.71 \text{ nm}$ [? ].

The growth of LCCs directly in SWCNTs is not possible as the host nanotube, with a diameter of 0.71 nm, will burn due to the high-temperature of the annealing process. Larger diameter nanotubes are more heat-resistant, however, they cannot be purified to a specific chirality as well as smaller diameter tubes. It
was found that using eDIPS-1.3nm host nanotubes, and optimal annealing conditions (1460°C, $\sim 10^{-6}$ mbar), LLCCs are grown with a large Raman signature at $\sim 1790 - 1800$ cm$^{-1}$. This low energy mode (non-ideal fabrication methods result in a Raman signature at $\sim 1850$ cm$^{-1}$), as confirmed in chapter 6, corresponds to the longest observed LLCCs to date, consisting of thousands of carbon atoms.

### 3.4 The Raman scattering process

Raman spectroscopy is a sensitive, non-destructive, inelastic scattering process. The general description of Raman scattering is described by three steps: (1) the absorption of an incident photon, (2) the creation or annihilation of a phonon, and (3) the emission of an inelastically scattered photon. Since energy and momentum must be conserved, the interaction with phonons reveals the vibrational energies of the material such that the Raman scattered photon can have lower energy after creating a phonon (Stokes scattered) or a higher energy after annihilating a phonon (anti-Stokes scattered), as shown by,
\[ \hbar \omega_s = \hbar \omega_i \pm \hbar \omega_q \quad \text{and} \quad k_s = k_i \pm k_q. \] (3.1)

Here, \( \hbar \omega \) is energy, \( k \) is momentum, and the subscripts \( s, i, \) and \( q \) correspond to the Raman scattered photon, the incident photon, and the phonon, respectively. Due to the very small momentum of photons, single photon Raman processes always involve phonons near the \( \Gamma \)-point (zero momentum).

Raman scattering is inherently a low-probability interaction with a quantum mechanical matrix element, \( K_{2f,10} \), describing the first-order Stokes Raman process, such that the Raman intensity is \( I \sim |K_{2f,10}|^2 \). The matrix element is given by,

\[
K_{2f,10} = \sum_{a,b} \frac{\langle \omega_s, f, i | H_{eR} | 0, f, b \rangle \langle 0, f, b | H_{ePh} | 0, 0, a \rangle \langle 0, 0, a | H_{eR} | \omega_i, 0, i \rangle}{(\hbar \omega_i - E_{ai}^e - i\gamma)(\hbar \omega_i - \hbar \omega_q - E_{bi}^e - i\gamma)}, \tag{3.2}
\]

where, the state \( |\omega_i, 0, i \rangle \) denotes the state with an incoming photon with energy \( \hbar \omega_i \), no phonon, and the initial electronic state \( i \) of the system. Following a scattering process, the state is given by \( |\omega_s, f, i \rangle \) where the Raman scattered photon has energy \( \hbar \omega_s \), there is a phonon in the state \( f \), and again the system is in the initial electronic state \( i \). \( H_{eR} \) is the electron-radiation Hamiltonian that describes the electron-photon interactions and \( H_{ePh} \) is the electron-phonon Hamiltonian. The sum is carried out over all possible intermediate electronic states \( a \) and \( b \), where \( E_{(a,b)i}^e \) is the energy difference between the states \( (a,b) \) and \( i \). The electronic state lifetime is given by \( \gamma \). The denominator reveals that electronic resonances can be utilized to enhance the Raman efficiency. This enhancement is present if the incident photon is electronically resonant \( (\hbar \omega_i \approx E_{ai}^e) \), if the scattered photon is electronically resonant \( (\hbar \omega_s = \hbar \omega_i - \hbar \omega_q \approx E_{bi}^e) \), or if both resonances are simultaneously present, as shown in figure 3.3.

Shown in figure 3.3a, neither the incident or Stokes scattered photon is resonant
Figure 3.3 – Sketch of (a) non-resonant, (b) incoming resonant, (c) outgoing resonant, and (d) double resonant Raman scattering. Electronic energy bands are shown in black lines, virtual states are shown in dashed gray lines, $\omega_{i,s}$ are the incoming and outgoing photons and $\omega_q$ is the phonon. These all represent Stokes processes.

With the electronic structure of the material. This process is termed non-resonant Raman and has the lowest probability of the possible processes. Resonant processes are shown in figures 3.3bc corresponding to electronic resonances of the incident and scattered photons, respectively. If both the incident and scattered photons are resonant, the processes is called double resonant and is shown in figure 3.3d.

For a system described by discrete electronic transitions between two parabolic energy bands the optical transition energies ($E_{ii}$) can be written as,

$$E_{ai}^e(k) = E_{bi}^e(k) = E_{ii} + \frac{\hbar^2 k^2}{2\mu}, \quad (3.3)$$

where, $\mu$ is the effective reduced mass given by $1/\mu = 1/m_e + 1/m_h$, where $m_{e,h}$ is the effective mass of the electron and hole, respectively. This allows the sum to become an integral in equation 3.2 and the Raman intensity to be evaluated as
\[ I \sim |K_{2f,10}|^2 \propto \frac{1}{\hbar \omega_q} \left( \frac{1}{\sqrt{\hbar \omega_i - E_{ii} - i\gamma}} - \frac{1}{\sqrt{\hbar \omega_i - \hbar \omega_q - E_{ii} - i\gamma}} \right)^2. \] 

(3.4)

If only a single discrete excitonic transition is considered, as is the case for LLCCs and carbon nanotubes, a further simplification to the evaluation of the matrix element \( K_{2f,10} \) can be made. This is allowed if there is only a single state with zero excitonic momentum such that \( E_{ei}(k) = E_{ei}(k) = e\hbar \). In the case that there are no other nearby excitonic states, there is no longer a sum over the states \((a,b)\) and the corresponding Raman cross section is given by,

\[ I \sim |K_{2f,10}|^2 \propto \frac{1}{\hbar \omega_q} \left( \frac{1}{\hbar \omega_i - E_{ii} - i\gamma} - \frac{1}{\hbar \omega_i - \hbar \omega_q - E_{ii} - i\gamma} \right)^2. \] 

(3.5)

Equation (3.5) is instructive as its simplified form allows for a clear understanding of the optical processes of the excitonic system. Additionally, there is a slight narrowing of the Raman resonances for both incoming and outgoing resonant processes due to the exciton that can be seen from the removal of the square root in the denominator, as compared to equation (3.4).

### 3.5 Raman properties of carbyne

Polyynes, which have alternating single-/triple-bonds, have a longitudinal optical Raman mode that is a function of the chain length \([? \ ? \ ? \ ?]\). This mode is described by a stretching of the C≡C \([? \ ? \ ? \ ?]\) which belongs to the \( D_{\infty h} \)-symmetry point group \([? \ ? \ ? \ ?]\), shown in figure 3.4. The mode has previously been referred to as the \( R \)-mode \([? \ ? \ ? \ ?]\). The frequency of this mode is dependent, ultimately, on the amount of bond-length alternation (BLA), or the relative lengths of the
alternating single-/triple-bonds, and is an ongoing field of theoretical research.

![Schematic of carbyne’s Raman vibrational mode.](image)

**Figure 3.4** – Schematic of carbyne’s Raman vibrational mode.

**Electronic properties of carbyne**

Raman spectroscopy is very sensitive to the electronic structure of the molecule being studied and all of the theoretical work for calculating the frequency of the Raman mode requires understanding the electronic properties of carbyne. As mentioned previously, carbyne in its relaxed state is cumulenic and conducting \[^1\]. As a BLA is introduced, the chain transitions into a semiconductor \[^2\] that always has a direct band gap \[^3\]. Increasing the amount of BLA increases the chain’s band gap \[^4\].

As it turns out, the amount of BLA present is also a function of the length of the chain \[^5\], such that the BLA reduces with chain length. Computationally, it has been found that the band gap of end-capped polyynes can range from 8.5 – 0.2 eV \[^6\], although experimental values have ranged between 4.7 – 2.7 eV, corresponding to 4 – 44 carbon atoms \[^7\]. LLCCs inside of carbon nanotubes are generally considered to be hydrogen-capped, which has a minimal impact on the BLA, but are subject to charge transfer from the nanotube and a mechanical restructuring due to van der Waals’ interactions \[^8\]. There is a net negative charge transfer to the chain that results in a reduced BLA and, correspondingly, a reduced band gap \[^9\]. The experimentally determined value for the band gap of a nearly infinite length carbyne chain has previously remained elusive due to both the limited length of chains and interactions with large end-capping groups. The
band gap of infinite carbyne inside of a SWCNT has been estimated at 2.2 eV [? ] and 3.3 eV [? ].

The resonance Raman profiles of LLCCs, in ensemble far-field measurements, have revealed a band gap ranging from approximately 2.20 – 2.05 eV, although the exact physical length of the chains are unknown [? ]. The direct band gap could not be measured with absorption spectroscopy due to the combination of weak LLCC absorption and strong nanotube absorption [? ]. Additionally, resonance Raman profiles suggest that there is a singlet excitonic gap, with simulations predicting an exciton binding energy of 0.1 eV [? ].

**Polyyne Raman shifts**

The energy of the Raman mode varies with the BLA and therefore also the band gap, softening with decreasing band gap. This has been experimentally observed with ensemble measurements where it has been found that the Raman mode softened with decreasing laser excitation energy [? ]. These results are indicative of a near-resonant Raman excitation of the polyynes. Theoretical calculations have reproduced the Raman shifts observed in studies of chemically synthesized polyynes of known size, showing that longer chains have a lower energy Raman mode [? ]. Recent calculations of the Raman frequency of an infinite, hydrogen capped, polyyne chain have shown flaws in DFT calculations and are in very good agreement with experimental results [? ].

Agarwal *et al.* [? ] have experimentally synthesized and measured the Raman response of a wide range of polyyne lengths, ranging from 4 – 20 triple bonds. Their results have confirmed a softening of the Raman mode between 2300 – 1900 cm$^{-1}$ with increasing chain length. Even Raman measurements of cumululene forms have observed a violation of the IR/Raman mutual exclusion principle, suggesting that even cumulene forms are physically non-linear [? ? ]. Other
studies have shown that although cumulene forms can be synthesized, any finite-length chain at a finite temperature exhibits a small amount of dimerization due to a Peierls transition [? ]. Recently, Pan et al. [? ] have reported the first observations of the single-bond stretching mode at $\sim 1050 \text{ cm}^{-1}$ for short chains.

LCCs in nanotubes, first presented via an arc discharge fabrication [? ], have shown similar Raman properties. A Raman frequency of $1850 \text{ cm}^{-1}$ was observed, corresponding to an approximately 40 atom carbon chain, as predicted by Kastner et al. [? ]. This red-shift of the Raman emission for LCCs in nanotubes is attributed the combination of long chains and the net negative charge transfer to the chain. Additional Raman frequencies, corresponding to the LLCC-band of different chains, were found as well. All of these modes demonstrated very narrow full-width half-maximums (FWHMs) of $\sim 10 \text{ cm}^{-1}$, indicative of a very ordered crystal structure [? ], and considerably narrower than had been previously observed [? ].

The carbyne chains studied in this work, the LLCCs, have been measured in detail with ensemble far-field optical microscopy, discussed in this paragraph and the following [? ? ? ]. These measurements have observed a Raman shift between $\sim 1850 – 1790 \text{ cm}^{-1}$, and several interesting properties of this mode. The most notable is that a continuum of LLCC-band Raman frequencies is not observed, but instead there are distinct frequencies and some narrow bands. This suggests that interactions with the inner host nanotube greatly determines the Raman mode, otherwise each additional atom in a chain would reduce the frequency of the Raman mode and a continuum of frequencies would be observed. Additionally, resonant Raman has shown that lower energy Raman modes have lower energy band gaps.

Simultaneously observing nanotube radial breathing modes (RBMs) and LLCC-band Raman has allowed a tentative assignment of a specific LLCC-band frequency to a specific chirality of nanotube. Temperature dependent Raman mea-
measurements have shown that the LLCC-band not only narrows with decreasing temperature but also shifts to higher energies. This data has been explained by a model of two coupled modes, namely the LLCC-band and the inner nanotube RBM. Additionally, supporting that model, it was observed that the presence of LLCCs enhances the photoluminescence of the inner nanotube. The relative intensity of the LLCC-band to the G-band is also observed to increase by a factor of nearly 6 as the sample is cooled from 325 K to 38 K.
4  Near-field biological imaging

Studying biological samples with optical light is ideal due to the inherent compatibility between biological organisms and light; however, as mentioned previously, standard optical imaging techniques are limited in spatial resolution due to diffraction. The resolution provided by standard optical techniques is therefore insufficient to resolve many sub-cellular features that have a spatial extent of only a few nanometers and exist in high densities, such as proteins. In this work, NSOM was used to map the distribution of complement receptor 1 (CR1/CD35) in human erythrocytes. The text and figures in this chapter are largely reproduced, with permission, from reference [?].

4.1  Complement receptor 1 (CR1/CD35)

Several studies have implicated CR1 as a possible risk factor for developing Alzheimer’s disease (AD), a terminal neurodegenerative disease [?]. CR1 is a type 1 transmembrane glycoprotein that is predominantly expressed in erythrocytes [?], with as many as 1,300 CR1 per cell [?]. The role of CR1 is to clear immune opsonized complexes and deliver them to the liver for degradation [?]. One specific example of this pathway is the binding of free amyloid-beta (Aβ_{1-42}) peptides by C3b, followed by CR1, such that the peptides are removed from the
brain [? ]. The build-up of Aβ_{1-42} in the brain is a known pathognomonic for AD.

One major finding to implicate abnormalities in CR1 in patients with AD is a negative correlation between level of cognitive impairment and amount of bound Aβ_{1-42} within erythrocytes [? ]. This does not directly require a problem with CR1, however, genetic studies support that CR1 may play a role in the development of AD. A genome-wide association study found variants of CR1 that were associated with AD [? ] and four single nucleotide polymorphisms (SNPs) near CR1 have also been correlated with increased levels of Aβ_{1-42} in cerebrospinal fluid (CSF), suggesting that these SNPs affect the ability for CR1 to effectively bind Aβ_{1-42} [? ]. The exact impact of the SNPs is unknown and therefore it is necessary to understand the relationship between CR1 function and expression within human erythrocytes.

Prior to this work, two electron microscopy (EM) studies of CR1 have been performed and both have revealed a clustering nature of CR1 within human erythrocyte membranes [? ? ]. EM studies are often very appealing for biological samples because of the high spatial resolution they offer; however, it is very difficult to ensure that the samples measured are physiologically relevant. The samples need to be prepared with toxic fixative agents (e.g. glutaraldehyde, paraformaldehyde, OsO₄, etc.) and are imaged in a non-physiological environment (e.g. vacuum, high-energy electrons, etc.) — both may alter the native distribution of proteins under investigation. Additionally, the necessary immunogold labels are often larger than the molecule under investigation and may further disrupt the native or pathophysiologic conformation. It is generally assumed that EM studies do preserve the key aspects of biological systems under investigation, but disparities between fixed and unfixed samples still cause concern with this technique.
4.2 Sample preparation

Biological samples were prepared similarly as described by Höppener and Novotny [? ]. Blood was provided by a healthy male in his mid-twenties with no signs of or family history of dementia. Erythrocytes were isolated from \( \sim 50 \mu L \) of human blood by centrifugation in an ice cold 150 mM KH buffer (150 mM potassium chloride, 20 mM HEPES, 24 mM sucrose; pH 7.4). The erythrocytes were diluted 30-fold with the KH buffer and 300 \( \mu L \) of diluted erythrocytes were placed on an APTES (3-aminopropyltriethoxy-silane) functionalized glass coverslip, allowing a monolayer of cells to adhere to the coverslip. After rinsing, \( \sim 200 \mu L \) of a 2% w/w solution of BSA (bovine serum albumin Cohn-V fraction) in the KH buffer was placed on the coverslip for 3 hours to reduce future nonspecific labeling of the remaining exposed APTES functionalized substrate.

The cells were then lysed with a 0.2% w/w solution of BSA in a 5 mM sodium phosphate buffer (5 mM NaH2PO4, 1 mM Free EDTA; pH 7.4) under pressure from a syringe. Membrane ghosts were used to allow the optical antenna to image a rigid surface as well to minimize the background biological fluorescence of the sample. The exposed cytoplasmic side of the erythrocytes was labeled against CR1 with an H-300 rabbit anti-CR1 primary antibody (Santa Cruz Biotechnology, Santa Cruz, CA), diluted 1:400. Finally, membrane ghosts were labeled with an Alexa Fluor 633 conjugated F(ab')2 goat anti-rabbit antibody (Invitrogen, Carlsbad, CA), diluted 1:800. Both antibodies were placed in the 0.2% w/w solution of BSA in 5 mM sodium phosphate buffer and the samples were washed thoroughly between each step with the appropriate buffer. All samples were kept wet and at room temperature for the entire preparation. Control samples were prepared by not adding the primary antibody.

The experimental geometry of the as-prepared biological sample is shown in figure 4.1. The extracellular side of the erythrocyte lipid bilayer is attached to the
Figure 4.1 – Schematic of the CR1 measurement geometry. CR1 (green) extends through the cell membrane (orange) and is labeled on the intracellular size with a primary antibody (black) and a fluorescently labeled secondary antibody (brown). An 80 nm gold particle tip is used as the near-field antenna to image the fluorescent label.

surface of a glass substrate. CR1 was then labeled on the intracellular side with a primary antibody (black) followed by a fluorescently labeled secondary antibody (brown). The particle antenna was then approached from above for near-field imaging. The far-field optical excitation and detection (not shown) come from below, as in figure 2.1

4.3 Real-time optical background suppression

In this work, the sample being imaged was fluorescent molecules surrounded by a biological matrix. The combined background fluorescence of the biological matrix and the high density of labeled proteins greatly masked the near-field contribution of labeled proteins directly under the optical antenna. In order to enhance the signal-to-background ratio, a real-time optical background suppression technique was employed [? ]. The background suppression technique works by modulating the tip-sample separation and then demodulating the recorded optical signal, at the same frequency. In this way, when the optical antenna is directly above a
fluorescent molecule, the recorded optical signal is enhanced when the tip is close the sample and reduced when the tip is retracted. When there is no molecule present, there is little difference in the optical signal between the tip-approached and tip-retracted positions.

It was experimentally determined that a 100 Hz modulation of the tip-sample separation, between $\sim 5$ nm and $\sim 65$ nm, gave a large signal-to-background ratio in the demodulated optical image. As described previously, the tip-sample separation is determined by the oscillation frequency-shift of the tuning fork relative to its free-space oscillation frequency. The tip-sample modulation was achieved by adding a sinusoidal offset (as a voltage) to the frequency-shift input of the SPM controller. This caused the SPM controller to respond as if there was a sinusoidally varying, large, topography on the sample, and therefore correspondingly lift the tip from the sample and then re-approach the surface. The topographic height perceived by the SPM controller is a function of the tuning fork quality factor, feedback-loop, and modulation parameters. This height was directly measured by recording the voltage applied to the tip-sample separation piezo as the tip was modulated.

The optical fluorescence signal was detected with a single-photon counting avalanche photodiode (APD) that produced a discrete TTL pulse for each photon detected. The APD output was the input to a lock-in amplifier (SR830, Stanford Research Systems, Sunnyvale, CA). The low-frequency of the modulation allowed for a sufficient number of charges to accumulate in the lock-in amplifier before the signal was demodulated, facilitating the use of the discrete TTL input. The photon counts were demodulated at the first harmonic and recorded as a voltage in the raster-scanned image, simultaneously with the integrated photon count rate and topography, at each raster pixel.
4.4 Results

Prepared erythrocyte membrane ghosts were imaged in the near-field microscope. Figure 4.2ab shows a representative topographic and near-field image of a membrane ghost labeled against CR1. A corresponding far-field optical image of the same membrane is shown in figure 4.2c. Membrane ghosts have an area of ∼45 µm², accounting for between one-third and one-half of the surface area of an intact erythrocyte. A near-field optical spatial resolution of 56 nm was achieved, allowing for the spatial extent of CR1 clusters to be measured, but not individual protein spacings. Since the antibodies used are only a few nanometers in area, fluorescent peaks with a spatial extent larger than the resolvable optical resolution are due to several closely spaced CR1 proteins, or clusters.

Control samples were imaged to understand the role of non-specific labeling by the secondary antibody. Shown in figure 4.3ab, there is significantly less optical signal (∼85% reduction) in both the confocal and background suppressed near-field images. A histogram was made, shown in 4.3c, to understand the spatial extent of each of the measured fluorescent spots (since this is the control sample, it must be assumed that these spots are not related to CR1). A distribution is
observed that peaks with an area of a single image pixel (35×35 nm²) and does not extend beyond 3 pixels. Since the small area spots can be attributed to non-specific labeling from the control experiments, they have been disregarded in subsequent analysis of the inter-cluster spacing distribution of CR1. Additionally, the spatial extent of these spots (<3 pixels) is likely too small to represent a cluster of CR1 proteins.
Figure 4.4 – Histograms of CR1 cluster areas in four measured cell membrane ghosts. Units are given as the spatial extent of each measured cluster in units of image pixels, corresponding to an area of $35\times35\text{ nm}^2$. Adapted from [? ].

The inter-cluster spacing of CR1 in four cells is shown in figure 4.5. The number of CR1 clusters per erythrocyte ghost ranged between 61 and 124, with a mean value of 92. The mean inter-cluster spacing across all of the cells measured is confirmed to be unresolvable by conventional diffraction limited optical techniques. The average inter-cluster spacing of CR1 increased from 184 nm to 256 nm as the number of CR1 clusters decreased. Notably, regardless of the number of measured clusters and the mean inter-cluster spacing ($203\pm85\text{ nm}$ across all membranes), the standard deviation of the inter-cluster spacing remained nearly constant across all four membrane ghosts analyzed, with a value $79\pm9\text{ nm}$. 
**Figure 4.5** – Histograms of the CR1 inter-cluster spacing for four measured cell membrane ghosts. There is a large variation between the number of CR1 clusters and their mean spacing, however, it is observed that the standard deviation of the spacing is nearly constant across all membrane ghosts. Adapted from [? ].

### 4.5 Conclusions

NSOM was used to quantitatively measure the spatial extent and spacing of CR1 clusters in erythrocytes from a healthy man in his mid-twenties with no symptoms of or family history of dementia. The methods used were designed to optimally preserve the physiological distribution of CR1 within the erythrocyte membrane. Erythrocytes were promptly adhered to an APTES functionalized glass coverslip to allow the dense monolayer of APTES to hold lipids and proteins on the surface without chemical fixing of the membrane. Additionally, labels were small and all labeling was performed after the membranes were adhered to the surface so as to prevent any alterations of the physiological CR1 distribution.
The results of this method of biological sample preparation can be compared with that of EM studies. While the clustering nature of CR1 is observed, the distributions presented here are different than previously reported [? ? ?]. The two cited reports vary slightly with respect to each other, but in this work many more clusters per membrane were observed. Paccaud et al. [? ?] measured an average of 6.7 – 81.8 CR1 clusters per erythrocyte, with more clusters representative of cells with more CR1 and an average cluster size of ∼4 CR1 per cluster. Chevalier et al. [? ?] reported only 3 – 8 CR1 clusters per erythrocyte, however they found there were 37 or 67 (for each donor) CR1 per cluster. NSOM is capable of determining the number of proteins per cluster; however, this requires photobleaching experiments or statistical approaches, including photon anti-bunching along with the appropriate monoclonal antibodies. The area and number of CR1 clusters was measured, observing between 61 and 124 clusters per membrane ghost. This suggests that the total number of CR1 clusters per erythrocyte could be as large as ∼350.

Although measurements were performed with dehydrated samples, the sample preparation embraced physiological conditions as much as possible to ensure that the measured distribution was the same as the physiological distribution. The differences between NSOM and EM studies, as well as inconstancies between fixed and unfixed samples within EM studies, suggests that the method of sample preparation may influence the measured distribution. The physiological sample preparation allowed by NSOM may have a significant advantage over EM in probing the physical expression of proteins, such as CR1, that may be affected in disease states.

The distribution of CR1 within the erythrocyte membrane was also quantified, revealing the cellular organization of the protein. This is observed by the nearly constant standard deviation of the inter-cluster spacing of CR1. A random two-dimensional distribution demonstrates the importance of the constant standard
deviation of the CR1 inter-cluster spacing distribution. If all of the clusters were randomly distributed, reducing the number of clusters by a factor of four would increase the mean cluster spacing and the standard deviation of the distribution by the square root of four, which was not observed. The cell tightly regulated the distribution of CR1 clusters within the membrane.

Additionally, the smaller area spots that could not be justified as clusters of CR1 are generally randomly distributed. Comparing the mean spacing between spots, both with and without the small spots, an inter-spot spacing increase of less than 5% for the latter distribution was observed. This indicated that the small area spots are generally randomly distributed while the larger area clusters have a spatial distribution that is maintained by the erythrocyte.

A continuation of this study to better understand the distribution of CR1 clusters in both healthy individuals and individuals with AD would allow quantitative analyses of any alterations in the expression of CR1 and its correlation with AD to be performed. This could fuel the development of new and accessible biomarkers for patients with mild cognitive impairment and AD.
5 Development of improved optical antennas

In this chapter, I worked to confirm theory regarding optical antenna design, as well as develop a mass-producible, high-performance, optical antenna. The work presented in this chapter is largely reproduced from references [? ? ].

5.1 Motivation

As shown in chapter [4], the simple particle antenna can have applications in quantitative imaging, however, the resolution of the 80 nm particle used was only 56 nm, making it insufficient to resolve individual proteins. One can propose simply using a smaller gold particle as the antenna, however, as shown by Anger et al. [? ], the near-field enhancement is reduced as the particle size is decreased, making small particles unfeasible. Therefore another antenna geometry needs to be considered.

As can be quickly seen from equations [2.1] and [2.2], there is a delicate interplay between the physical amount of material present in the optical antenna as well as the antenna’s minimum dimensions. An ideal antenna would have a large amount of material to increase the interaction of the antenna with the incident optical field, but then have a very small minimum feature size to localize the excitation radiation. One obvious step in this direction is simply an etched metallic
wire. Using such a geometry, several simulations have confirmed that field enhancements can be on the order of $10^3$ \cite{? ??}, but in practice, tips that provide such large field enhancements are challenging to reproducibly fabricate, primarily due to the crystal structure of the metallic wire. Additionally, for imaging and spectroscopy applications (i.e., Raman or fluorescence), the antenna can either enhance or quench the emission of the sample \cite{? }. These competing processes were briefly discussed in chapter 2. While the etched metallic probe is very desirable for Raman spectroscopy, it turns out to be nearly unusable for fluorescence spectroscopy.

In order to make NSOM more reproducible and useable as a tool to researchers outside of the optical physics community, it was clear that a new type of optical antenna was needed.

### 5.2 The cascaded particle antenna

Originally proposed by Li et al. \cite{? }, the idea behind the cascaded particle antenna is that a plasmonic nanoparticle with a large scattering cross section can localize incident fields to excite a particle with a smaller scattering cross section, which in turn would again excite a progressively smaller particle. This calculated cascaded enhancement of the optical field presented in \cite{? } is not directly applicable to visible light, but they have shown a field enhancement of nearly $|E/E_0| \approx 50$ in the ultraviolet.

#### 5.2.1 Fabrication

Using the expertise that I established in single particle picking, I fabricated cascaded particle antennas using a similar serial process. The first step was to prepare an 80 nm particle tip as described in section 2.1.1. A quartz pipette was heated
and pulled into a sharp tip. The tip was then reshaped in the SEM to produce an 80 nm diameter pocket to place the largest gold particle. The tip was functionalized with APTMS prior to attaching it to a tuning fork for AFM. An 80 nm gold particle was then attached to the pipette by AFM, as described previously. The 80 nm gold particle was chemically functionalized by dipping it into a solution of 1,6-hexanediol (0.05% w/w in acetone). The dithiol functionalized gold particle was then used to pick a 40 nm gold particle using the same AFM picking method. This fabricated dimer antenna was either used as-is or was again functionalized in the dithiol and used to pick a third, 20 nm gold particle. Dimer and trimer antennas were characterized in the SEM as necessary.

5.2.2 Imaging and spectroscopy

In the same experimental geometry introduced earlier (figure 2.1), the dimer and trimer particle antennas were used for imaging and spectroscopy of single dye molecules. Dye molecule samples were prepared by spin casting 20 µL of a \( \sim 5 \times 10^{-9} \) M sample of Nile blue dye molecules in water onto a Poly(methyl methacrylate) (PMMA) coated (2 – 5 nm) glass coverslip spinning at 2,000 rpm. The exact dye concentration can be modified to adjust the density of dye molecules that adhere to the surface.

Figure 5.1a shows the imaging results obtained using a dimer antenna (80-40 nm cascade) to image the single molecules. The image demonstrates a spatial resolution of \( \sim 25 \) nm and a fluorescence enhancement of \( \sim 20 \). To ensure that there were no near-field spectral artifacts, figure 5.1b depicts a single molecule emission spectrum both with and without the dimer antenna, for the same molecule. No spectral modification of any molecule was observed.

The trimer antenna was also used to image single molecules, shown in figure 5.2a. The extreme localization at the apex of the trimer antenna gave an
Figure 5.1 – Single molecules imaged with the cascaded dimer antenna. (a) An image of single Nile blue dye molecules acquired in the near-field of a dimer antenna. A cross section (inset) shows a spatial resolution of 23 nm for the molecule marked with the arrow. (b) The emission spectrum of a single molecule both with the dimer tip approached (red) and retracted (blue). The spectra show a near-field enhancement of a factor of 20. ($\lambda_{ex} = 632.8$ nm) Reproduced from reference [? ].

imaging resolution of $\sim 15$ nm. In order to better understand the local field enhancement, the collected fluorescent rate of a single molecule was recorded as a function of the timer-molecule separation (figure 5.2b). The collected fluorescence rate increased by a factor of $\sim 40$ in the presence of the trimer antenna.

Simulations (figure 5.3) show that the field enhancement at the apex of an 80-40-20 nm cascaded gold particle antenna is $|E/E_0| \approx 10.5$. This suggests that a fluorescence rate enhancement of $\sim 100$-fold should be observed; however, the model used does not account for quenching due to the particle antenna and therefore a lower fluorescence enhancement was expected. Previous work has shown that the amount of quenching increases as the particle antenna diameter decreases. In fact, a lone 20 nm gold particle will lead to no fluorescence enhancement for a high-quantum efficiency molecule [? ]. For the 80-40 nm dimer, a four-fold fluorescence rate increase, as compared to a single 40 nm particle antenna, was measured. That number is $\sim 40$ for the 80-40-20 nm cascaded trimer antenna.

In order to fully understand the experimental geometry, gold particle dimers
Figure 5.2 – Single molecules imaged with the cascaded trimer antenna. (a) An image of single Nile blue dye molecules acquired in the near-field of a trimer antenna. A cross section (inset) shows a spatial resolution of 15 nm for the molecule marked with the arrow. (b) The collected fluorescence rate of a single longitudinally oriented molecule as a function of the timer-molecule separation, showing a collected fluorescence enhancement of ~40. Inset shows the experimental geometry. (λ_ex = 632.8 nm) Reproduced from reference [? ].

Figure 5.3 – Simulations of the fields at the apex of a trimer antenna. (a) The simulated geometry of the 80-40-20 nm cascaded gold particle trimer antenna. (b) Simulated phase (blue) and intensity enhancement (red) as a function of wavelength at the tip apex. Reproduced from reference [? ].
were fabricated with the same chemistry, colloidally. The dimers were then imaged in the tunneling electron microscope (TEM) with atomic resolution to ensure that there was no electrical contact between the individual gold particles. As shown in figure 5.4, there is indeed a particle-particle gap of \( \sim 2 \text{nm} \).

### 5.3 The pyramid antenna

In section 5.2, the interaction between the polarizable volume of an optical antenna and the size of the antenna apex were both theoretically and experimentally explored. Unfortunately, the cascaded particle antenna is experimentally difficult to fabricate and structurally rather delicate. In collaboration with Prof. Sang-Hyun Oh’s group at the University of Minnesota, I have developed template-stripped gold pyramid antennas for near-field microscopy [5]. The goal behind this project was to take the knowledge acquired while developing the cascaded particle antenna and previous work with etched gold wire antennas, to develop a robust, high-performance, and reproducible near-field antenna.
The requirements of such an antenna are clear: (1) large scattering cross section, (2) sharp antenna apex, and (3) large cone angle. The large scattering cross section was achieved in the cascaded particle antenna by using a large gold particle, while the sharp apex was achieved with a small particle. The large cone angle is a requirement to reduce quenching, which is of great importance for fluorescence applications. This is understood from etched metallic wires that are excellent for TERS but have been found to quench fluorescence. As discussed in section 2.1.1, an antenna with a small cone angle simulates a small particle, meaning that there are many higher-order, nonradiative modes in the particle that can quench fluorescence. Raman scattering, due to its small cross section and low quantum efficiency, is not easily quenched. An antenna with a large cone angle has a larger mode miss-match between supported surface plasmon modes and the molecule dipole emission, leading to less quenching. The work by Sun et al. is a very nice theoretical work that describes the differences between the near-field enhancement in fluorescence and Raman spectroscopy applications.

### 5.3.1 Pyramid fabrication

The well understood properties of single crystal silicon has allowed for tremendous technological development of nanoscale silicon devices, the techniques of which have subsequently been applied to silicon template fabrication. The ability to wet etch silicon along its crystal facets to nearly atomically flat surfaces and atomically sharp edges, combined with the low adhesion between silicon and noble metals, allows nano-structured metal films with sub-nanometer rms surface roughness to be stripped from silicon templates.

Figure is a schematic of the pyramid fabrication methodology. In this process, a 100 nm SiN$_x$ mask was grown on a [1 1 1]-oriented silicon wafer. MEGA-POSIT SPR-955 photoresist (Rohm and Haas) was deposited by spin coating and 20 μm diameter circles were exposed into the resist using standard photolithogra-
The resist was developed for 70 sec in MF CD 26 (Rohm and Haas) using a CEE 200X (Brewer Science) spray developer. The exposed SiN\textsubscript{x} was then removed by RIE etching with CF\textsubscript{4} (STS model 320). An oxygen plasma was used to remove the photoresist and the wafer was wet etched in a 30:10:60, KOH:isopropyl alcohol:water (\% v/v) solution for 90 min. The wafers were then rinsed in water and cleaned in a piranha solution before 200 nm of gold was evaporated onto the template. The SiN\textsubscript{x} mask was removed by soaking the whole wafer in a 49\% hydrofluoric acid solution for 20 min. This process yielded isolated gold pyramid shells inside of the silicon template.

Large pyramids (20 µm base) were fabricated so that they could be easily attached to wires and implemented as an AFM probe. This was achieved by gluing a thin (15 µm diameter) tungsten wire onto a quartz tuning fork, the same as the glass pipettes described previously. The tip of the wire was cleaned in methanol and then dipped into a two-part epoxy (UHU Schnellfest) such that a small bead of glue formed at the wire apex. Using a micrometer stage, the tip of the wire was placed into a single gold pyramid shell. After the glue cured, the wire was retracted from the wafer surface and, correspondingly, the pyramid shell was removed and ready to be used as a near-field antenna.

### 5.3.2 Pyramid near-field imaging

The pyramid antenna was first evaluated by mapping individual fluorescent molecules on a glass coverslip as was demonstrated for the cascaded particle an-
Figure 5.6 – Single molecule fluorescence imaging with a pyramid antenna. (a) A confocal fluorescence image of single Atto 647N molecules and (b) the corresponding near-field image. A cross section (inset) shows a spatial resolution of 18 nm for the molecule marked with the arrow. (c) An approach curve showing a ∼200-fold emission rate enhancement of a single molecule as a function of the tip-sample separation. Scale bars are 200 nm. (λ_{ex} = 632.8 nm) Reproduced from reference [?].

tenna. The samples were prepared using the same parameters, except the dye molecule Atto 647N was used for its photostability. Figure 5.6a depicts a 1 μm² confocal image of single Atto 647N molecules excited with a radially polarized 632.8 nm laser excitation. Individual molecules cannot be resolved. The large fluorescence enhancement of the pyramid antenna makes it easy to resolve individual molecules in the dense sample with a resolution of less than 20 nm (figure 5.6b). The collected fluorescence rate of an individual longitudinally oriented molecule as a function of the tip-molecule separation is shown in figure 5.6c. An enhancement of ∼200-fold is observed and, it is important to note, quenching was never observed for a single molecule imaged with a sharp pyramid antenna.

TERS imaging of carbon nanotubes was also demonstrated with the pyramid tip and further explored hyperspectrally in chapter 6. Presented in figure 5.7 is near-field G-band imaging of a highly-enriched sample of (10,3) nanotubes on a glass substrate. The sample was excited with a 632.8 nm He-Ne laser, which is resonant with the nanotube, and the Raman G-band image was formed by raster-scanning the sample and filtering the scattered light through a narrow bandpass filter centered on the G-band. An optical spatial resolution of 19.9 nm was mea-
The full spectrum, both in the near-field and far-field, was used to calculate a local field enhancement, corresponding to the collected Raman scattering rate, at the antenna apex of 7.6.

5.3.3 Pyramid simulations

Given the experimental geometry, where the sample is excited from below and the scattered light is collected with the same objective, finite-difference time-domain (FDTD) calculations of the backwards radiation efficiency of a single dipole emitter were performed, shown in figure 5.8. Here, the backwards radiation efficiency is defined as the radiation flux through the lower-half-space of the figure normalized by the radiation flux for an isolated dipole. A longitudinally oriented dipole (figure 5.8a) was chosen as it exhibits the largest enhancement. Simulations were then performed to understand how the pyramid geometry, specifically the cone angle $\alpha$, determines the backwards radiation efficiency as a function of wavelength, figure 5.8b.
It was found that the large cone angle afforded by the silicon crystal structure allowed for a large enhancement of the backwards radiation efficiency. Specifically, if the tip couples to the emitter in the so-called adiabatic limit, corresponding to small $\alpha$, it is expected that there will be a maximum amount of radiation coupled into propagating surface plasmons on the antenna. The mode mismatch between non-radiative modes of the dipole and propagating surface plasmons along the pyramid surface, provided by the sharp antenna apex and large cone angle, result in a large enhancement. Similar results were also found for a cone antenna (not shown).

### 5.4 Conclusions

As demonstrated in chapter 4, the single particle antenna was insufficient for some applications and it was necessary to develop an antenna that was equally reproducible but offered a greater enhancement-to-confinement ratio. This was demonstrated first with the cascaded particle antenna where large particles allowed for large optical cross sections while smaller particles localized the field into
a small volume. That work paved the way for the pyramid antenna that could easily be mass fabricated and offered a similar enhancement-to-confinement ratio.

The pyramid antenna, which provided a large local field enhancement at the antenna apex performed well for TERS applications. Rather surprisingly, however, the pyramid antenna also performed very well, exceeding the cascaded particle antenna, for applications in near-field fluorescence microscopy. The surprise came in contrast to the etched metallic wire that, due to the inherently small cone angle, generally provides an overall quenching of fluorescence emission at short tip-molecule separations. Correspondingly, simulations did show that a significant amount of energy was passed into the pyramid antenna. Three properties of the pyramid prevented a net fluorescence quenching: (1) a nearly plane-mirror geometry that allowed for an enhancement of collected fluorescence emission of up to a factor two by the redirection of radiation and the combined effects of (2) the large cone angle and (3) sharp antenna apex that created a strong mode mismatch between fluorescence emission and propagating surface plasmons on the metal film. Altogether, the pyramid allowed for fluorescence enhancement at very short tip-molecule separations.
6 Optical spectroscopy of carbyne

Long linear-chain carbons in double-walled carbon nanotubes (LLCCs) are an ideal structure to study with near-field microscopy. As discussed in chapter 3, LLCCs have a length dependent Raman response and an electronic resonance that is in the visible spectrum. Prior to the work in this thesis, only ensemble far-field optical measurements of these LLCCs have been performed [3, 4, 5], and no other long LCCs in other systems have been individually studied.

Ensemble measurements have shown many interesting properties of the LLCCs, including the temperature dependence of the LLCC-band intensity, frequency, and FWHM along with a possible coupling between the linear chain and the host nanotube Raman modes. What has been lacking in previous work is fundamental to ensemble measurements: it is impossible to determine, with certainty, the subset of the sample being measured. A direct experimental study of individual LLCCs was required to confirm results, and in fact go beyond the ensemble measurements by identifying experimental outliers. The results presented in this chapter do just that, both identify that the majority of measured LLCCs behave as expected while there is a small subset with properties that may require an additional theoretical understanding. The work presented in this chapter has been published in references [3, 4, 5].
6.1 Individualized LLCC sample preparation

Given the previous development of the near-field microscope and optical antennas, the biggest challenge of studying LLCCs is the sample preparation. The bulk LLCC sample, as prepared in [? ? ], is a dense sheet of mostly doubled-walled nanotubes that are partially filled with LCCs. The sample requires individualization by dispersion and suspension in a fluid. Standard nanotube dispersion procedures generally use ultra-sonication in water with a surfactant. It is, however, well known that carbon nanotubes are physically cut by ultra-sonication [? ? ], and I have experimentally observed that ultra-sonication greatly reduces the present LLCC-band signal, suggesting that the LLCCs are highly-susceptible to breaking.

Despite this challenge, initial samples were successfully suspended in 2% w/w sodium dodecyl sulfate (SDS) or deoxycholate (DOC) in water. Following ultracentrifugation (14,400 g for varying times) it was possible to isolate individual DWCNTs with generally short (<100 nm), but intact, carbon chains. In order to preserve longer chains, different solvents including ethylene glycol (EG) [? ] and 1,2-dichloroethane (DCE) [? ] were used. It was found that EG did disperse the nanotubes better than other chemicals, however, it also left a thick residue that rendered the sample unusable for TERS.

Nanotubes were dispersed in DCE for most of the results presented. For this, the raw nanotube sample was placed in DCE for several days and periodically bath sonicated for 5 min periods until the sample appeared dispersed by eye (a brown fluid). At this point an additional bath sonication for 30 min was performed. The sample was then centrifuged for 2 hrs at 14,400 g. The supernatant had large amounts of catalyst and it was therefore removed. Below the first quarter of fluid, there were many individualized tubes and small bundles that were spin cast onto a glass coverslip spinning at 1,500 rpm.
In a hope to study even longer LLCCs (on the order of 1 µm), I suspended nanotubes in chlorosulfonic acid (CSA) \([? ? ?]\). In this method, CSA reversibly protonates the sp\(^2\) hybridized bonds, causing the nanotubes to repel each other and spontaneously suspend without sonication. Once suspended, the nanotubes can be deposited on a glass surface by drop coating. Specifically, the CSA solution was placed on a coverslip for 15 min and then quenched with chloroform for 30 min. The sample was baked at 115°C for 20 min to promote surface adhesion of the nanotubes before deprotonating the nanotubes by rinsing in diethyl ether for 5 mins. The sample was dried at 115°C for 20 min before being rinsed in deionized-water and dried with N\(_2\). This method did provide both physically long nanotubes (no sonicative cutting) and an abundance of LLCCs. Unfortunately, all of my sample preparations were performed in an open environment (not in a water-free glove box) which reduced the acidity of the CSA. Optimization of the sample preparation in an Argon glove box is an ongoing collaboration.

The concentration of nanotubes in their solvent was not quantified. This was because I did not have access to a sensitive balance and therefore could not quantify the concentrations. If the concentration of nanotubes was too high to be fully suspended, the unsuspended nanotubes were removed by the ultracentrifugation step or, in many cases, simply by settling for a few days.

### 6.2 Raman spectroscopy results

Much of the study of individualized LLCCs can be done by far-field optical methods. Far-field measurements allow for the control of parameters (including excitation power and polarization) on an absolute scale. In contrast, the absolute intensity at a near-field antenna apex is difficult to quantify and there is no control of the polarization properties for the standard pyramid antenna. In this way, a combination of near-field microscopy (to identify individual LLCCs and their
lengths) combined with far-field microscopy (to study power and polarization properties) is ideal.

6.2.1 Far-field Results

Individual LLCC far-field measurements were taken in an inverted confocal microscope, in the same configuration as the near-field setup described in figure 2.1; however, in this case the AFM was not installed and the polarization of the laser excitation could be freely modified. This experimental geometry allowed for both power and polarization dependent characterization of the LLCCs. Figure 6.1 shows the typical behavior of a single LLCC in the far-field. In figure 6.1a, the spectrum of the G-band ($\sim 1590 \text{ cm}^{-1}$) and LLCC-band ($\sim 1800 \text{ cm}^{-1}$) are shown. It is clear that the intensity of the LLCC-band far exceeds the G-band, and the FWHM of the LLCC-band is much narrower. The Raman intensity of the LLCC-band (figure 6.1b) shows that there is a linear increase in Raman mode with power. This is the same for the G-band as shown by the ratio of the two Raman modes in figure 6.1c. These results were observed for all chain lengths and excitation powers.

![Figure 6.1](image)

**Figure 6.1** – Typical behavior of an individual LLCC as a function of far-field excitation power. (a) The spectrum of the G-band ($\sim 1590 \text{ cm}^{-1}$) and LLCC-band ($\sim 1800 \text{ cm}^{-1}$) with increasing laser excitation powers. (b) The integrated intensity of the LLCC-band and (c) the integrated intensity ratio of the LLCC-band to G-band, as a function of excitation power. ($\lambda_{ex} = 647.1 \text{ nm}$)

For all LLCCs measured, there was also an observed relationship between
the LLCC-band intensity, frequency, and FWHM, shown in figure 6.2. As the excitation power was increased, the emission intensity increased linearly, shown in figure 6.2a. Correspondingly, there was a softening of the Raman mode and an increase in the FWHM (figure 6.2b). This behavior of the LLCC-band was also observed as a function of the polarization of the far-field excitation. It is seen that the intensity of the LLCC-band (figure 6.3a) is modulated as a \( \cos^2(\theta) \) function \( (R^2 = 0.98) \), where the small offset (12 a.u.) is likely due to physical nonlinearities in the LLCC. The frequency and FWHM of the LLCC-band are also modulated as a shifted, offset \( \cos^2(\theta) \) function \( (R^2 = 0.80 \text{ and } 0.92, \text{ respectively}) \), shown in figure 6.3b. Here, the frequency softening and linewidth broadening are attributed to sample heating as has been observed in different Raman modes of carbon nanotubes [?].

![Figure 6.2](image)

**Figure 6.2** – Typical behavior of an individual LLCC as a function of far-field excitation power. (a) The integrated intensity of the LLCC-band increases linearly with the excitation power. (b) The LLCC-band softens with the excitation power (red) and, correspondingly, the FWHM of the mode increases (blue). \( (\lambda_{ex} = 647.1 \text{ nm}) \)

### 6.2.2 Near-field Results

TERS of the LLCCs goes beyond far-field measurements by enabling a study of the localized interaction between the various Raman modes present in the sample. For example, current theory [? ] suggests that the Raman mode of the LLCC
Figure 6.3 – (a) The intensity (black) and (b) the frequency (red) and FWHM (blue) of the LLCC-band as a function of the excitation polarization. \((P = 750 \mu W, \lambda_{ex} = 632.8 \text{nm})\)

can be modeled as a coupled system between the inner nanotube RBM and the LLCC, such that they are both excited simultaneously. Additionally, the high spatial resolution of TERS allowed for the measurement of the physical size of the LLCC along with its spectrum.

Before any quantitative statements can be made, it is necessary to understand in what way, if any, the near-field spectrum of the LLCC may differ from the far-field spectrum. Shown in figure 6.4 are the normalized near-field and far-field spectra of two unique LLCCs. A softening of the LLCC-mode \((\sim 1 \text{ cm}^{-1})\), along with a slight broadening of the mode, is always observed. This near-field interaction can be understood as an effect from the enhanced excitation fields, the same as was observed in far-field optical measurements (figures 6.2, 6.3).

For all of the measurements presented, it was necessary to first experimentally ensure that only individual, continuous, LLCCs were being studied. TERS has the ability to characterize and correlate the physical size of samples with their optical properties. This is especially important for LLCCs since they are too long to be directly measured in the TEM and still too short to be measured with far-field optical methods. The length, and corresponding spectrum, of 11 LLCCs measured in the near-field are shown in figure 6.5. It can be seen that many of the data...
Figure 6.4 – The normalized near-field (blue) and far-field (orange) spectrum of two (a,b) unique LLCCs. A softening of the Raman mode (∼1 cm⁻¹) is observed in the near-field, along with a slight broadening of the mode. (P = 575 µW, λ_ex = 647.1 nm)

points show a Raman frequency that is harder than theory predicts and three data points are significantly shifted in frequency. For measurements that only deviate from theory by a few wavenumbers, it is possible that theory has predicted the minimum Raman mode energy. Experimentally, it was observed that the Raman mode softens with increasing excitation power, so it is possible that with an increased excitation power the experimental results would agree better with theory. Currently, it is unclear why some data points deviate more significantly. This is an area of ongoing work and a discussion of possible explanations is presented in the conclusions.

Near-field hyperspectral imaging of the LLCCs has, indeed, revealed localized interactions between the LLCC-band and the Raman modes of the DWCNT. Shown in figure 6.6a is the superposition of a near-field Raman image (color) of the LLCC-band and the corresponding DWCNT topography (grayscale). The physical lengths of the LLCCs in the image (200 – 800 nm) are correlated with their respective Raman shifts (1804 – 1786 cm⁻¹), the results of which are included in figure 6.5. The TERS spectrum of the LLCC is presented in figure 6.6b for the points labeled with the diamond, circle, and square. Depending on the
Figure 6.5 – The distribution of the TERS measured physical lengths of LLCCs plotted with respect to the corresponding TERS frequency. The blue line presents the predicted values based on theory.

sampled position, the relative intensity of the different Raman modes varies, with some modes nearly vanishing at specific locations. In general, the observed modes include the outer nanotube RBM at $\sim 204 \text{ cm}^{-1}$, the inner nanotube RBM at $\sim 362 \text{ cm}^{-1}$, the D-band at $\sim 1315 \text{ cm}^{-1}$, and the G-band at $\sim 1590 \text{ cm}^{-1}$, in addition to the LLCC-band at $\sim 1800 \text{ cm}^{-1}$.

Figure 6.7a shows the hyperspectral intensity for an approach curve on a single LLCC for both the LLCC-band and the G-band. The fluctuations in the G-band intensity are a result of the relatively weak G-band signal when an LLCC is present. A shift in the Raman frequency of the LLCC-band is observed as the tip-sample separation is decreased, likely related to the enhanced excitation fields
at the antenna apex (figure 6.7b). The same effect is observed in cross sections of near-field hyperspectral images, where the antenna is effectively approached from the side of the LLCC instead of above the LLCC (not shown).

### 6.3 Conclusions

Despite the wealth of information on the optoelectronic properties of LLCCs acquired through ensemble measurements, it was necessary to observe the behavior of individualized LLCCs to fully understand their optoelectronic properties. Far-field measurements, as presented above, offer a wealth of information, but near-field measurements are the only way to confirm that individual LLCCs are being studied, and therefore validate results from far-field measurements.
TERS has also been necessary to confirm the existence of long LLCCs. The sample is too long for a single chain to be completely measured in the TEM and too short for far-field optical measurements, leaving TERS as the only method to measure lengths of hundreds of nanometers with nanometer precision. TERS confirmed the existence of LLCCs with lengths on the order of 1 µm. Theory has successfully predicted the Raman frequency of many of the observed chains; however, there were experimental outliers that demonstrate the current theory may be incomplete.

Initially, it was considered that the outlying data points may represent a single LLCC that has fractured into many smaller, but closely spaced, LLCCs. In this case, there would be a significantly broadened FWHM since each chain segment would emit at its own, unique, frequency. The measured FWHMs ranged between $\sim 7 - 14 \text{ cm}^{-1}$, and no relationship between the deviation of the Raman frequency predicted by theory and the FWHM was observed. Other possible explanations for their frequency include charge transfer from the specific chirality of inner nanotube (ongoing theoretical work) or even the possibility of a fully suspended chain, such that the ends of the chain are supported by two separate inner nanotubes, and
the length of the chain is only contained by the outer nanotube. One experiment that could determine the relative contribution of the chain length and the host nanotube to the Raman frequency would be to measure an LLCC in the near-field, experimentally cut it (i.e., helium-ion FIB), and then measure it again. If the host nanotube determines the Raman shift, it would remain constant, but if the Raman shift is determined by the LLCC length, both segments should have a higher-frequency mode after cutting.

The length dependent measurements also revealed a complex interaction between the different Raman modes of the system. This highlights the need for the high spatial resolution afforded by near-field techniques. Studies of LLCCs in nanotubes have both predicted [?] and measured [?] shifts in the RBM upon filling, while other studies have noticed a dramatic decrease in the RBM of a Mo-filled nanotube [?]. Unfortunately, the precise interaction between the different modes has remained elusive due primarily to the limited number of chains sampled inside of nanotubes with resonant RBMs.

As demonstrated in chapter 5, an approach curve can be used to measure the fields at the antenna apex. Additionally, as demonstrated by Beams et al. [?], it is possible to discern the spatial coherence properties of a sample with an approach curve. The weak G-band signal makes it difficult to make a quantitative analysis between the functional form of the approach curve for the two modes. This method, however, remains a possibility for determining the LLCC coherence properties, especially if a resonant nanotube is found, such that the G-band signal is greater.
7 Measuring partial optical coherence

Thomas Young’s experiments are perhaps the most well-known study of optical field correlations that can be measured with interference fringes \( ? \). The interference fringes that are observed are explained by the superposition of optical waves, one each coming from two spatially separated sources \( ? \). The contrast between the bright and dark fringes defines the visibility and contains information of the degree of correlations (amplitude and phase) between the optical fields \( ? \). For two points in space, the degree of optical correlations is termed the spectral degree of coherence \( ? \). I propose that the LLCC system offers the potential to demonstrate a non-zero spectral degree of coherence at length scales approaching a single wavelength, at room temperature.

This idea stems from the observation that the length of the LLCC determines its Raman frequency \( ? \), suggesting that the chain is aware of its length. It is therefore conceivable that the Raman active vibration is delocalized along the length of chain. For LCCs, experimentally there appears to be a saturation of the Raman frequency after around 50 carbon atoms \( \sim 6.5 \text{ nm} \) \( ? \), but there are still shifts in the Raman frequency of 10s of wavenumbers for 150 nm and longer chains \( ? \). Considered classically, the length of chain that determines its Raman frequency \( > 150 \text{ nm} \) would emit as an antenna, such that each Raman scattered photon, that is by definition fully coherent with itself, is delocalized across the
given length of chain. This suggests that there will be partial coherence on even longer length scales.

In order to probe these distance (that are likely too large to be measured in the near-field by the method presented by Beams et al. [? ]), I developed a simple, but robust, method to perform a two-pinhole diffraction experiment with diffraction-limited resolution.

\section*{7.1 Coherence measurement methods}

Several research groups have developed methods to measure the spectral degree of coherence of excitonic systems [? ? ? ]. These systems exhibit coherence on lengths scales that are on the order of a few wavelengths and therefore are a good reference point of possible methods to measure the spectral degree of coherence of the LLCCs. One demonstrated method to map the coherence function of polariton condensates is shift interferometry. In this method, two images of the source are superimposed (in space and time) and then controllably shifted, in either space or time, relative to each other. The appearance of interference fringes, and their visibility as a function of displacement, maps the system’s complex degree of coherence.

Several geometries for shift interferometry are possible. Kasprzak et al. [? ] used a Michelson interferometer to superimpose and then shift two magnified images of a Bose-Einstein condensate. They also used a retroreflector to invert one of the images to map the coherence function in a single interference pattern. High et al. [? ] used a Mach-Zehnder interferometer to introduce a small angular deviation in one of the beam paths and extract the coherence function. These methods demonstrate the versatility of shift interferometry, but both methods are difficult to align, require several measurements which costs time and requires stability, and use only half of the available photons due to the necessary use of
beam-splitters.

For the LLCCs, that are on the order of 1 – 3 diffraction-limited spot widths in length, it is only necessary to look at the spectral degree of coherence between two specific points on the chain (either the ends or points with a given separation) and to do so without losing any photons (as there are only few available Raman photons). Due to the short length scales being measured, it is necessary to ensure that there are no coherence artifacts introduced by defocus and that the locations of interest are in fact the locations sampled.

A Young’s double-slit experiment, for example the one implemented by Deng et al. [?], is very appealing, however the one-dimensional nature of the LLCC favors a two-pinhole experiment. In a double-slit interference measurement, generally the spatial extent of the light source along the length of the slits is large enough that diffraction effects, due to the finite extent along that dimension, can be neglected. These effects cannot be neglected for the linear chain and therefore a non-intuitive diffraction pattern is observed. Replacing the slits with pinholes removes all ambiguity in the diffraction pattern (spherical waves are emitted from each pinhole).

### 7.1.1 Experimental methods

A two-pinhole interference experiment, similar to the geometry introduced by Deng et al. [?], has been implemented. This is done by modifying the standard microscope geometry described in figure 2.1. First, a wide-field laser excitation is used to illuminate the whole LLCC and the detection pathway is modified as shown in figure 7.2. The microscope creates an intermediate image defined by the objective and the microscope tube lens. That intermediate image is then imaged with a two lens afocal imaging system, creating the “image”. The image plane is then either imaged or Fourier transformed onto a CCD for detection. An inten-
Figure 7.1 – Schematic diagram of the experimental setup used for coherence measurements. An external two lens afocal system is placed outside of the microscope, forming an image in the “image plane”. The image plane can be spatially filtered with two-pinhole mask and either imaged or Fourier transformed onto a CCD for detection.

The diffraction mask pinholes were fabricated by FIB milling into a 300nm thick chromium or titanium film on a glass substrate (figure 7.2). Using the FIB allowed for a thick, opaque, metal film to be used without the problems associated
with lift-off from EBL fabrication methods. Discussed in the following section, the physical diameter of each pinhole was fabricated so that it was smaller than the point spread function (PSF) of the whole system, such that it was transmitting light from a diffraction-limited spot in the sample plane. The pinhole spacing was determined by scaling the distance between the two points of interest in the sample plane by the system magnification, ensuring that the inner edge of the pinholes is never closer than the FWHM of the PSF. As such, it was decided to keep the system magnification fixed and fabricate pinholes of the desired spacing.

Measurements were performed by first imaging the sample onto the CCD. Then, the pinholes were positioned into the image plane such that the sample emission was illuminating the two pinholes. This was confirmed by imaging the illuminated pinholes directly onto the CCD. Finally, the imaging lens in front of the CCD camera was replaced with the Fourier transform lens such that a diffraction pattern was recorded by the CCD camera. The Fourier transform of the pinholes, the interference pattern, was then computationally analyzed (discussed below) to extract the spectral degree of coherence.

**Figure 7.2** – SEM image of fabricated 15 μm diameter pinholes with a 40 μm center-to-center separation in a 300 nm thick chromium film.
7.1.2 Theoretical methods

The theoretical background for accurate coherence measurements depends critically on a well calibrated optical system. The challenge rests in coherence artifacts introduced by the system’s PSF. Specifically, a point in the object plane will be imaged to an Airy function in the image plane due to diffraction from the optical elements. The size of the Airy function also depends critically on any defocus present in the system. For a diffraction limited system, the FWHM of the Airy function is defined by the lowest resolution optic and the system’s magnification. A detailed computational analysis of my system’s PSF, along with direct measurements of the PSF, is presented in appendix A. In practice, the spectral degree of coherence of the sample will in fact be a measure of the spectral degree of coherence of the sample convolved with the system’s PSF.

The spectral degree of coherence is calculated from the image of the pinholes illuminated by the sample and the recorded interference pattern. The pinhole image will be used to extract the intensity illuminating each pinhole which, ideally, would be equal. The interference pattern will be computationally two-dimensionally Fourier transformed to extract the energy in the zero-order and first-order frequency components. The full theoretical background for the necessary calculation is derived in reference [225], and the magnitude of the spectral degree of coherence $\mu_d$, hereafter referred to as the visibility, is given by,

$$|\mu_d| \approx \frac{(k_L + k_R) \int |\alpha| df_x df_y}{\sqrt{k_L k_R} \int |\beta| df_x df_y}.$$  \hspace{1cm} (7.1)

Here, $k_{L,R}$ is the integrated intensity of the illuminated left and right pinholes, respectively, $\alpha$ is the integrated energy in one of the first-order lobes, and $\beta$ is the integrated energy in the zero-order lobe.

Calculations of the expected visibility, for the experimental geometry in figure [7.1], of a completely incoherent 1 $\mu$m long linear source emitting at 715 nm
(simulating the LLCC) are 5.12% and 11.25% for pinholes that are 15 µm in diameter with a center-to-center separation of either 60 µm or 40 µm, respectively. These pinhole separations correspond to 800 nm and 533 nm in the object plane, respectively. The anticipated non-zero visibility, as discussed in appendix A, is an artifact of diffraction.

7.2 Reference measurements

In order to validate measurements of the LLCC coherence, it is first necessary to ensure that the optical system is performing as expected. This means that the system needs to be calibrated with a perfectly coherent and a completely incoherent source. I have demonstrated both sources by using a gallium arsenide nanowire (GaAsNW). The coherent source is Rayleigh scattered, coherent, laser light at 715 nm from a cw-Ti:Sapph laser. The incoherent source is the GaAsNW photoluminescence at 715 nm after being excited by a 632.8 nm He-Ne laser.

The results from the coherent source are shown in figure 7.3. For this measurement, a dark-field geometry was employed by using a low-NA excitation and a high-NA collection, facilitated by inserting a Fourier mask into the Fourier plane of the collected light. It can be seen that a perfect dark-field geometry is not achieved, adding to noise in the recorded optical signal. Still, a visibility of 91.2% is measured for the 15 µm diameter pinholes with a center-to-center separation of 60 µm, approaching a perfectly coherent optical source. In fact, simulations show that a small amount of random noise can reduce the measured visibility by 10% or more.

Figure 7.4 shows the same measurement for the photoluminescence of the GaAsNW excited with a He-Ne laser. The same pinholes are used but an optical interference filter is used instead of the Fourier filter in the detection pathway. In this case, it is quite clear from the optical Fourier transform (figure 7.4c) that
there is only minimal optical coherence. The visibility was 5.3%, only slightly higher than the anticipated coherence for an incoherent source. This error could be due to noise or a small amount of defocus. From several measurements I have concluded that my measured visibility varies with a value of ±1%.
Figure 7.5 – Coherence of the LLCC-band Raman scattered light. (a) A real space image of the LLCC-band Raman scattered light. (b) A real space image of 15 μm diameter pinholes with a 60 μm center-to-center separation illuminated by the scattered light. (c) The optical Fourier transform of the illuminated pinholes. The measured visibility is 5.2%. (λ = 715 nm).

7.3 LLCC coherence

With a well calibrated optical system, the remaining challenge was simply to isolate a continuous, long, LLCC. Shown in figures 7.5a and 7.6a is a real space image of such a chain. Although the chain is curved, it has a length of over 900 nm and therefore the linear portion of the chain is ideal for the coherence measurements. Measurements were first made using the 60 μm center-to-center spaced pinholes, shown in figure 7.5. While the strong Raman scattering of the LLCC did allow for wide-field Raman imaging, the measured visibility was only 5.2 ± 1%, again representative of a completely incoherent source.

In order to further probe the optical coherence of the LLCC, additional pinholes, with a center-to-center separation of 40 μm were fabricated, corresponding to 533 nm in the object plane. Those measurements, shown in figure 7.6, found a spectral degree of coherence of 10.5 ± 1%. Again, those results are consistent with a completely incoherent source.
Figure 7.6 – Coherence of the LLCC-band Raman scattered light. (a) A real space image of the LLCC-band Raman scattered light. (b) A real space image of 15 µm diameter pinholes with a 40 µm center-to-center separation illuminated by the scattered light. (c) The optical Fourier transform of the illuminated pinholes. The measured visibility is 10.5%. ($\lambda = 715$ nm).

7.4 Conclusions

I have developed an experimental geometry to measure the spectral degree of coherence of a one-dimensional sample for length scales on the order of a single wavelength. The system is based on a two-pinhole diffraction experiment but is designed such that the pinholes can be carefully, and reproducibly, aligned with respect to the sample. The method has the potential to out-perform shift interferometry methods when photons are scarce and the spectral degree of coherence is of interest.

The optical system was calibrated by measuring the coherence of Rayleigh scattered laser light (perfectly coherent) and photoluminescence light (completely incoherent). Good agreement is found between the measured visibility and that predicted by calculations (<1% error for incoherent measurements, and $\sim$10% error for coherent measurements). Measurements are highly reproducible ($\pm$1%) with all samples.

The spectral degree of coherence of an LLCC was measured by first performing wide-field Raman imaging of a single LLCC. The Raman emission was then diffracted through pinhole pairs (of two different separations) in order to study
the spectral degree of coherence at different separations (as small as 533 nm) in
the LLCC. So far no optical coherence, beyond that expected from the PSF of
the system, has been observed. This may be due to the unique properties of the
chain measured or that there is no optical coherence on these lengths scales in the
LLCC.

The motivation for studying optical coherence in the LLCC is based on the Ra-
man mode softening as the chain length increases. This is explained by a decrease
in the BLA as the chain length increases and may not cause a delocalization of
the Raman scattered photon. Further measurements and theoretical calculations
are needed to fully understand the system.
8 Conclusions and outlook

As demonstrated in chapter 5, it is now technologically feasible to reproducibly fabricate and employ optical antennas with a large enhancement-confinement ratio for near-field imaging and spectroscopy. The antennas presented in this thesis regularly achieve a spatial resolution of 15 – 20 nm, provide a fluorescence enhancement of up to 200, and a TERS enhancement of more than 10. These parameters, not achievable with earlier antenna geometries (see chapter 4), will allow for the characterization of the next generation of carbon nanophotonic devices.

As was demonstrated by using the particle antenna for biological imaging, there is potential for near-field microscopy to study clinically relevant samples, provided that the resolution and reproducibility of the method is improved. Theoretical studies have proposed a possible improved antenna geometry that I have experimentally confirmed with the cascaded particle antenna. Although the antenna provided a large enhancement-confinement ratio and was reproducible, its fragile geometry and challenging serial fabrication made it impractical for general imaging and spectroscopy. Building on the theoretical understanding of the cascaded particle antenna, and utilizing the knowledge-base of silicon fabrication and template stripping, a new highly-reproducible mass-fabricated pyramid antenna was developed. The pyramid antenna provides similar performance to the cascaded particle antenna and its fabrication methodology makes it very usable.
to researchers outside of the optical physics community.

The main value of near-field microscopy is in the high spatial resolution and spectral sensitivity that it provides. While not all systems require high spatial resolution (exceeding traditional optics by more than an order-of-magnitude), it is vital to isolate single molecules, characterize them, and therefore validate far-field optical measurements. I demonstrate the necessity of near-field microscopy in my study of LLCCs.

The optoelectronic properties of nanocarbons are dependent on their shape, chemical bonds, and defect density. These inherently nanoscale features are ideally suited for study with near-field microscopy as has been previously demonstrated [?]. The antennas developed in this thesis have been able to reproducibly isolate and study a novel nanocarbon system, the LLCCs. While many of the results presented are from far-field optical measurements, near-field microscopy is the only way that an individual LLCC can be isolated. The measurements not only provide diagnostic capabilities, but also are necessary for understanding the system to support the development and improvement of the theoretical framework.

The antennas developed within this thesis represent a pathway to potentially more complex and interesting antenna geometries and experimental systems. For example, the recent interest in chiral photonics inspires a desire for chiral antennas and near-field chiral sensing. Such antennas should be possible using template stripped fabrication methods [?]. Additionally, these antennas are ideal for studying other material systems such as superconducting photodetectors, where the spatial resolution provided by the antenna could potentially validate the vortex entry-assisted detection model [?]. Commercialization of these antennas will greatly promote near-field microscopy by making the field accessible to a wide range of researchers.
A Coherence simulations

As presented in figure 7.1, the specifications of my system are as follows: the sample is placed on a glass–air interface ($n_{\text{glass}} = 1.518$, $n_{\text{air}} = 1$). A high-NA (NA/1.4) oil ($n_{\text{oil}} = 1.518$) objective is used to collect light emitted into the substrate. The objective has a focal length of 2 mm and a back aperture of 5.6 mm. The light then propagates only through air and is focused by a tube lens ($f_{\text{tube}} = 200$ mm) before being re-collimated by an additional lens ($f_{\text{lens}} = 200$ mm). The collimated light is then focused onto the two-pinhole mask by a lens ($f_{\text{image}} = 150$ mm). For all of the calculations considered here, the propagation of a collimated beam is said to be free from diffraction and the two 200 mm lenses are neglected. The wavelengths considered are 632.8 nm and 715 nm corresponding to a He-Ne laser emission and the LLCC-mode for a chain excited with a He-Ne laser, respectively. Experimentally, 715 nm laser light is obtained from a tunable cw-Ti:Sapph laser.

A.1 Calculating the system’s PSF

In order to find the PSF of the system, I propagated the fields of a dipole emitting at a glass-air interface into the objective and then refracted the optical emission to find the fields in the back aperture plane of the objective. Then, neglecting
diffraction through propagation and the two 200 mm lenses, refracted the light again for the final focusing element and propagated the light to the focus. The following derivation follows from Novotny and Hecht [? ].

A.1.1 Dipole emission at a glass-air interface

There are several ways to do this step analytically. Here, I begin with the electric field $\mathbf{E}(\mathbf{r})$ at a position $\mathbf{r}$, from a dipole located at a position $\mathbf{r}_0$, as,

$$ \mathbf{E}(\mathbf{r}) = \frac{\omega^2}{\epsilon_0 c^2} \mathbf{G}(\mathbf{r}, \mathbf{r}_0)p. \quad (A.1) $$

Where, $\omega$ is the angular frequency of light, $\epsilon_0$ is the permittivity of free space, $c$ is the speed of light in vacuum, and $p$ is the dipole moment. The Green’s function $\mathbf{G}(\mathbf{r}, \mathbf{r}_0)$ is given as,

$$ \mathbf{G}(\mathbf{r}, z_0 = 0) = \frac{i}{8\pi^2} \int_{-\infty}^{\infty} \int \mathbf{M} \exp ik_x x + k_y y dk_x dk_y, \quad (A.2) $$

where, $x, y$ and $k_x, k_y$ are the real space and Fourier space coordinates perpendicular to the optical axis, respectively, and $\mathbf{M}$ is a matrix defined below. The Green’s function is also given as,

$$ \mathbf{G}(\mathbf{r}, z_0 = 0) = \frac{i}{8\pi^2} \mathcal{F}^{-1}\{\mathbf{M}\}. \quad (A.3) $$

The equation can be simplified by,

$$ \mathbf{E}(k_x, k_y; z = 0) = \mathcal{F}\{\mathbf{E}(\mathbf{r}; z = 0)\} \quad (A.4) $$

$$ = \mathcal{F}\left\{ \frac{\omega^2}{\epsilon_0 c^2} \frac{i}{8\pi^2} \mathcal{F}^{-1}\{\mathbf{M}\}p \right\} \quad (A.5) $$

$$ = \frac{\omega^2}{\epsilon_0 c^2} \frac{i}{8\pi^2} \mathbf{M}p. \quad (A.6) $$
The field at the source can be related to the field on the reference sphere by,

\[ E(k_x, k_y; z = 0) = \frac{ir \exp -ikr}{2\pi k_z} E_\infty(\frac{k_x}{k}, \frac{k_y}{k}), \tag{A.7} \]

where, \( k_z \) is the Fourier space variable along the optical axis. Finally, it is found that,

\[ E_\infty(\frac{k_x}{k}, \frac{k_y}{k}) = \frac{\omega^2}{\epsilon_0 c^2} \frac{k_z}{r} \exp ikr \bar{\mathbf{M}}. \tag{A.8} \]

The matrix \( \bar{\mathbf{M}} \) is given by,

\[ \bar{\mathbf{M}} = \bar{\mathbf{M}}_s + \bar{\mathbf{M}}_p, \tag{A.9} \]

where,

\[ \bar{\mathbf{M}}_s = \frac{t_s(k_x, k_y)}{k_z^2(\frac{k_x^2}{k_z} + \frac{k_y^2}{k_y})} \begin{bmatrix} k_y^2 & -k_x k_y & 0 \\ -k_x k_y & k_x^2 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{A.10} \]

and,

\[ \bar{\mathbf{M}}_p = \frac{t_p(k_x, k_y)}{k_1 k_2 (\frac{k_x^2}{k_z} + \frac{k_y^2}{k_y})} \begin{bmatrix} k_2 k_z & k_x k_y k_z & k_x (k_x^2 + k_y^2) k_z / k_z^2 \\ k_2 k_y k_z & k_y^2 k_z & k_y (k_x^2 + k_y^2) k_z / k_z^2 \\ k_x (k_x^2 + k_y^2) & k_y (k_x^2 + k_y^2) & (k_x^2 + k_y^2)^2 / k_z^2 \end{bmatrix}. \tag{A.11} \]

\( t_s \) and \( t_p \) are the standard Fresnel transmission coefficients given by,

\[ t_s(k_x, k_y) = \frac{2\mu_2 k_{z_1}}{\mu_2 k_{z_1} + \mu_1 k_{z_2}}, \tag{A.12} \]

and,

\[ t_p(k_x, k_y) = \frac{2\epsilon_2 k_{z_1}}{\epsilon_2 k_{z_1} + \epsilon_1 k_{z_2}} \sqrt{\frac{\mu_2 \epsilon_1}{\mu_1 \epsilon_2}}. \tag{A.13} \]

Here, \( \mu_{1,2} \) and \( \epsilon_{1,2} \) are the permeability and permittivity of the two media, respectively. With this, there is an analytic solution for the field of a dipole at an interface on a reference sphere.
Figure A.1 – The intensity of the emission of a y-dipole in the back focal plane of the objective. The outer ring represents NA 1.4, while the inner ring is NA 1.0.

A.1.2 Refraction

Again, there are a few ways to deal with refraction. The simplest method is to convert the $\theta$ component of the electric field into the $\rho$ component (or vice versa), while keeping the $\phi$ component of the field unchanged. Additionally, the amplitude of the fields needs to be scaled by $\sqrt{\frac{n_1}{n_2} \cos \theta}$. This mapping between spherical and cylindrical coordinates requires an aplanatic lens and paraxial fields. Refraction at the objective is then given by,

$$E_{bfp} = \frac{1}{\sqrt{\frac{n_1}{n_2} \cos \theta}} [E_\infty(\theta, \phi) \cdot n_\rho] n_\rho + [E_\infty(\theta, \phi) \cdot n_\phi] n_\phi,$$  \hspace{1cm} (A.14)

and, refraction at the final lens is given by,

$$E_\infty^2 = \sqrt{\frac{n_2}{n_3} \cos \theta} [E_{bfp}(\theta, \phi) \cdot n_\theta] n_\theta + [E_{bfp}(\theta, \phi) \cdot n_\phi] n_\phi.$$  \hspace{1cm} (A.15)

Figure A.1 is the intensity at the back focal plane of the objective for a y-dipole (simply a rotated x-dipole).
A.1.3 Forming an image

This is a step where an integral cannot be avoided. Although, due to the low-NA focusing of the final optical element, it may be possible to simply do a Fourier transform for this step (or a Fourier transform with a modified kernel); however, I found it best to do it with a Riemann sum so that the physical coordinates in the optical focus are clearly defined.

This integral is as follows,

\[
E(x, y, z) = \frac{i f \exp(-ikf)}{2\pi} \int \int_{(k_x^2 + k_y^2) \leq k^2} E_\infty(k_x, k_y) \exp \left( i(k_xx + k_yy \pm k_zz) \right) \frac{1}{k_z} dk_x dk_y,
\]

(A.16)

where, \( f \) is the focal length of the focusing lens.

Figure A.2 is the intensity at the focus for an in-plane vertical and an out-of-plane (longitudinal) dipole emitter.

![Figure A.2](image)

**Figure A.2** – The total PSF of the optical system for a given dipole orientation. Images are 200×200 µm².
A.2 Measuring the system’s PSF

The PSF of the system is measured by placing a sub-diffraction-sized object into the optical focus and imaging it directly onto a CCD. Two options exist: the coherent PSF and the incoherent PSF.

A.2.1 The coherent PSF

The coherent PSF is challenging to measure since this needs to be done with Rayleigh scattering of a laser source. This measurement was done by placing a single 80 nm gold particle into the optical focus and exciting it with a linearly polarized low-NA excitation. The Rayleigh scattered light was collected and imaged onto a CCD. The low-NA excitation was used to limit the back-reflected light from the glass-air interface. Despite the low-NA excitation, there is still a considerable amount of back-reflected light (as compared to the Rayleigh scattered light from the particle). The back-reflected light and the Rayleigh scattered light coherently interfere on the CCD making it difficult, or impossible, to measure the true PSF.

Simulations shown in figure A.3 keep the back-reflected fields as 4% of the incident fields, and vary the scattered field strength. The experimental realization is shown in figure A.4. It looks qualitatively similar to the calculation between the 100% and 10% scattering strengths.

A.2.2 The incoherent PSF

The incoherent PSF can be measured for a given dipole orientation by measuring the photoluminescence of a gold nanorod. In this case, the plasmon mediated photoluminescence of the gold nanorod is highly polarized. Additionally, since we are looking at Stokes shifted light, the laser excitation can be filtered with an
Figure A.3 – The calculated coherent PSF of the setup for an x-oriented dipole. In both cases the glass-air interface reflects 4% of the incident light. The relative scattering strength of the particle is varied from 100% to 0.1%. Below 0.1% there is no qualitative change in the PSF. Images are 200×200 µm².

Figure A.4 – The experimental Rayleigh scattered image of an 80 nm gold particle with an x-polarized laser excitation.

interference filter and there is no longer the challenge of interference of the optical signal with the excitation light at the CCD.

Figure A.5 shows both a calculation and experimental measurement of the
incoherent PSF for a vertically oriented dipole.

![Figure A.5 – Comparison of the calculated and measure incoherent PSF for a vertically oriented dipole.](image)

**A.3 Diffraction calculations**

The ease of understanding the diffraction pattern for the two-pinhole case is demonstrated with simulations in figure A.6. The calculated diffraction patterns are for the PSF sampling a 1µm long chain of x dipoles, both coherent and incoherent. Since each pinhole is smaller than a diffraction-limited spot, the two-pinhole diffraction pattern gives the interference of two point sources, effectively removing diffraction artifacts (except coherence introduced by the PSF) from the recorded diffraction pattern.

**A.3.1 Calculating the degree of coherence**

The measurement of the degree of coherence can be done by knowing both the intensity of light illuminating each pinhole and the diffraction pattern. Ideally, the
two pinholes are illuminated uniformly and, if a two-dimensional Fourier transform of the diffraction pattern is calculated, the energy at zero frequency would be equal to the combined energy in the positive and negative frequency components (equivalently, twice the energy in the positive or negative frequency). The relative intensity scaling can then be modified by the intensity of light at each of the pinholes. The theory for this calculation is derived fully in reference [? ].

My calculations showed that the visibility for a completely incoherent object, emitting at 715 nm, will be 5.12% and 11.25% for pinholes that are 15 \( \mu \)m diameter with a center-to-center separation of either 60 \( \mu \)m or 40 \( \mu \)m, respectively. This corresponds to a separation in the object plane of 800 nm or 533 nm, respectively.