Electron Dynamics in Single-Walled Carbon Nanotubes

by

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ABSTRACT

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This thesis looks at three aspects of electron dynamics in single-walled carbon nanotubes (SWNTs): electron spin resonance (ESR), conductivity, and the dynamic Franz-Keldysh effect (DFKE). The temperature dependence of ESR in annealed SWNTs is presented. It is shown that the spin susceptibility is greatly increased due to the absence of oxygen. In addition, the electrons become more localized due to the annealing, leading to a change in the asymmetry of the ESR signal as a function of temperature. I observe motional narrowing of the ESR resonance. Temperature dependent conductivity of SWNT decant films is also presented. These measurements support the ESR data by indicating that electron movement is hindered as temperature is lowered. Last, this thesis describes the first attempt to observe DFKE in SWNTs. Using a free electron laser pump-white light probe and a fiber CCD detection scheme, I attempted to observe the DFKE in an DGU-enriched film.
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Chapter 1

Introduction

Low-dimensional structures have increasingly become a focus of condensed matter physics. Particular interest has been generated for two-dimensional (2-D) structures, such as graphene, and one-dimensional (1-D) metals. The reason for interest in 1-D metals (or materials which do not have a gap in the spin and charge excitation spectra [1]) stems from the pioneering theoretical studies of Tomonaga [2] and Luttinger [3], who showed that in 1-D, Fermi liquid theory is not a stable framework, due in part to electron-electron interactions [1, 4, 5]. The corresponding Tomonaga-Luttinger Liquid (or simply LL) theory for 1-D metals has been under theoretical development ever since those landmark papers were published. Unfortunately, the experimental confirmation has lagged far behind, due in main part to having a suitable system to explore. For example, Egger et al. [4] point out that experimentalists started working with 1-D organic chain compounds in the 1970's only to find that complications arose due to the crossover from 1-D to 3-D; in addition, phase transitions complicated observations in these 1-D compounds.

The discovery of single-walled carbon nanotubes (SWNTs) in 1991 [6] provided another system to study 1-D phenomena. In particular, the best experimental evidence for LL behavior among all physical systems has been observed in metallic SWNTs [4]. Transport measurements, which probe charge density changes, have been the primary vehicle for these observations in SWNTs [7, 8], although other experimental probes are also predicted to show LL behavior.
Despite tentative observations, much of LL theory has not been experimentally explored. For instance, LL theory predicts that electron modes are highly unstable and will decay into collective plasmon modes. For a spin 1/2 system, the spin and charge plasmonic modes will decouple from one another, with the ability to travel at different velocities. This phenomenon, often referred to as spin-charge separation, is one of the most striking predictions from LL theory [1]; it has yet to be convincingly observed.

To demonstrate spin-charge separation, experimentalists must look at more than just the charge of the electrons. One standard way to probe spin degrees of freedom is via electron spin resonance (ESR). This well-developed and well-characterized technique, looks at the spin coherence and susceptibility of a material, in a contact-less way. Furthermore, theoretical calculations show that ESR is able to resolve certain LL behaviors in nanotube, giving physicists another avenue besides transport type measurements to probe 1-D SWNT metals [9, 10]. In addition to anomalous power law scaling of critical exponents, these theoretical calculations of SWNT ESR discuss how at certain conditions an observation of spin-charge separation is expected.

1.1 Outline

In this thesis, I will primarily focus on experimental evidence of ESR of SWNTs. Though I will be discussing 3-D powder nanotube samples, this should be viewed as a first step towards a larger goal of measuring the intrinsic 1-D spin resonance of nanotubes. On a broader level, this thesis examines the electron dynamics of carbon nanotubes on an ensemble scale. I use magnetic resonance, transport, and ultrafast spectroscopic measurements on different nanotube samples to examine phenomena related to the unique electron properties
of SWNTs. To achieve results with these experimental techniques, projects on nanotube preparation were developed to produce high quality samples.

Chapter 2 looks mainly at ESR in metals from a theoretical point of view. Since ESR is such a large topic both theoretically and experimentally, I do not consider many of the details. Instead, I focus on Dysonian physics in traditional metals, as well as current theoretical predictions for ESR in nanotubes, especially as related to LL theory. Several of the current problems with ESR in SWNTs are also discussed so as to show how our results differ from previous works.

Chapter 3 describes my experimental observation of ESR in SWNTs. Specifically, I discuss how annealing nanotubes removes the adsorbed oxygen and water on nanotubes. By removing oxygen and water from the SWNTs, the conduction electrons being probed by ESR are prevented from being able to easily move from nanotube to nanotube. Thus, the energetic barrier between nanotubes (also known as a tube-tube barrier) is increased by the absence of water and oxygen molecules. At high temperatures (50 K and above), the thermal energy is larger than these tube-tube barriers, so the electrons are still delocalized. At low temperatures, tube-tube barriers act to localize the electrons to a given nanotube, since the tube-tube barriers are larger than the thermal energy. This temperature-dependent localization trend manifests itself in ESR as a change in the lineshape as a function of temperature. In addition, the movement of electrons from nanotube-to-nanotube produces a motional narrowing of the ESR linewidth as temperature increases. These ESR observations agree with tentative measurements of temperature-dependent sheet resistance on nanotube films. In both techniques, I find that electron movement becomes more difficult as temperature decreases.
In Chapter 3, I discuss work done to isolate metallic nanotubes from semiconducting nanotubes using density gradient ultracentrifugation (DGU). Though this project eventually became separated from ESR, DGU produced several important scientific results with regard to tunable resonant Raman scattering (RRS) spectroscopy and nanotube bundling reduction. Specifically, tunable RRS on metallic-enriched samples showed the first observation of all metallic species in the enriched solution. From the Raman excitation profiles obtained from the tunable RRS spectra, relative populations could be extracted. These population numbers indicate that SWNT species with a chiral angle above 19° are enriched by DGU, while those below this chiral angle are substantially suppressed.

Chapter 4 examines a non-perturbative, nonlinear optical phenomenon known as the dynamic Franz-Keldysh effect (DFKE). This project is still being developed, so many of the results are tentative. I demonstrate a proof-of-concept for (1) how to detect DFKE using a multi-fiber pump-probe spectroscopy detection scheme and (2) how DFKE can be experimentally probed using coherent far-infrared radiation and white-light. Additionally, I describe the development of t-carrageenan and carboxymethylcellulose (CMC) as a polymer matrices for use at mid-infrared (MIR) and far-infrared (FIR) frequencies. My work demonstrates that t-carrageenan is a strong polymer host choice for keeping nanotubes individualized as they are transitioned from an aqueous state to a solid one.
Chapter 2

Theoretical Background

This chapter provides the theoretical framework for electron spin resonance (ESR) in SWNTs. The chapter begins by introducing ESR in broad terms, but placing particular emphasis on conduction electron spin resonance (CESR). This narrowness is necessitated because of the breadth and depth of CESR, which itself has over a half century worth of measurements. Specifically with CESR, it is the diffusive action of the electrons moving in and out of the resonant microwave region (skin depth) that alters the lineshape; the form that results from this movement is often known as the Dysonian lineshape and is related to the Ramsey fringe experiments in atomic physics. In contrast, most ESR experiments are done on spins that spatially fixed (localized), producing a Lorentzian or Gaussian lineshape. Thus, CESR is fundamentally different from traditional ESR.

Dysonian physics relates to conventional three-dimensional metals in specific geometries with respect to the Zeeman splitting field. Since I am studying 1-D structures, the general Dysonian formulism does not apply to my system. Although the case of standard metals must be developed, this chapter distances itself from traditional CESR and moves towards two particular ends: theoretical predictions of ESR in SWNTs and previous experimental observations of ESR in carbonaceous materials, including SWNTs. With regard to the former, I focus on Luttinger Liquid (LL) behavior and how it could be manifested in an ESR-type measurement. As mentioned in the first chapter, LL theory relates to low energy properties of 1-D metals. This physical situation corresponds to the case of ESR measure-
ments on metallic SWNTs. The last part of Chapter 2 deals with previous experimental ev­
idence of SWNT ESR. Although ESR of SWNTs has been performed many times, a major
question that is unresolved is why the experimental community has not observed conduc­
tion electron spin resonance in undoped SWNTs. This hurdle currently is the largest barrier
to observing LL behavior in SWNTs via ESR, and must be resolved before exotic physics
can be probed.

2.1 Conduction Electron Spin Resonance

ESR is an extremely powerful technique for interrogating spins and spin dynamics within
solids (metals, semiconductors, and insulators), liquids, and even gases. The basic prin­
ciples of ESR were first demonstrated in the 1930s, but it was not until the 40s that the
microwave technology developed in World War II could be implemented to push ESR to
its full potential [11–15]. Early experimenters focused on power absorption, rotational
spectra (e.g., collisional broadening of ammonia), spectrometer design, and detectability.
It was only later that the four main tools of spin resonance became clear: measurements of
spin-orbit coupling via the g-factor tensor, relaxation time measurements (both $T_1$ and $T_2$),
measurements of spin susceptibility, and studies of electron dynamics (hopping, localiza­
tion, delocalization, exchange interaction, etc). Although comparatively few studies have
been done on ESR on metals (CESR), it continues to be one of the best techniques for in­
terrogating spins and spin dynamics in metals. Starting from a basic and cursory overview
of ESR, I explain CESR theoretically giving experimental results and data when available
in this section.
2.1.1 Basic Description

A natural starting point to discuss CESR is the derivation of spin susceptibility from Kittel [16]. When a static magnetic field, $H$, is applied to a metal at absolute zero, the concentration of the spins parallel to the field, $N_+$, are changed:

$$N_+ = \frac{1}{2} \int_{-\mu H}^{\epsilon_F} d\epsilon D(\epsilon + \mu H), \quad (2.1)$$

where $\epsilon$ is energy, $D(\epsilon)$ is the density of electron states at a given energy, and $\mu$ is the magnetic moment of a species, which can be taken to be $\mu_B$ (Bohr magneton) in almost all cases. Approximating Eq. 2.1 gives

$$N_+ \approx \frac{1}{2} \left\{ \int_{\mu H}^{\epsilon_F} d\epsilon D(\epsilon) + \mu HD(\epsilon_F) \right\}, \quad (2.2)$$

where the shift of $N_+$ downwards is $\approx \frac{1}{2} \mu HD(\epsilon_F)$. This change in the density of states in a $H$-field also occurs for spins anti-parallel to the field, except that the shift in $N_-$ is opposite that of $N_+$, as shown in Fig. 2.1. Because of the upward shift for $N_-$, the density of electron states for the anti-parallel case is $D(\epsilon - \mu H)$ where the integral is taken from $\mu H$ to $\epsilon_F$:

$$N_- \approx \frac{1}{2} \left\{ \int_{\mu H}^{\epsilon_F} d\epsilon D(\epsilon) - \mu HD(\epsilon_F) \right\}. \quad (2.3)$$

The net magnetization, which is an experimentally observable quantity, is defined as:

$$M = \mu (N_+ - N_-). \quad (2.4)$$

Typically, the net magnetization and spin populations ($N_+$ and $N_-$) are normalized by the volume of the system, $V$, which corresponds with the usual form of $M$ [17]

$$M = \frac{1}{V} \sum_{i=1}^{N} \mu_i, \quad (2.5)$$

where $\mu_i$ is the $i^{th}$ magnetic dipole and the sum is taken over all $N$ dipoles in a given volume, $V$. Putting Eqs. 2.2 and 2.3 into Eq. 2.4 gives

$$M = \mu_B^2 D(\epsilon_F) H, \quad (2.6)$$
Figure 2.1: The density of states shifts when a magnetic field is applied [16]. In (a), the lowest parallel spin states are energetically shifted downward to an energy $\mu B$ below the zero field case, while the anti-parallel states move energetically upward by $\mu B$. Because the number of parallel and anti-parallel spins are different as seen in (b), there is a net magnetization of the sample.

which can be further reduced into spin susceptibility by writing

$$\chi_{s}^{Pauli} = \mu_{B}^{2} D(e_{F}),$$  \hspace{1cm} (2.7)

where $\chi_{s} = \partial M / \partial H \approx M / H$. When normalized by mass and presented in cgs, this has units of emu/g (mass spin susceptibility); otherwise, it is typically given as emu or emu/cm$^{3}$ if one is talking about volume spin susceptibility. Figure 2.2 shows volumetric susceptibilities for several metals as a function of temperature.

A few things are important to note about the spin susceptibility of metals. First, Eq. 2.7 indicates that $\chi_{s}^{Pauli}$ exhibits no temperature dependence. This is a crucial distinction with the Curie law, which is described by $\chi_{s}^{Curie} \propto 1/T$. Hence, one major, but not definitive, test to see whether electrons are localized or free is to perform temperature dependent ESR.
Figure 2.2: Spin susceptibilities (in cm$^3$/g) of several metals as a function of temperature [16]. Several of the d-metals, such as Pd, Ti, and Zr, have some mild temperature dependence to them, though clearly not a Curie law ($\propto 1/T$) behavior. The more spherical the outer orbit, such as those seen in K and Na, the less temperature dependent $\chi$ is.
Second, the magnitude of $\chi_s^{\text{Pauli}}$ is affected by dimensionality through $D(\varepsilon)$. What Eq. 2.7 fails to do is to take into account electron-electron interactions, which are highly dimensionally dependent. Further, even in the three dimensional (3-D) case, this is a substantial correction to even the simplest alkali metals [18].

In addition to not accounting for strong correlations, the issue of dimensionality is also important. A simple examination of the one-dimensional (1-D) case, for instance, will find strongly peaked values of $D(\varepsilon)$ as a function of $\varepsilon$, since $D(\varepsilon) \propto \varepsilon^{-1/2}$. If $D(\varepsilon_F)$ is on (or near) one of those peaks (also known as van Hove singularities), $\chi_s^{\text{Pauli}}$ could easily be much larger than when $D(\varepsilon_F)$ is far away from a van Hove singularity. This dependence on the magnitude of $D(\varepsilon_F)$ can actually be seen in Fig. 2.2. In that figure, the transition metals, such as Ti and V, have the highest susceptibilities due their large density of orbitals. As Kittel points out, this is in agreement with heat capacity measurements [16].

The magnitude of $\chi_s^{\text{Pauli}}$ is small as compared to $\chi_s^{\text{Curie}}$, with $\frac{\chi_s^{\text{Pauli}}}{\chi_s^{\text{Curie}}}$ sometimes on the order of $10^{-2}$ [18]. If the temperature dependence of $\chi_s^{\text{Curie}}$ is considered, one can begin to see the origin of the differences in magnitude:

$$\chi_s^{\text{Curie}} = \frac{N\mu^2}{3k_BT}. \quad (2.8)$$

Here $\mu$ is the effective Bohr magneton ($\mu = p\mu_B$, where $p$ is the effective number of Bohr magnetons). Equation 2.8 can be converted to Eq. 2.7 by multiplying by $T/T_F$:

$$\chi_s^{\text{Pauli}} = \frac{N\mu^2}{3k_BT} \times \frac{T}{T_F}$$

$$= \frac{N\mu^2}{3k_BT_F}$$

$$= \mu_B^2 D(\varepsilon_F) \quad (2.9)$$
where \( p \approx 1 \) for a metal and \( T_F \) can be related to the Fermi energy, \( \varepsilon_F = k_B T_F \). Essentially, this says that only the electrons within \( k_B T \) of the Fermi energy \( (k_B T_F) \) can contribute to the spin susceptibility in metals [16]. Thus, even though Pauli spin susceptibility can be described in a similar manner as the Curie law, the inability for spins far away from the Fermi level to align with the applied field prevents metals from becoming strongly magnetized. In contrast, with Curie law behavior, it is only thermal energy that causes spins to become unaligned, which explains why at very high temperatures, \( \chi_{\text{Curie}} \rightarrow 0 \). Put another way, the Pauli exclusion prevents total spin alignment with the applied field far better than thermal disordering does [18]; this effect is sometimes called Pauli-blocking.

### 2.2 Dysonian Lineshape

A unique feature of CESR is the Dysonian lineshape whose particular form results from the diffusion of the flipped, precessing spins in and out of the magnetic rf field (often, the magnetic rf field is denoted as \( H_1 \)) [19]. Dyson developed the mathematical form and theoretical interpretation [19] in concert with the experimental work of Feher and Kip [20] to explain the lineshape resulting from the CESR of Na and Li. His work is largely based on Ramsey’s pioneering work with atomic phases [21], which is where I will begin the discussion of Dysonian physics.

#### 2.2.1 Ramsey Fringes

In his classic experiment, Ramsey ingeniously showed that by spatially (and thus temporally) separating coherent rf pulses, a linewidth corresponding to the natural linewidth of the species could be resolved. The spacing of these coherent rf pulses is similar to how...
diffusive spins interact with the perturbing magnetic field in magnetic resonance. In both situations, it is not the duration of the rf pulses which ultimately determines the linewidth read out by the detector; rather, with the appropriate theoretical considerations, the natural linewidth can be resolved. I will spend some time describing Ramsey’s experiment and its geometry, as it is the basis for the Dysonian physics.

In Ramsey’s original experiment, a furnace is used to heat up Li atoms. After a series of slits, the gaseous atoms form a beam to which a static magnetic field, \( H_0 \), is applied. At a time \( t_0 \), a certain section of this beam is hit with a short rf pulse with a time duration of \( \tau \), which excites the atoms out of thermal equilibrium. These excited atoms then proceed down the vacuum chamber, unaffected by any other field besides \( H_0 \), until a second rf pulse is applied at the end of the chamber. This spatial propagation acts as a time delay, during which the atoms undergo collisions and some loss of coherence. The propagation time, \( T \), is much longer than the rf pulse time, and contrary to what one expects, the absorption and emission linewidths are determined not by the time spent in the rf pulse, but by this propagation time.

The uncertainty principle should give a broad linewidth, \( 1/\tau \). If the Fourier transform of the single rf pulse is taken, a diffraction spectrum centered on the rf frequency, \( \omega_0 \), with a width of \( 1/\tau \) is produced [23]:

\[
F_{t_0}(\omega) \propto e^{i\omega t_0} e^{\frac{e^{i(\omega-\omega_0)\tau} - 1}{\omega - \omega_0}}.
\]  (2.11)

Here, \( t_0 \) is the time when the pulse is applied, \( \omega \) is frequency, and \( \omega_0 \) is the rf pulse frequency. When another pulse at \( T \) time later is applied, though, destructive interference occurs, leaving a width of \( 1/T \) centered at \( \omega_0 \) on a background of \( 1/\tau \). Thus, the timing between the rf pulses creates the uncertainty broadening instead of being dominated by the
Figure 2.3: Schematic of Ramsey's experiment. S denotes the atomic source, while magnets A and B are inhomogenous magnets used to steer the atoms to the detector, D. For Ramsey's experiment, the coherent rf pulses are applied at the beginning and end of the C magnet. Because of a Maxwellian distribution of velocities and the different states that are produced because of them, the atoms have a distribution of trajectories, as indicated by the dashed line next to the detector. These trajectories, which correspond to the transition probabilities, are known as Ramsey fringes [22].

Figure 2.4: Pulse scheme used by Ramsey [22]. Each pulse is of a duration $\tau$ applied a time $T$ apart, where $T$ is the propagation time of the atoms.
rf pulse time [23]. In this way, Ramsey was able to resolve the atomic lifetimes of the
gaseous atoms using short rf pulses.

As one can see by Fig. 2.5, there is much more structure than just a simple linewidth.
The fringe pattern that is observed is due to the Maxwellian distribution (Eq. 2.12) of Li
atom velocities [24]

\[ \phi(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}}, \]  

(2.12)

where \( \phi(v) \) is the probability of a given velocity, \( v \) is velocity, \( T \) is the gas temperature,
and \( m \) is the mass. The fringe pattern can be understood by looking at the precession of a
magnetic moment, \( \mu \) about the center field, \( H_0 \). The precession begins with a phase, \( \phi \) (not
to be confused with \( \phi(v) \)), of 0 at the first rf excitation at time, \( t_0 \). If all the atoms traveled
at the same velocity, the phases at \( t_0 + T \) would be coherent and the transition probability
would be exactly the same for each atom, resulting in a sinusoidal pattern in the transition
probability as a function of oscillating field frequency. In reality, the velocity distribution,
\( \phi(v) \) in the rf-free region (magnet C in Fig. 2.3), produces a spread of phases at the second
rf pulse. This spread creates a two slit-like interference pattern of fringes which are shown
in Fig. 2.5 [25]; these are often referred to as Ramsey fringes.

2.2.2 Dysonian Physics

Dyson’s work draws upon Ramsey’s experiment to explain why a resonance should be seen
at all with a metal. Platzman and Wolff note the following in their treatment of CESR [23]:
if we assume a free electron gas with a Fermi velocity of \( v_F = 10^8 \) cm/s and a skin depth
of \( \delta \approx 10^{-5} \) cm, then the time that an electron spends inside the skin depth (interaction
region with rf pulse) is \( t_s \approx 10^{-13} \) s. As with Ramsey’s work, one should naïvely expect
the resonance width to be \( 1/t_s \), which make an observation of CESR impossible using a
The conceptual breakthrough that Dyson saw was that the conduction electrons diffuse not only out of the skin depth, but also back into it [19, 23]. As with a random walk, the diffusion of the electrons randomly goes in and out of the rf pulse region. Thus, as with the Ramsey two hairpin experiment, the electrons "see" a series of randomly spaced rf pulses of a varying length. As such, the pulse of Eq. 2.11 reduces to the coherence linewidth of the conduction electrons, $T_2$, on a background of $1/t_s$.

But even if this resonance can be observed, it is unclear what the lineshape will look like. The diffusivity of the conduction electrons suggests a modification of the localized Lorentzian lineshape by some addition of dispersion, inhomogeneous broadening, or both.

Figure 2.5: Ramsey fringes [22].
A necessary step, therefore, is to calculate the energy (power) absorbed by spins which diffuse in and out of the rf field.

2.2.3 Geometric Dependence of the Dysonian Lineshape

In an ESR experiment, the geometric configuration of the metal in the cavity is important for understanding the type of ESR lineshape that results. In particular, two key temporal ratios are involved in the Dysonian lineshape. The first is the ratio between the time it takes an electron to diffuse through the skin depth, $T_D$, to the the time it takes an electron to traverse the entire sample, $T_T$. The skin depth, $\delta$, that I refer to is the depth (in the direction of electromagnetic propagation) that an electromagnetic wave can penetrate matter before being reduced by a factor of $e^{-1}$:

$$\delta = \frac{c}{\sqrt{2\pi\rho}} \text{ (cgs)}.$$  \hspace{1cm} (2.13)

Here $c$ is the speed of light and $\rho$ is the conductivity. Therefore, if we assume that the mean free path, $\Lambda$, is smaller in comparison to $\delta$, and if the average electron velocity is $v$, then $T_D$ can be explicitly calculated in the 3-D case [20]:

$$T_D = \frac{3}{2} \frac{\delta^2}{v\Lambda}.$$  \hspace{1cm} (2.14)

$\Lambda$ can be replaced by using the DC conductivity relation for a free electron gas: $\sigma = Ne^2\Lambda/m^*v^2$. These results are valid when a normal situation is examined, that is, when $\Lambda \ll \delta$ (i.e., the mean free path is much smaller than the skin depth). For the anomalous skin effect, $\Lambda \sim \delta$ or $\Lambda > \delta$; Dysonian lineshapes can be calculated here as well. For the purposes of this thesis, I will stay with the initial assumption, $\Lambda \ll \delta$.

For $\frac{T_D}{T_T} \gg 1$, the metal sample can be considered to be fully immersed in the perturbing
rf field, \( H_1 \). No diffusion or dispersion effects should be seen at this point, since the electrons are not moving in and out of the skin depth. In other words, the electrons appear to be localized within \( H_1 \). Thus, the resulting lineshape is Lorentzian \[20\]

\[
\frac{dP}{d\omega} = -\frac{\omega H_1^2}{4} V \omega_0 \chi_0 T_2 \frac{2(\omega - \omega_0) T_2^2}{[1 + (\omega - \omega_0)^2 T_2^2]^2},
\]

where \( P \) is the absorbed power, \( \omega \) is the rf frequency of the linearly polarized magnetic perturbing field, \( H_1 \), \( T_2 \) is the coherence time, \( V \) is the sample volume, \( \chi_0 \) is the static spin susceptibility, and \( \omega_0 \) is the resonant frequency. This comports with physical intuition since the spins are not traveling out of the microwave region. In effect, they still “appear” to the cavity to be localized within the sample, despite their actual physical movement. This apparent localization is simply a geometric effect of the skin depth being much larger than the travel distance (in the direction of rf power delivery) of the electrons.

When \( \frac{T_2}{T_F} \ll 1 \), diffusion effects modify the lineshape by adding a dispersion component. The rf field is screened by the charged carriers in the conducting medium. There is a phase shift between the electric and magnetic components of the rf field due to this screening. The phase shift, \( \varphi \), creates a lineshape with a mixture of dispersion and absorption components \[26,27\].

In the diffusive regime, the second temporal ratio, \( \frac{T_2}{T_F} \), becomes important. Two limits exist for the dispersive case, as defined by this ratio. When \( \frac{T_2}{T_F} \rightarrow 0 \), the diffusion through the skin depth is extremely fast as compared to the dephasing time, \( T_2 \). This situation applies to high conductivity metals, low temperatures, and/or extremely long spin-spin relaxation times. As might be expected, the lineshape is mostly dispersive. In the notation of Feher
and Kip [20]

\[
\frac{dP}{d\omega} = -\left[\frac{\omega H^2}{4} T_2 \delta A \omega_0 \chi_0 T_2\right] \left\{ \frac{T_2}{2} \sqrt{\frac{T_D}{T_2}} \left[\frac{2 - (1 + x^2)^{1/2}}{(1 + x^2)^{1/2} + 1} \right]^{1/2} \right\},
\]

(2.16)

where \(A\) is the surface area of the sample and \(x = (\omega - \omega_0)T_2\). Likewise, the case \(\frac{T_D}{T_2} \ll 1\) yields a similar result as Eq. 2.16, except that there is a correction term. For both sub-cases, the longevity of the spin lifetime as compared to the diffusion time substantially alters the lineshape, so that it no longer takes the form of a Lorentzian.

The other limiting case for will be when \(\frac{T_D}{T_2} \gg 1\), which corresponds to slowly diffusing dipoles, intermediate or low conductivity, and/or paramagnetic impurities distributed throughout the metal [20]. Because of their relatively low conductivity (as compared to a metal like aluminum or copper), SWNTs are described by this case. Thus, I expect that the ESR lineshape I experimentally obtain will be well-described by the theoretically derived power derivative. This power absorption derivative is given in closed form as [20]:

\[
\frac{dP}{d\omega} = \left[\frac{\omega H^2}{4} T_2 \delta A \omega_0 \chi_0 T_2\right] \left\{ \frac{T_2}{2} \frac{T_2^2 (\omega - \omega_0)^2 - 2 T_2 (\omega - \omega_0) - 1}{[1 + T_2^2 (\omega - \omega_0)^2]^2} \right\}.
\]

(2.17)

As with other ESR lineshapes, the curve described by Eq. 2.17 contains information on the \(g\)-factor (Zeeman splitting energy), \(T_2\) (linewidth or dephasing time), and spin susceptibility (amplitude). One important and differentiating measure of the Dysonian lineshape from the Lorentzian or Gaussian case is the so-called \(A/B\) ratio, which measures the ratio of the high point on the positive peak (\(A\)) to the lowest point on the negative peak (\(B\)). In a typical ESR spectrum, this ratio would be 1, whereas when diffusion is present, the ratio is larger reaching, in certain cases, above 9 for highly conductive metals. The \(A/B\) ratio can be related to the \(\frac{T_D}{T_2}\) ratio, which is shown in Fig. 2.7. This plot will be useful in Chapter 3 to extract \(T_D\) once \(T_2\) and \(A/B\) are obtained.
Figure 2.6: Theoretically calculated derivative of power \( \frac{dP}{dH} \) absorbed for different \( T_D/T_2 \) ratios [20] versus \( \gamma(H-H_0)T_2 \), where \( \gamma \) is equal to \( \frac{\mu_B}{h} \). As the \( T_D/T_2 \) ratio trends towards 0, the lineshape loses more of the symmetric Lorentzian lineshape and becomes more fully dispersive.

One very important point about the Dysonian form is that it can be divided into its Lorentzian and dispersion components in the low conductivity regime. The ability to do this allows one to calculate the imaginary part of the transverse susceptibility, which can in turn be related to the static susceptibility. The transverse spin susceptibility can be written as [26, 27]

\[
\chi = \chi'' \cos \varphi + \chi' \sin \varphi, \quad (2.18)
\]
Figure 2.7: $\sqrt[\frac{T_D}{T_2}]$ versus A/B ratio for power absorption derivative [20]. As the $\frac{T_D}{T_2}$ ratio goes to zero, the asymmetry (as seen in the A/B ratio) of the Dysonian lineshape increases. This behavior corresponds to the fact that $T_D$ decreases as conductivity increases, thus allowing electrons to acquire a greater dispersive component. One can see this trend reflected in Fig. 2.6.
where $\chi''$ is the imaginary part of the transverse susceptibility and $\chi'$ is the real part. Rewriting the Dysonian lineshape as a composite of these real and imaginary terms, we have [26, 27]

$$\frac{d\chi}{dH} = \left(\frac{\cos\phi}{\Delta^2}\right) \frac{-2y + (1 - y^2)\tan\phi}{(1 + y^2)^2},$$

(2.19)

where $y = \frac{H - H_0}{\Delta H}$. When $\phi = 0$, a Lorentzian lineshape is recovered, indicating electron localization. For $\phi = \frac{\pi}{2}$, the only dispersive lineshape remains. The weak Dysonian lineshape behavior as a function of $\phi$, is plotted in Fig. 2.8. As can be seen, altering $\phi$ effectively tunes the $A/B$ ratio, showing that the two are coupled quantities.

![Figure 2.8: Dysonian spin susceptibility derivative ($\frac{d\chi}{dH}$) as a function of phase angle, $\phi$. When $\phi = \pi/2$, the lineshape is fully dispersive. Roughly speaking, this corresponds to the case of $\frac{d\phi}{dH} \rightarrow 0$. The opposite limit, $\phi = 0$, is the fully absorptive limit; the lineshape in this extreme is a Lorentzian, indicating electron localization.](image)
The lineshapes from the Dysonian model and the Ramsey model have certain similarities, such as a linewidth proportional to the inverse natural lifetime and a background whose bandwidth is inverse to the diffusion time. Yet, three major differences can be noted. One is that the spins can penetrate the rf region multiple times, as opposed to Ramsey’s case, where only two rf pulses are typically applied. Two, eddy-current losses are important in a metal; no such concern exists for the two hairpin experiment [19]. Third, although the diffusion into the skin depth is random in Dyson’s model, the molecular velocities in Ramsey’s experiment do not have the same randomness.

2.2.4 CESR Experimental Results

The most important experimental results for the Dysonian lineshape have been with the alkali metals. The first reported evidence of CESR was seen by Griswold et al. [28] in Na. Later studies focused primarily on simple metals such as Li [20] and K [20]. Since these metals have a nearly spherically symmetric Fermi surface, they behave like ideal metals, which made the alkalis good candidates for study. Also, purity can be very high with the correct processing. In addition, the spin-orbit coupling of these elements is fairly low because of the small nuclei present. These attractive features made for an active research area for several years. More challenging were large Z metals, such as Ag and Au, and highly conductive samples such as Cu and Al. It was not until the 1960s and 1970s that several of these elemental metals were finally resolved using CESR.

The significant delay in observing metals using CESR is due to the experimental difficulty in obtaining a good, repeatable lineshape. Three major reasons stand out as inherent hurdles to detecting CESR: one, the skin depth of metals/conductors in the microwave fre-
quency range is small (roughly 100 nm - 10 \(\mu\)m), which means most of the microwave energy is simply reflected by the sample; two, in general, spin relaxation times are very short [29], which can make the width of the resonance as a function of \(H_0\) extremely large (on the order of \(10^2 - 10^3\) G); and three, \(\chi\) (spin susceptibility) is small (typically on the order of \(10^{-6}\) emu) due to the large degree of electronic state degeneracy [30]. Because of the third reason, it is often the case that a strongly paramagnetic impurity will have a much larger signal than the metal.

Several avenues have been taken to get around the difficulties of measuring CESR. One method is to employ a transmission type cavity [in the literature, this is called transmission conduction electron resonance (TESR)], in which both dispersion and absorption properties can be measured with accuracy. This is the most accurate way to study CESR, since the phase shift of the transmitted microwaves can be resolved due to observation of both the reflected and transmitted signals [23, 31]. The problem with TESR is that the signals are usually small and difficult to resolve. Typically, most researchers build their own TESR systems, since no commercially available system currently exists. For a good experimental review of TESR, see Lewis and Carver's article [32]. An example of a TESR spectrum is given in Fig. 2.9 for 100 \(\mu\)m thick gold film at 13.5 K [33].

### 2.3 ESR in Carbon Nanotubes

This section looks at the current state of ESR in SWNTs. I start with theoretical predictions of what ESR of SWNTs should yield; I emphasize that the 1-D aspect of nanotubes alters many properties of a typical metal. Specifically, the presence of strong electron-electron correlations in 1-D manifests itself in the ESR lineshape of SWNTs, in addition to providing the conditions for spin-charge separation.
In addition to describing the previous theoretical work on ESR of nanotubes, I discuss prior experimental studies on both graphite (3-D analog of nanotubes) and SWNTs. Because the experimental work on SWNTs is so contradictory, I stay mostly with the more recent publications, which claim less and show more than earlier works. To be fair, SWNT sample quality has improved considerably over the last fifteen years, so a true comparison of newer works to older ones is flawed on many levels.

2.3.1 Theoretical Predictions of the ESR of Carbon Nanotubes

The Luttinger model for a 1-D electron system extends the Tomonaga model put forward in 1950 [2, 3, 34]. Together, the Tomonaga-Luttinger paradigm provides a way to work with low energetic phenomena on a 1-D constrained Fermi surface. A complete review of
this is outside the scope of this thesis, but several references are available if the reader is interested, such as Mahan [34], Giamarchi [5], and Voit [1].

The Tomonaga-Luttinger model, more commonly referred to as Luttinger liquid (LL) theory, is invoked for metallic carbon nanotubes due to their 1-D nature, as well as experimental evidence that show strong electron-electron correlations exist [7]. As a consequence, any theoretical description of dynamic correlations (such as spin susceptibility) in nanotubes has its starting point with LL theory. However, for LL theory to be influential, the energy scale, \( E \), must be much less than \( D \), the electronic bandwidth in nanotubes [4], where \( D \approx \hbar v_F / R \) and \( R \) is the nanotube radius. A rough estimate for nanotubes finds \( D \) on the order of \( eV \). For the case of optics, the relevant energy scales are also on the order of \( eV \), which means that LL theory is not an applicable model. For ESR, the perturbations are on the order of 10 \( \mu eV \), which satisfies \( E \ll D \). Therefore, much like transport experiments, ESR should encounter the effects of strongly interacting electrons.

Recent theoretical work done on ESR in nanotubes has concentrated on explaining two major facets: one, how the resonance should behave when electron interactions are present, and two, spin-orbit coupling in nanotubes. The observation by Kuemmeth et al. [35] that the spin-orbit coupling in nanotubes is much greater than previously thought [36] has raised a number of questions about the source of the coupling. Spin-orbit mechanisms in nanotubes have been attributed to curvature [37–39], chirality [39], and fluctuations in orbital moments [40]. Though Kuemmeth and co-workers precisely measured spin-orbit coupling of one nanotube, they failed to show how adding nanotubes alters SO coupling. Thus, their work, though influential and important, does not have correspondence to work done on ensembles of SWNTs.
More importantly for this thesis are the theoretical predictions of the nanotube ESR line-shape. Further, even if an ensemble of nanotubes is treated as a 3-D metal, there are still questions about what kind of ESR signal one should expect and whether or not it should be temperature independent in the presence of strong electron-electron interactions in a LL type model. In what follows, I present the derivation given in Dóra et al. [10] as the most pertinent calculation of what to expect for the ESR signal of an ideal nanotube system with electron interactions.

The expected signal intensity, \( I(\omega) \), at a magnetic field strength of \( B \), an energy of \( \hbar \omega \), and a temperature of \( T = 0 \) is [10]:

\[
I(\omega) = A \left( \frac{\alpha}{2v_s} \right)^2 \sin^2(\pi \gamma) \frac{\Gamma^2(1 - \gamma)}{\gamma(1 + \gamma)} \frac{2|\omega|(\omega^2 + b^2)}{(\omega^2 - b^2)^{1-\gamma}},
\]

(2.20)

for \( |\omega| > b \) and zero everywhere else. Here, \( \alpha \) is a LL parameter, \( v_s \) is the spinon velocity, \( \Gamma(x) \) is the gamma function, \( b \) is equal to \( K_s B \), and \( \gamma = (K_s + 1/K_s - 1)/2 \). \( K_s \) is the spin renormalized coupling constant, which along with \( K_C \) (charge analog), can determine all the LL correlation functions [1]. On a general level, when \( K_v < 1 \), repulsive interactions are being described, and when \( K_v > 1 \), the interactions are attractive; these relations are true both before and after bosonization [5]. The general form for \( K_v \), where \( v = s \) or \( c \) is defined as [1]

\[
K_v \equiv e^{2\xi_v(p)} = \sqrt{\frac{\pi v_F + g_4 v(p) - g_2 v(p)}{\pi v_F + g_4 v(p) + g_2 v(p)}},
\]

(2.21)

where a \( g_4 \) process indicates a coupling of two fermions on the same side of the Fermi surface and \( g_2 \) is the coupling strength of two fermions on different sides of the Fermi surface [5]. After the fermion interaction, a \( g_2 \) coupling will leave both fermions on their respective sides (forward scattering, \( q \sim 0 \)), whereas with a \( g_1 \) coupling, the interaction
will find an exchange of sides leading to a backscattering process \((q \sim 2k_F)\). The different processes are depicted in Fig. 2.10.

Figure 2.10 : Graphical depiction of the different electron excitation processes that can occur in a LL. Different \(g\) values indicate coupling between fermions either on the same side of the Fermi surface \((g_4)\) or on different sides \((g_1\) and \(g_2)\) [5]. The \(g_3\) process is left out because it happens so rarely.

Notable about Eq. 2.20 is that \(I(\omega)\) cannot be described in terms of Lorentzian functions.
Also, there is a sizable asymmetry of the signal around the resonances at $\omega = \pm b$, with the signal disappearing from $|\omega| < b$ and falling off as a power-law from $|\omega| > b$. What is not clear is how one can observe this strongly peaked behavior in real systems. For instance, at $T = 10$ K, the thermal energy scale is $860 \mu$eV. If one is dealing with a typical X-band microwave system ($\nu = 10$ GHz), then $\hbar \omega = 41 \mu$eV and $\mu_B B = 23 \mu$eV for a field of 0.4 T. Therefore, a more relevant energy regime would be $T \gg \omega, B$. For this limit, the lineshape consists of two Lorentzians centered on $\pm K_S g \mu_B B$ [10]:

$$I(\omega) = A 2 \pi (\hbar \omega)^2 \left[ \frac{\eta}{(\hbar \omega - K_S g \mu_B B)^2 + \eta^2} + \frac{\eta}{(\hbar \omega + K_S g \mu_B B)^2 + \eta^2} \right], \quad (2.22)$$

where $\eta = 2 \gamma \mu_B k_B T$. The significance of Eq. 2.22 becomes clear when it is compared to the non-interacting spin case (Fermi liquid), where $K_S = 1$ and $\gamma = 0$. In the non-interacting case, the intensity reduces to the summation of two delta functions resonant at $g \mu_B B$, showing that there is correspondence between the interacting and non-interacting regimes. The fact that the model can also explain the non-interacting case shows its robustness and overall soundness.

The other important point that Dóra et al. demonstrated is that the width of the resonance is governed by $\eta$ [10]. This, in turn, creates a linewidth with a linear dependence on temperature and the interaction parameter, $\gamma$. Thus, the resonance is broadened by the electron interactions, as compared to the non-interacting case. (Note that for both situations, the overall signal intensity, should be the same.) Last, the position of the resonance is slightly shifted due to the interactions, as seen by the addition of $K_S$ and $\eta$ in the denominator of Eq. 2.22. A graph of the normalized intensity for the generalized case (i.e. not explicitly for Eq. 2.22) at a fixed value of $K_S$ is shown in Fig. 2.11 to give some idea of how temperature affects linewidth.
Figure 2.11: ESR signal intensity for $K_s = 1.1$ and $\gamma = 0.0045$. The blue curve corresponds to $k_B T/\hbar \omega = 0.1$, 1 (red), 5 (black), and 25 (magenta). Notice that the resonance occurs at $1/K_s \approx 0.91$ [10].

Up to this point, I have not talked about ESR observations of spin-charge separation. There are no theoretical predictions of a direct observation of this effect with ESR. What has been shown is that in the presence of spin-orbit coupling, a double peak can be produced for 1-D metals [9]. The two peaks will be of differing heights, but centered symmetrically around the resonance with the spacing between the two peaks equal to $|\lambda_+ - \lambda_-|$, where $\lambda_{\pm} = \vec{B} \pm \vec{\lambda}$ and $\vec{\lambda}$ is the spin-orbit coupling vector [9]. This double peaking of the resonance is not due to spin-charge separation. Rather, because of the electron-electron interactions, the double peaks will only be present if spin-charge separation is also present.
Thus, spin-charge separation is a necessary condition for a double-peak to occur in a 1-D metal with a finite spin-orbit coupling. Therefore, one can expect a dramatic change in the ESR signal upon the onset of spin-charge separation from a broadened, single-peaked resonance to a narrowed, double-peaked structure centered symmetrically around the resonance. Provided one can observe the phenomena described by Dóra et al. showing the presence of strongly correlated electrons in 1-D, it should be possible to also detect spin-charge separation in the ESR spectrum given the right experimental conditions (i.e. temperature and magnetic field).

2.3.2 Previous Experimental Work: Graphite

CESR in carbon structures can be traced back to Wagoner’s pioneering work on graphite [41, 42]. Graphite is the 3-D analog of the 1-D SWNTs, and graphene (one layer of graphite) is the 2-D form. Graphite has a CESR signal whose linewidth and spin susceptibility are both temperature dependent. Two interesting things emerge about graphite: first, there is a strong $g$-factor anisotropy relating to the large (on the order of $10^2$) conductivity difference between the $a$ and $c$ axes of the crystal; and two, the shift of the $g$-factor from the free electron value ($g = 2.0023$) is related to the fact that the Fermi level is close to a degenerate band edge. The latter point is significant because the magnitude of the shift is large. Wagoner observes that $\Delta g = 0.125$, where $\Delta g = g - g_{\text{free}}$, can be directly compared to Elliott’s work, where $\Delta g = \frac{\lambda}{A}$ ($\lambda$ being the magnitude of the spin-orbit coupling and $A$ the energy separation of the state being mixed in by the spin-orbit coupling) [43].

More recent work has looked at different types of graphite [Kish, highly-oriented pyrolytic graphite (HOPG), and pyrolytic graphite (PG)] at low temperatures [44]. In the Matsubara and co-workers paper [44], the spin-orbit coupling constants, $\lambda_{12}^z$ and $\lambda_{33}^z$ are estimated
to be $-4.29 \times 10^{-4}$ eV and $-5.01 \times 10^{-4}$ eV, respectively. These negative spin-orbit couplings constants are tentatively explained by not correctly taking into account low ($n = 0, 1$) Landau levels in the calculation of $\Delta g$. Also crucial is the acknowledgement of two species within the graphite: one being the conduction electrons (Pauli Law), and the other being localized electrons (Curie law). It is this model of two different spin types within a given graphitic sample that most closely explains the increasing $\chi$ as temperature decreases that is seen in graphite. It may be that the temperature dependence of spin susceptibility in carbon nanotubes may also be roughly explained by this paradigm.

Figure 2.12: ESR trace of graphite [41], left, and graph of $\Delta g$ as a function of temperature for single crystal and polycrystalline graphite [42], right. The $g$-factor of graphite is temperature dependent, which makes the presence of graphite in ensemble SWNTs easily detectable.

2.3.3 Previous Experimental Work: Carbon Nanotubes

ESR in SWNTs has taken many twists and turns. Early on, it was claimed that CESR in purified SWNTs had been observed [45, 46]. In these works, oxidation and annealing created what was identified as the CESR peak in arc-discharged SWNTs. The main
support of this claim was that the spin susceptibility remained constant as a function of
temperature. Surprisingly, $\chi$ was estimated at $4.5 \times 10^{-8}$ emu/g [46], which is three times
larger than graphite [44]. Curiously, the lineshape in both of Kosaka’s works were dis­
tinctly Lorentzian. It was not until later that the Dysonian lineshape was observed in nan­
otubes [47]. It is unclear why early accounts did not see the presence of dispersion in their
samples.

Petit et al. put forth one of the most convincing cases for CESR in SWNTs [47]. To date,
no other group has measured the temperature dependent resistivity, $\rho(T)$, at both DC and
10 GHz. By determining the electrical resistivity, the skin depth (and hence $T_D$) could be
reliably estimated. In addition, Petit et al. also observed Pauli spin susceptibility down to
$\approx 100$ K. Interestingly, the Dysonian lineshape was lost upon grinding the SWNT material,
indicating that particle size and tube-to-tube contacts were fairly important. As with the
work of Kosaka et al. [46], Petit et al. [47] annealed their sample; but unlike Kosaka et
al., Petit and co-workers purified their laser oven nanotubes using a heavy acid treatment.
In both cases, it is unclear if the researchers are probing itinerant carriers, because of the
doping of the acid. Further, Petit and co-workers’ study is limited in that the claim Pauli
law susceptibility was obtained by only changing the temperature a factor of 3. If itinerant
carriers were being probed, only band structure effects such as Pauli law spin susceptibility
would be present. In addition, itinerant effects imply that carriers are not being supplied
from dopants. Itinerant effects are necessary for a LL paradigm to apply, since it is the
reduced nature of the Fermi surface in 1-D that is crucial for LL theory. Thus, the point
about whether or not itinerant carriers are being observed is important.

Later work indicates just how fickle spin resonance in SWNTs can be. Salvetat et al. [48]
Figure 2.13: $\chi_s(T)$ versus temperature for laser-oven SWNTs [27]. A Curie law fit, with a Pauli law offset, is shown on the graph. Below 15 K, though, the fit fails to explain the noticeable drop, as seen in the inset.

reported that the spin susceptibility as a function of temperature was neither Pauli nor Curie Law. The lineshape they observed was a “hyper-Lorentzian” with no asymmetry, which they claimed represented a distribution of relaxation times. The hyper-Lorentzian lineshape, which has no theoretical backing, has not been observed by other groups. It seems reasonable to say that it was chosen to comport with their odd lineshape. Interestingly enough, Salvetat et al. state that their attempts to create defects via irradiation only marginally changed the spin resonance behavior, implying that the electrons are not substantially hindered by physical defects.
More recently, Likodimos et al. [27] claim to observe the opening of a spin gap at temperatures below 10 K; this identification can be seen by the precipitous drop in the spin susceptibility in Fig. 2.13. Their work is the first reported instance of a spin gap in SWNTs using ESR. It is unclear why other groups, using similar SWNTs (laser oven) and similar equipment, did not observe this behavior. The lineshape that Likodimos discusses is not quite Dysonian and not Lorentzian, in contradiction to all other works. $\chi(T)$ has both Curie and Pauli-like features along with the previously noted drop below 10 K due to the spin gap. The spin susceptibility of the conduction electrons in his work is estimated to be $\chi_0 = 1.06 \times 10^{-9}$ emu/g, which is a full order of magnitude less than Kosaka et al. [46].

All in all, a consensus has developed around three main things: one, the $g$-factor of carriers in SWNTs is between $2.003 \pm 0.001$ [27,46–48]; the linewidth, $\Delta H < 10$ G [27,48]; and the lineshape is highly dependent on preparation methods (e.g. type of nanotubes, grinding, oxidation, acid purification, etc.). Other direct types of doping, such as potassium-doping [49] and hydrogen adsorption [50], also have an effect on the spin resonance in SWNTs. Generally speaking, it is widely believed that CESR has not been unambiguously observed for undoped SWNTs [10,27].

**Remaining Problems in SWNTs**

Compared to studies of CESR in simple metals, the subfield of CESR in carbon nanotubes has barely been plumbed. It is unclear, for instance, whether CESR has even been observed in SWNTs. For instance, Pauli-like spin susceptibility has never been seen down to liquid helium temperatures in undoped nanotubes. For all intensive purposes, this is the major indication that true CESR is being observed, since Pauli-blocking is occurring when spin susceptibility as a function of temperature is constant. Another major parameter...
determined by ESR, the spin coherence time, $T_2$, typically does not vary with temperature in nanotubes [27]. Temperature independence implies the absence of the Elliott-Yafet relaxation mechanism, where spin-orbit coupling facilitates relaxation via phonons [43, 51]. Further, the claimed spin relaxation mechanism has not been satisfactorily explained. Many authors attribute the spin relaxation mechanisms to ferromagnetic catalysts within the nanotubes. While this reasoning does have some credibility, no hard evidence has ever been presented. Estimates of catalyst size, distribution, and type are all lacking, as is a clear demonstration that different concentrations and types of catalysts actually alter $T_2$.

The mystery of the spin-orbit coupling has been an increasingly difficult issue. Although most reports have the $g$-factor somewhere in the range of 2.002 to 2.004, a recent publication by Kuemmeth et al. [35] observes a $g$-factor of 2.14 using Coulomb blockade spectroscopy on a single semiconducting nanotube; this discrepancy has yet to be explained. Similarly, there still remains the question of the effect that ferromagnetic catalysts have. Conceivably, if they are acting as spin-flip centers, then it would make sense that this interaction would have some effect on the $g$-factor. Indeed, the small magnetic field generated by this ferromagnetic (or super-paramagnetic) catalyst should cause the $H$ field needed to create the Zeeman splitting to be lower by some small amount, in effect, pulling the $g$-factor away from the free electron value. This seems not to be the case given how close the SWNT observed $g$-factor is to the free electron value.
Chapter 3

Electron Spin Resonance of Single-Walled Carbon Nanotubes: Experimental

This chapter gives a very brief experimental overview of ESR. My temperature dependent ESR results on annealed SWNT powders are presented after this experimental review. A tentative model of conducting quasi-1D polymers is used to explain the SWNT ESR data. Last, I show our results for the metallic enrichment of SWNTs via density gradient ultracentrifugation, which I was previously thought to be a good route to take to observe CESR in SWNTs.

3.1 Experimental Methods: Electron Spin Resonance Overview

Electron spin resonance is a very well developed magnetic resonance technique that measures the absorption of power by a sample due to spin flipping. I will attempt here to quickly summarize the salient major features of ESR, while also describing in some depth the use of a resonant cavity in the measurement process. In no way is this meant to be comprehensive. If the reader is looking for a deeper understanding of this method, one should consult Poole [52] and/or Wertz and Bolton [53].

3.1.1 Quick Summary of Electron Spin Resonance

In the simplest description of ESR, a strong magnetic field (usually on the order of 0.1 to 1 T) is used to magnetize the sample by aligning the spins either parallel (diamagnetic)
or anti-parallel (paramagnetic or ferromagnetic) to it. The applied field produces Zeeman splitting for the spin states:

$$\Delta E = h\nu = g\mu_B H_0,$$

(3.1)

where $\Delta E$ is the energy separation between two states in a spin 1/2 system, $\nu$ is the Larmor frequency, $g$ is the g-factor, and $\mu_B$ is the Bohr magneton.

Linearly polarized microwaves of a fixed frequency are sent to a coupled resonant cavity, which generates a perturbative magnetic field, $H_1$, on the order of 100 to 1000 times smaller than $H_0$. Since the frequency, $\nu$, is fixed, $H_0$ is slowly changed such that Eq. 3.1 is satisfied at some point during the sweep. When this energetic condition is met (or nearly met), the resonant cavity absorbs energy differently, partially destroying the coupling between it and the microwave waveguide. This alteration of the coupled condition reflects microwaves back through the waveguide and into a detector. It is essential that the microwave energy sent back through the waveguide is directed to the detector and not to the microwave source, since microwaves incident on the source will severely harm the source and/or affect the microwave source stability.

Thus, ESR spectrometers measure the cavity coupling to the waveguide, which in turn depends on the power absorbed by the sample. To improve the signal-to-noise ratio, a magnetic jitter is added on top of $H_0$, which is on the order of 1-10 G. This jitter, also known as magnetic modulation, allows the use of phase sensitive detection, which greatly improves the signal-to-noise ratio. Modulation of the magnetic field produces the characteristic derivative lineshape that is seen with magnetic resonance experiments.
3.1.2 Cavities

A resonator is a necessary component of any traditional ESR system. Almost all modern ESR spectrometers use a resonant cavity to create a $H_1$ field from incident microwaves contained inside a transmission line (usually in the form of a microwave waveguide). The resonant cavity has several functions: (1) to convert incident microwave power to a standing, circularly polarized perturbation field, $H_1$; (2) to separate the $E_1$ and $H_1$ fields spatially; (3) to allow a modulation field (on the order of 1-10 G) to penetrate the sample and (4) to be able to maintain a narrow resonance (high Q). In this section, I will describe some important facets of resonant cavities and how they relate to quantitative ESR.

Any discussion about resonant cavities must mention Feher’s phenomenological construct of the lumped RLC circuit. A simple RLC circuit has all the elements of a resonator: resonance, stored electric and magnetic fields, separation of magnetic and electrical energy, and a resistive (energy absorbing) element. Solving the prototypical RLC circuit for its characteristic impedance gives:

$$Z = R + \frac{1 - \omega^2 LC}{j\omega C}$$

(3.2)

This results in a resonance at $\omega = \frac{1}{\sqrt{LC}}$, which is the frequency at which the Gunn diode attempts to output. The width of the resonance is extremely important in ESR spectroscopy, since it determines how well power is stored and dissipated in the cavity. The so-called cavity Q is given by:

$$Q = \frac{\omega L}{R} = \frac{v}{\Delta v}$$

(3.3)

where $R$ is the resistance caused by losses from the cavity walls and sample. Phenomenologically, we can understand the wall losses, $R$, by imagining an $H$-field at the walls of the cavity. To satisfy Maxwell’s equations at the surface of a good metal, a surface current is
generated in the cavity walls, thus causing loss. The $Q$ given in Eq. 3.3 is referred to as the unloaded $Q$. If the sample is lossy, therefore, the $Q$ will be low (typically, losses in the wall are minimized by design). The relation of $Q$ to frequency, $v$, and frequency spread, $\Delta v$, is how to physically relate the idea of a cavity $Q$. This physical paradigm can be abstracted for use in lasers and acoustics, where bandwidth at a given energy is important to know or measure. One can also interpret $Q$ as a ratio between stored energy (as given by $v$) to energy dissipated per cycle ($\Delta v$).

The loaded $Q$ is a more complete description of the real resonator, since it incorporates

![Equivalent circuit configuration of ESR cavity and waveguide](image)

Figure 3.1: Equivalent circuit configuration of ESR cavity and waveguide [54]. $R_0$ represents the transmission line impedance, while the $n$ turn transformer models the coupling iris. The cavity impedance is denoted as a resistance $R$, while the separation of electric and magnetic fields within the cavity are modeled using a capacitor and inductor, respectively.

the transmission line into the theoretical description. One can view this adding a transformer with a turns ratio of 1 : $n$. The transformer corresponds to the coupling iris, which
tunes the impedance match between the transmission line and the cavity. At a critical coupling condition, the cavity appears to the transmission line as an infinite extension of itself. Critical coupling allows the power transfer from the source to the resonator to be at a maximum, and the cavity to be both stable and sensitive. Figure 3.1 shows how to model the microwave transmission line \((R_0)\), iris coupling \((n \text{ turn transformer})\), and cavity \((R, L, \text{ and } C)\). By altering \(n\), the effective resistance \(R_0\) can be matched with the cavity resistance, \(R\) [54]. The expression for the loaded cavity \(Q\) thus incorporates the turns ratio and the transmission line resistance into the resistance of that the microwaves experience [54]:

\[
QL = \frac{2\pi vL}{R_0 n^2 + R}. \tag{3.4}
\]

The loaded \(Q\) and the unloaded \(Q\) both take into account the effects of the sample. What the loaded \(Q\) does differently is to incorporate the transmission line and the coupling effect. It produces a good physical insight into the iris and iris screw (coupling unit) and their relation to the transmission line and cavity.

Figure 3.2 : RF electric (left) and magnetic (right) fields in a TEM\(_{102}\) cavity [54]. The darker areas in the middle of the white rings are where the fields have their greatest amplitudes; those on the inside of the dark rings have the smallest amplitudes. Typically, the static magnetic field, \(H_0\) is directed along the \(x\)-direction, while the sample is inserted vertically in the \(z\)-direction in the middle of the \(z-y\) plane, where the RF magnetic field is both maximal and undisturbed by the walls.
More detailed calculations are required for understanding the actual cavity behavior, since complex interactions are present. A rich interplay between geometry, sample, walls, and frequency makes calculations of the field distribution difficult, so numerical methods are required. Two finite element solutions are graphically shown in Fig. 3.2 indicating the electric and magnetic fields generated in a typical rectangular TEM$_{102}$ cavity. As can be seen in these figures, the magnetic perturbing field, $H_1$, is at the center of the cavity, where the sample is situated. The static $H_0$ field is applied in the $x$-direction, while the sample is inserted in the middle of the $z-y$ plane. The electric field, $E_1$, is described by the 102 indices of the cavity: it is labeled so that the half-waves of the $z, x,$ and $y$ are denoted by the first, second, and third subscripts in the rectangular geometry. Good cavity design and modeling are very important for ESR since the $H_1$ field strength is necessary for quantitative spin counting. As such, the literature on this subfield is immense. Two good references for further reading are Poole [52] and Weber [54].

3.2 Experimental Methods: Sample Preparation

In comparison to most nanotube experiments, the sample preparation for this experiment is very minimal. Essentially, the main step that I perform is annealing the SWNT powder. Despite the lack of sample preparation, it is still important to make mention of the type of nanotubes which I am using, since the SWNTs themselves have gone through a fair amount of processing which rid the sample of most of its ferromagnetic catalysts; a key step that is necessary for observing spin resonance in bulk nanotubes.

3.2.1 Pre-Experiment Preparation

The type of nanotubes I use for ESR is purified laser oven single-walled carbon nanotubes in powder form. Laser oven refers to how they are created, which is of little concern in this
thesis. What is relevant is that laser oven nanotubes typically have a diameter distribution that ranges from 0.6 to 1.6 nm, which is fairly broad and signifies that many different types of nanotubes will be included. As such, my sample will have both semiconducting and metallic nanotube chiralities in it.

The sample also undergoes purification, which means that an acid was used to dissolve the metal catalysts in powder. This step was carried out by the nanotube producer (NASA). By weight, there is still a substantial amount of metallic catalyst left, as seen in Fig. 3.3. The metallic catalyst amount was measured by thermo-gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) to be 5.5% of the sample by mass.

The extra step in the preparation process came about after seeing that roughly 9% of the powder by mass was burned off at 100°C. It thus became imperative to drive off these non-nanotube, weakly adsorbed substances via an annealing treatment. To anneal the sample, I place the nanotube powder inside a capillary tube measuring 1.1 mm in diameter and a length of 2.5-5 cm. To hold the powder in place, I place quartz wool inside the capillary tube such that it is somewhat loosely abutting the powder.

The thermal treatment consists of heating the nanotube powder at 250°C for 12 hours under a 75 sccm flow of argon. This flow produces a blanket to prevent H₂O and O₂ from penetrating into the sample. Once the anneal is done, I typically flow argon with the vacuum closed until the inside of the chamber is close to atmospheric pressure. After quickly pulling out the sample, I fill the capillary (with the sample inside) with helium. Immediately after stopping the helium, I flame seal the capillary with a butane torch. Next, I place the flame sealed capillary tube inside a 3 mm ID ESR quartz tube and back fill that tube.
Figure 3.3: TGA curve of weight loss as a function of heat under air after having dried the tubes at 120°C for one hour. The weight percentage left (metal catalyst) can be used in conjunction with XPS information and the typical formation of cobalt and nickel oxides to calculate the catalyst concentration. Data taken by A. Leonard in Jim Tour’s lab at Rice University.

with helium. Last, I cap the quartz tube and seal with paraffin wax. This ensemble is what I place into the ESR spectrometer.

3.3 ESR Results

For a very long time, I could not reliably and reproducibly obtain a stable ESR resonance for nanotubes. However, when annealed, the ESR signal not only became stable and reproducible, but it also increased by roughly a factor of 10. This section presents my recent successes on temperature dependence of annealed SWNTs. The four major subsections
depict what we are able to gather from the ESR spectra; I will leave discussion of our conceived physical model until the next section.

3.3.1 Numerical Processing and Fitting

In all cases, I have subtracted a very broad ($\Delta H_{pp}$ on the order of 1000 G) ferromagnetic resonance (FMR) due to the catalyst particles in the nanotube powder. Since I was scanning only 200 G (for greater point density), I fit this FMR background with a 3rd order polynomial function using a Levenburg-Marquadt algorithm. This background fit has the same functional form used by Likodimos et al. [27]. The FMR peak was temperature dependent, which is reflected in the monotonic variation of the polynomial coefficients with temperature. As can be seen in Fig. 3.4, the full form of the FMR is incomplete, since even at 0 G, there is still an offset. What is more is the FMR does not fit any easy functional form (i.e. Gaussian, Lorentzian, Dysonian, etc.). Thus, even if I scanned the entire range (0-6000 G), I would still need a background subtraction to remove the SWNT ESR from the data.

The polynomial fit I used did not include the ESR peak when it was applied. Specifically, the polynomial fit the aggregation of points ±45 G from the center resonant field, $H_0$; in other words, all points except for $H_0 \pm 45G$. Concurrently, the Dysonian lineshape given in Eq. 2.19 was fit to the resonance peak in the excluded range. Thus, the ESR signal I obtained from the spectrometer was fit with the additive sum of a 3rd order polynomial (background) and Dysonian lineshape (resonance). Corrections due to field offsets were employed later using a DPPH standard, which came out to be $-2.39$ G for all temperatures except for room temperature, for which the correction was $-2.50$ G.
Figure 3.4: Annealed and non-annealed ESR signal from purified laser oven SWNTs at low temperatures. The linewidth of FMR peak is roughly 2000 G long, indicating a very fast relaxation time on the order of picoseconds. The small signal at 1500 G is related to the Fe$^{3+}$ ion in the capillary tube. The shift in the position of the resonances is due to slightly different X-band frequencies. Notice how large the annealed SWNT resonance is as compared to the FMR. The non-annealed curve was multiplied by 2000 (due to a different gain setting) and offset for visual clarity.

3.3.2 Initial Impressions

When the nanotubes were not annealed, the observed resonances are small, as seen in Fig. 3.4 and as evidenced by the low signal-to-noise ratio in Fig. 3.6 as compared to Fig. 3.7. More importantly, the non-annealed SWNT resonances are difficult to reproduce, since small fluctuations and vibrations markedly change the signal. This may be due to the fact that the resistance in SWNT networks in uncompressed powders can be altered considerably by small perturbations. Surprisingly, other researchers have published on similarly
Figure 3.5: A very small ESR resonance, as compared to the FMR signal, was observed by Likodimos et al. [27]. This ESR resonance is typical of non-annealed SWNTs.
small resonances, as shown in Fig. 3.5, where the FMR dominates the spectrum. Only upon annealing does the SWNT ESR signal become comparable to the FMR peak, as seen at 4.2 K in Fig. 3.4. The ratio of the SWNT peak to the FMR peak qualitatively shows that annealing produces a substantial change in the spin susceptibility of SWNTs.

![Graph showing ESR intensity vs. applied magnetic field](image)

**Figure 3.6**: Dysonian lineshape fits to subtracted ESR resonances for non-annealed purified laser oven SWNTs. Below 40 K, the Dysonian lineshape does not describe the data very well.

In Fig. 3.6, a Dysonian is fitted to each subtracted SWNT resonance temperature curve. Up until 40 K, the Dysonian fits well to the subtracted ESR signal. Below this temperature, the Dysonian form does not fully describe the observed peak. It seems as if either a perturbation occurred at 40 K or another resonance is developing. In either case, the information from the fits that I obtain will be skewed by this fact.
Figure 3.7: Background subtracted ESR traces as a function of temperature (intentionally offset for clarity). The red dots indicate actual data taken, while the black lines are Dysonian lineshape fits to the data. All curves are well-described by a Dysonian lineshape, despite changes in magnitude, linewidth, and asymmetry.

In contrast, the annealed SWNT ESR signals are well-described by a Dysonian at every temperature. In Fig. 3.7, several background subtracted resonance signals are displayed showing the evolution of the ESR with temperature. At each temperature, the signal-to-noise ratio is very high, because of the increase of the signal size after anneal. Importantly, the signal grows inversely with temperature, indicating that I am not observing a Pauli law spin susceptibility. In addition, as temperature decreases, the linewidth increases, although not in the manner seen in the non-annealed sample, since there is only one resonance. The position of the peak seems not move as temperature is varied, which corresponds to the non-annealed case.
3.3.3 \textit{g-factor}

The \textit{g}-factor can be related to the spin-orbit coupling in a material [52], though, that relationship may not be clear cut. However, the relative change with respect to a certain variable (e.g., temperature, frequency, solvent, etc.) can tell us how the spin-orbit coupling is being affected. For my spectra, I fit a Dysonian lineshape to each trace at a set temperature. The fit is crucial to determining the actual \textit{g}-factor, since a simple derivative or integral test (as can be used with a Lorentzian or Gaussian) will not give the correct center of the resonance.

The results before annealing showed minimal temperature dependence with the \textit{g}-factor moving higher as temperature decreased, as seen in Fig. 3.9. At high temperatures ($T > 150$ K), the \textit{g}-factor was below 2.0030; at lower temperatures, it (on average) crept higher. A reasonable estimate of the experimental precision of this measurement is ±0.0001, based on the calibration (at one temperature) of the magnetic field.

![Figure 3.8: \textit{g}-factor as a function of temperature for non-annealed purified laser oven SWNTs.](image-url)
Besides the general trend noted above, no further temperature dependence of the $g$-factor is observed. The point density is insufficient for tracing out the finer features of the curve. The small dips and rises are within or close to the error bars for the measurement. The values are similar to those obtained by Likodimos et al. [27], though, slightly lower than the 2.0035 average value seen in that work.

After annealing, the $g$-factor shifted downward by 0.0003-0.0006. The observed $g$-factor has an average value of 2.0025, which is very close to the free electron value of 2.0023. Here, I have added the error bars to show that within the error of the experiment, the $g$-factor is relatively constant as a function of temperature. This constancy is in direct conflict with the observed behavior of graphite [41], and much more inline with studies related to SWNTs [27,45–47].

![Figure 3.9: g-factor as a function of temperature for annealed purified laser oven SWNTs.](image)
3.3.4 Linewidth

One of the most important parameters that I can extract from the data is the linewidth, $\Delta H$, which can be extracted easily from fitting the lineshape using Eq. 2.19. The coherence time can calculated from $\Delta H$:

$$\frac{1}{T_2} = \frac{g |\mu| B}{h} \Delta H.$$  \hfill (3.5)

To conform with the literature, I plot $\Delta H$ and not $T_2$, with the recognition that they will be inversely proportional to one another.

For the non-annealed sample, $\Delta H$ is close to 6 G at temperatures above 150 K. Starting at 40 K, though, the linewidth significantly broadens from 7 G to nearly 14 G at 5 K. This anomalous broadening relates to the emergence of what appears to be a second resonance (Fig. 3.6). The single Dysonian lineshape paradigm appears to be meaningless below 40 K for this data. The second resonance causes the Dysonian lineshape fit to become less and less applicable as temperature is lowered to 5 K.

Because the resonance was not very stable for the non-annealed SWNTs, it is difficult to tell exactly what is occurring. One hypothesis is that the powder was disturbed at 40 K disrupting the SWNTs and changing the cavity coupling. Another hypothesis is that the relaxation mechanism is undergoing a significant change somewhere around 30-50 K.

Annealing the powder produces a dramatic effect in the temperature dependence of the linewidth. At high temperatures ($T > 100$ K), the linewidth is below 7 G, which is comparable to the most recently reported linewidth in SWNTs of 6.5 G [27]. As temperature is decreased, the linewidth marginally increases until 70 K. Once below 70 K, $\Delta H$ begins
Figure 3.10: $\Delta H$ as a function of temperature for non-annealed purified laser oven SWNTs.

to exponentially increase from below 7 G until above 9 G. This marked rise slows after $T$ drops below 10 K, inching up from 9.09 G at 10 K to 9.29 G at 4 K.

The shape of the linewidth curve is startling, as it has never been seen for ESR in SWNTs. It does, however, fit the general profile of motional narrowing. For motional narrowing, one expects the highest temperatures to have the narrowest linewidths (in Gauss), since the electron movement, which is greatest at the highest temperatures, narrows the linewidth. The mechanism of motional narrowing will be elaborated on further in the Discussion section.

One important point that should be mentioned is that the data points above 100 K were
shifted downwards by 0.672 G. This shift corresponds with data taken between 100-150 K, as well as multiple data points at 300 K. I am currently working to resolve this discrepancy, which I attribute to an incomplete anneal.

3.3.5 Dysonian Lineshape Asymmetry

The asymmetry of the signal, or $A/B$ ratio, indicates the degree of mixing between the absorption and dispersion components of the Dysonian lineshape. Recall Eq. 2.18 in which $\phi$ denoted projection angle of $\chi$. The ratio of dispersion to absorption is given by [27]:

$$\alpha = \tan \phi.$$  

(3.6)
The $A/B$ ratio can be related to $\alpha$ when $\alpha$ is small: $A/B \approx 1 + \alpha$ [26]. Thus, seeing large asymmetries in the derivative lineshape signify a larger dispersion component.

![Graph showing $A/B$ ratio and $\alpha$ as functions of temperature for annealed purified laser oven SWNTs.](image)

Figure 3.12: $A/B$ ratio (left axis) and $\alpha$ (right axis) as functions of temperature for annealed purified laser oven SWNTs.

I plot the $A/B$ ratio and $\alpha$ as functions of temperature in Fig. 3.12. It is immediately obvious that they follow each other closely, which agrees with my previous claim for small $\alpha$. Also apparent is that the degree of asymmetry is decreasing as temperature decreases. $\alpha$ drops from roughly 0.4 at 300 K to less than 0.2 at 4 K. At low temperatures, $\alpha$ is close to 0, which signifies that we are observing a mostly Lorentzian signal. (If the components of dispersion and absorption were completely equal, for instance, then $\alpha$ would be 1.) Thus, I am observing a marked change in the movement of the spins from more delocalization...
at high temperatures to a more localization at low $T$. The physical meaning of this will be elaborated on in the Discussion section.

In comparison to my work, Likodimos et al. [27] also reported a decreasing $\alpha$ with decreasing temperature. Their value of $\alpha$ is higher than mine, starting at roughly 0.6 at 300 K and decreasing to 0.4 below 10 K. For both my work and Likodimos et al., the difference of $\approx 0.2$ in $\alpha$ from 300 K to 4 K is small when compared to the differences that Petit et al. [47] observed. In Petit et al.'s work, they report an $A/B$ ratio of 8-9, which is large when compared to my ratio of 1.2-1.5. No temperature dependence is discussed in their work, so no further comparison can be made.

### 3.3.6 Spin Susceptibility

The spin susceptibility was calculated from the Dyson lineshape fitting. The spin susceptibility, $\chi_s$, is related to the magnitude of the rf spin susceptibility, $A$, by

$$\chi_s = 3 \sqrt{3} \frac{A \cos \phi}{\omega_0 \Delta H^2},$$

where $\omega_0$ is the center angular frequency. The spin susceptibility relates the magnetization, $M$, to a static magnetic field, $H$, by $M = \chi_s H$. The two temperature paradigms, Pauli law and Curie law, were discussed at length in Chapter 2.

In Fig. 3.13, I plot the spin susceptibility as a function of temperature for the annealed nanotubes. The values above 100 K are shifted downwards to match the low temperature data, since I used a different resonant cavity for this temperature range. All the values are scaled so that the 100 K static spin susceptibility is a value of 1.00. I employed a CuSO$_4$ calibration standard to translate the relative spin susceptibility into units of emu/g (see Appendix A for more details).
Figure 3.13: $\chi_s$ as a function of temperature for annealed purified laser oven powder.

It is clear from the figure that the spin susceptibility has temperature dependence. This fact implies that a localized spin system with a Curie law temperature behavior may be present. To investigate this point, I fit a line to $\chi_s$ versus $1/T$. If Curie behavior is occurring, then a line should be a good description of the spin susceptibility. However, as Fig. 3.14 shows, $\chi_s$ does not follow a $1/T$ dependence at low temperatures when a numerical fit is applied. The fit shown in Fig. 3.14 was done for temperatures above 8 K and then extrapolated for the lower temperatures, since a full linear fit to the data produces a poor fit to all temperatures. The majority of points, which lie at small values of $1/T$ and $\chi_s$, are not represented well in a full fit, because the error of the fit is biased to the larger values (lower
Figure 3.14: $\chi_S$ as a function of inverse temperature for annealed purified laser oven powder (circles) is given. A line was fit to $\chi_S$ for temperatures above 8 K; the curve was then extrapolated for the rest of the temperature range (dashed line). From 8 K to 4 K, the behavior is distinctly non-Curie-like, as evidenced by the considerable mismatch between the actual data and the fit. A linear fit to the entire data set produces a very poor fit due to the lower temperature values.

Interestingly, from 300 K to 20 K (one order of magnitude in temperature), Curie-law is observed. For these points, the general form displays both Curie and Pauli law behavior giving a $\chi_S$ a functional form:

$$\chi_S = \frac{C}{T} + \chi_0.$$  \hspace{1cm} (3.8)

Here $C$ is the Curie coefficient and $\chi_0$ is the Pauli susceptibility component. For my data, I extract a Curie coefficient of $C = 1.89 \times 10^{-5}$ emu K/g and a Pauli contribution of $\chi_0 = -1.63 \times 10^{-8}$ emu/g.
$\chi_S$ is the most widely varying of all the parameters in the nanotube ESR literature, so a strict fit of either the Pauli or Curie law paradigm could be misleading. I will discuss in the next section what other factors could lead to deviations at low temperatures from Eq. 3.8. Strikingly, the values of $\chi_S$ that I observed are on the order of $10^{-6}$ emu/g, which nearly three orders of magnitude above Likodimos et al. [27] and two orders of magnitude over other reports [46, 55]. Likodimos and co-workers also give their Curie and Pauli contributions as $C = 4.7(1) \times 10^{-8}$ emu K/g and $\chi_0 = 1.06(3) \times 10^{-9}$ emu/g. As expected, my values of both $C$ and $\chi_0$ are much higher than Likodimos et al. Oddly, my $\chi_0$ is negative. Further measurements with a precise standard at high temperatures may correct this discrepancy.

3.3.7 Sheet Resistance Results

The sheet resistance of decanted HiPco films is presented in Fig. 3.15. Resistance measurements in the ohmic regime were made on thin films (on the order of 100 nm) as a function of temperature. The sheet resistance, $R_s$, is defined as

$$R = \frac{\rho}{A} \quad \text{and} \quad R_s = \frac{\rho}{W}$$

where $L$ is the distance between two contacts, $A$ is the cross-sectional area that the current passes through and is equal to the thickness of the film times the width, $W$, and $\rho$ is the resistivity.

The sheet resistance rises as temperature is lowered, which agrees with the typical understanding of carriers from the narrow gap semiconducting nanotubes depopulating the
conduction band. The results I obtained are in agreement with previous reports in both magnitude and temperature behavior [56]. The observed temperature trend is more important than the exact value of $R_s$, since the film composition is different from our ESR samples in many respects, such as nanotube diameter distribution, catalyst impurity concentration, density, and intertube contacts. The increase of $R_s$ with decreasing temperature signifies that the skin depth is increasing. Thus, the two time scales for the Dysonian lineshape, $\frac{\Delta f}{f}$ and $\frac{\Delta f}{f^2}$, are both changing as a function of temperature. As a consequence, one should expect the degree of asymmetry in the observed ESR signal to be reduced (more Lorentzian-like) as temperature decreases, which is what I observe. Temperature dependent measurements on acid treated powders in a magnetic field will be performed on both

Figure 3.15: Sheet resistance as a function of temperature for a HiPco nanotube decant film.
non-annealed and annealed samples to clearly examine charge transport behavior. By ex­amining the temperature dependence of the conductivity, I will be able to make a claim as to whether or not hopping behavior is occurring. This determination via transport is impor­tant in lieu of the proposed variable-range hopping model, deduced from ESR data, that I will discuss in the next section.

3.4 Discussion

In this section, I will discuss my proposed model, which seems to explain most of the data. Further experimentation is necessary to fully confirm the model.

3.4.1 1D Conducting Polymer Model

Conducting polymers are quasi-1D systems, whose conductivity and spin susceptibility can both be fairly high [57]. Conducting polymers have similarities to carbon nanotubes, which is why both have been thought of as good candidates for LL behavior, as mentioned in Chapter 2. Thus, numerous studies have been performed on conducting polymers to examine their transport and spin properties [58]. I will examine the spin dynamics of two polymers, polyacetylene and polyaniline, to examine how quasi-1D systems affect ESR.

These polymers can be described as 1-D, disordered metals in which variable-sized “metal­lic islands” are surrounding by insulators [57]. In this model, two types of conduction are possible: intra-chain (along the polymer chain) diffusion, denoted as $D_{\parallel}$, and inter-tube (or interchain) hopping, $D_{\perp}$. Diffusion applies to the randomized movement of particles (electrons, phonons, etc.) from one position to another, primarily driven by a potential (e.g.
electric or chemical). The diffusion equation in its simplest form (1-D) is
\[ \frac{\partial u}{\partial t} = D(x, t) \frac{\partial^2 u}{\partial x^2}, \] (3.10)
where \( u \) is a wavefunction describing the particle, \( t \) is time, \( x \) is position, and \( D \) is the diffusion constant, which can be a function of position and/or time. For the case of 1-D disordered metals, despite two different avenues of diffusion, one can safely assume that hopping (interchain "jumping") is much slower than intra-chain conduction, leading to \( D_\perp < D_\parallel \). A typical order of magnitude for \( D_\parallel \) in trans-polyacetylene is \( 10^{13} \) rad/s with \( D_\perp / D_\parallel \geq 10^6 \) [59].

The movement of the spins affects the linewidth via motional narrowing by altering the total spin time correlation function, \( G(t) \) [58, 59]. This correlation function can be related to the spectral lineshape via a Fourier transform [58]:
\[ F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t) e^{-i\omega t} \, dt. \] (3.11)
For the quasi-1D case, \( G(t) = \exp[-\Delta \omega t] \), where \( \Delta \omega \) is the linewidth. Motional narrowing, as first described by Bloembergen et al. [60] and later by Anderson [61], is the process by which the observed resonance linewidth is reduced due to the rapid motion (relative to the relaxation frequency) of the spins. The probed spins experience small precessional phase shifts as they move due to slightly different magnetic environments [16]. These phase shifts act as a dephasing mechanism. Yet, the dependence of the coherence time, \( T_2 \), on the magnetic perturbation, \( B_i \), is not \( B_i^{-1} \) as is typical, but \( B_i^{-2} \):
\[ T_2 = \frac{1}{\gamma^2 B_i^2 \tau}. \] (3.12)
Here \( \tau \) is a measure of the time that a spin senses the magnetic perturbation, which can be interpreted as electron hopping conduction in the case of polymers. For magnetic reso-
nance, one roughly estimate the temperature behavior of $\Delta H$ and assume a simple thermal activation type behavior

$$\Delta H = \Delta H_0 e^{\Delta E/k_B T},$$

(3.13)

where $\Delta H_0$ is the rigid lattice linewidth [16] and $\Delta E$ is the barrier energy that one hop encounters. The rigid lattice, or static, case is for a motionless electron, and represents the asymptotic limit of the linewidth. Equation 3.13 is an estimate of motional narrowing, since the actual functional form depends on the mechanism of the motion. In the SWNT system that I am studying, the most accurate form of $\Delta H$ is that of a 1-D environment with traps [62]. In this model, the energetic barriers between 1-D chains is taken into account, as well as the concentration of localized (trapped) and diffusive (mobile) spins. Yet, the information required to use such a model is far beyond the experimental capabilities that I have at my disposal, such as frequency dependence and nuclear magnetic resonance (NMR).

How the electrons hop chain-to-chain (or tube-to-tube) is also important. For instance, to describe a disordered metal such as polyaniline, one often uses variable-range hopping (VRH) as the specific conduction mechanism. VRH is a dimensionally dependent model in which the location of the hop is contingent upon the energetic distribution of the thermal bath (phonons). Having a larger hopping distance helps to find a better hopping location, but also limits the energetic transfer to that state [63]. Thus, a competition is setup between “searching for” and “transferring to” a given location. For a given dimension, $d$, the VRH conductance can be written as [63]

$$\sigma_{hop} = \sigma_h \exp\left[\left(-T_0/T\right)^\nu\right],$$

(3.14)

where $\sigma_{hop}$ is the hopping conductivity, $\sigma_h = e^2 D(\varepsilon_F) R^2 v_{ph}$, $R$ is the hopping distance, $v_{ph}$ is the phonon frequency, $T_0$ is a constant that scales inversely with $D(\varepsilon_F)$, and $\nu$ is roughly
equal to $1/(d + 1)$. The exponent, $v$, is not exact, since electron interactions and fractal networks can modify this relation.

One important point that should be stressed is that the spin dynamics of polyaniline are strongly affected by both water and oxygen [57]. Indeed, oxygen is known to be a good trapping molecule for 1-D polymers [58]. Consider a situation where the moving spins in a polymer, denoted as $A$, are being affected in some way by another species, $B$. Two different line broadening cases are possible for this situation: slow exchange and fast exchange. For the former case, the spin flip-flop frequency, $\omega_x$, is very much smaller than the difference in the Larmor frequencies of the two different interacting species, $A$ and $B$: $\omega_x \ll | \omega_A - \omega_B |$. For the other case, $\omega_x$ is much larger than the difference of frequencies. In this situation, the $B$ spin species is strongly coupled to the $A$ spin species. For both cases, the linewidth is broadened, but for the strongly coupled case, the linewidth broadening, $\delta(\Delta \omega)$ has the specific relation [58]

$$\delta(\Delta \omega) = pC_BD,$$

where $p$ is the efficacy of the collisions at spin flipping, $C_B$ is the concentration of $B$, and $D$ is the hopping frequency of the spins. Thus, as concentration is increased, the linewidth is proportionally broadened. For polyaniline, the presence of oxygen (in particular, the dipole-dipole interactions of the triplet state in oxygen) is directly proportional to the ESR linewidth [57].

### 3.4.2 Comparison of Model to Results

Returning back to carbon nanotubes, I will see if any of the features from 1-D polymer chains can explain the SWNT data. Examining spin susceptibility first, I found that upon annealing, a marked increase in the signal intensity occurred, which I roughly estimated
as a factor of ten. Annealing the powder and sealing it to be air tight, seem to cause a remarkable change in the sample properties. If conducting 1-D polymers are any guide, one can hypothesize that this is a fast exchange between the oxygen species and the nanotube electrons. This strongly coupled interaction would produce a very broad second resonance, since the triplet state of oxygen would act as a fast relaxation mechanism [57, 58]. The strong coupling may be seen in the $g$-factor shift that I noted in the results section above, in which the $g$-factor dropped from 2.003 to 2.0024 upon annealing.

![Graph](image)

Figure 3.16: Relative static susceptibility for nine trials. After trial 4, pure oxygen was added to the sample for 10 minutes. Each trial was completed at $\approx 30$ minute intervals.

To examine this hypothesis, I tested whether or not the presence of oxygen has an effect on the resonance. For this experiment, I measured the ESR spectra of the annealed sample
for two hours (one test every 30 minutes for a total of four trials). Next, I broke open the flame-sealed tube and inserted a 99.99% pure oxygen flow for ten minutes. For the next two hours, I measured the signal every 30 minutes; this is plotted in Fig. 3.16.

The signal shows a factor of two drop in the relative spin susceptibility within an hour of when the oxygen has been added. Such an observation is a strong indication that oxygen has a strong influence on the spin dynamics in nanotubes. Moreover, I can conclude that the presence of oxygen in SWNTs severely limits the spin density being probed by ESR. Although I initially expected a factor of ten signal decrease, one can surmise that the oxygen was originally situated between nanotubes. Upon annealing, the oxygen was de-adsorbed from their interstitial locations, which allowed the tubes to attract one another via van der Waal’s forces. The lack of space between the nanotubes prevents the oxygen from being re-adsorbed, which thus explains why the signal does not decrease by a factor of ten.

What the proposed 1-D polymer model does not explain (and what is still under evaluation) is the functional form of the spin susceptibility. Although Eq. 3.8 describes the spin susceptibility from 20 K to 300 K, there is a large discrepancy between the fit and the data at lower temperatures (see Fig. 3.14). The odd behavior of $\chi_S$, which is mentioned as a possible explanation for non-Curie law behavior in Salvetat et al. [48], may be due to electron-electron interactions and/or a changing band gap. Both of these would modify the strict $1/T$ dependence for a Curie law. Regardless, SWNT ESR is widely expected to be a probe of metallic SWNTs, so a Pauli law is typically predicted, and in early publications, has been observed down to 77 K [47]. Yet, as Náfrádi et al. [55] point out, the spin susceptibility for a LL is not clearly Pauli law as one naively expects. Thus, a different functional form may be more appropriate for $\chi_S$, even if metallic SWNTs are being probed.
What is clear for my data, though, is that I am not seeing any spin gaps opening at low temperatures, such as seen by Likodimos et al. [27]. In that situation, a sharp, sustained drop in $\chi_s$ is observed at a given temperature. For my data, a drop below 20 K may occur, but it is not sustained. Interestingly, the measured magnitude of the spin susceptibility is roughly a factor of 100 larger than previously reported [46, 55]. This huge increase of the spin susceptibility upon the removal of oxygen would seem to imply that the presence of oxygen is acting as a spin trap. A broad resonance, due to fast relaxation, could be present in the non-annealed case; a broad resonance would be very difficult to detect if it is fairly
broad (i.e. larger than 100 G wide). Upon removing the oxygen, the spin population would no longer be influenced by oxygen and would contribute fully to the observed resonance.

The absence of oxygen also manifests itself in the linewidth and asymmetry of the ESR signal. This behavior is similar to the case of polyaniline, where lineshape both sharpens and becomes more symmetric upon removal of oxygen and water [57, 58]. Figure 3.17 shows that motional narrowing of the linewidth is occurring as temperature is increased. Equation 3.13 can be fitted to $\Delta H$ to obtain a rough estimate of the static linewidth ($\Delta H_0$) and the energetic barrier height ($\Delta E$). To better utilize that simple model, I plotted $\ln(\Delta H)$ versus $1/T$ and then fit a line through the resulting point. The linear fit gives $\Delta H_0 = 6.75$ G and $\Delta E = 0.134$ meV or $\Delta v = 32.5$ GHz. The hopping frequency calculation that I used employs a simple thermal activation model that is compatible with the notion of phonon-assisted conduction from nanotube-to-nanotube or metallic nanotube-to-nanotube (metallic island model). It allows me to extract a hopping frequency ($\Delta v$), which is the first estimate of the intertube hopping rate in SWNTs. Although just an estimate based on a crude model, it does give insight into the energy scale of the hopping barrier between bare nanotubes.

The rigid linewidth I obtain is 6.75 G, which represents one of the shortest linewidths ever measured for SWNTs (Likodimos et al. [27] holds the honor of the shortest linewidth ever reported with a $\Delta H$ of 6.5 G). The narrow linewidth indicates that my coherence time, $T_2$, is longer than previous reports. If one believes the current model of relaxation by the ferromagnetic catalyst particles [48], the longer coherence time implies that my sample is fairly pure. The relaxation mechanism and the purity of the sample are both topics that are being evaluated.
The temperature dependence of $\alpha$ is another important measure of spin localization (or delocalization). Specifically, I can make a rough estimate of conductivity ($\sigma$) from $\alpha$ based on Feher and Kip's work [20]:

$$\alpha \propto \sqrt{\frac{1}{T_D}}$$

$$T_D \propto \frac{1}{\sigma}$$

$$\alpha^2 \propto \sigma.$$  \hspace{1cm} (3.16)

Looking at the power law fit ascribed to $\alpha(T)$ in Fig. 3.18, one can see that $\alpha = AT^\beta$, where $\beta$ is 0.201. Thus, I have $\sigma = CT^{2\beta}$, where $2\beta$ is 0.402. This fit is fairly good, but the actual theoretical model I would like to use does not explicitly follow this form. Instead,
I would like to fit a VRH model to the data; this fit is shown in Fig. 3.19. The fit is not as good as I would have hoped, but it does correctly explain the experimental trend. It is clear the data that the SWNT ensemble is acting as a 1D system, as seen by $v \approx 0.5$, which gives $d \approx 1$. The fitted coefficient shows that the SWNT system has a low $\alpha$ even for high temperatures. The low $\alpha$ implies that the lineshape is not very Dysonian, since one would expect $\alpha$ to approach 1 or higher if metallic-like behavior is being observed [20,27].

![Power law fit to temperature dependent $\alpha$ values.](image)

$$y = 0.373 \times \exp\left[ \left(-0.917/T\right)^{0.637} \right]$$
SSE: 0.232
$R^2$: 0.359

My interpretation that SWNTs show quasi-1D VRH after annealing is consistent with the interpretation given by Pint et al. [64], who saw similar behavior in nanotube carpets. Although they did not extract a hopping frequency, their temperature trend strongly follows
Eq. 3.14. It would seem reasonable that the conductivity of the annealed powders used in my experiment should follow a similar behavior as Pint et al. and $\alpha(T)$; as previously mentioned, I plan on doing this experiment in the very near future.

3.4.3 Concluding Remarks

The strong coupling of oxygen to SWNTs has a powerful effect on the spin dynamics of electrons in nanotubes. A parallel between 1-D conducting polymers, such as polyacetylene and polyaniline, and nanotubes is drawn to show that the theoretical and experimental results in that community can be used to explain the remarkable results we have obtained. As such, I believe that motional narrowing is to account for the temperature dependence seen for the ESR signal linewidth. This motional narrowing is further identified as VRH hopping, which is similar to the inter-chain or inter-metallic island hopping, seen for polyaniline. My interpretation of quasi-1D VRH is consistent with previous reports on annealing in SWNTs [64]. Further, I am able to extract an estimated hopping frequency of $\approx 32.5$ GHz from the temperature behavior of the linewidth.

The increase of the spin susceptibility upon annealing can be ascribed to linewidth broadening caused by the presence of oxygen. I hypothesize that oxygen acts as a spin trap for SWNT electrons, creating a fast relaxation due to the oxygen triplet state; this, too, has previously been noted for 1-D conducting polymers [58]. Such a situation would create a broad, nearly unobservable resonance, which would account for why we have not detected this peak. Not all the spin population would be trapped in the presence, thus leaving a resonance with a substantial amount of delocalization, which may be the resonance previously been ascribed to CESR of SWNTs [46, 47].
3.5 Density Gradient Ultracentrifugation Results

A necessary component of any study into the magnetic, electrical, or optical properties of SWNTs is understanding what is actually in the sample. As of yet, no group has successfully created an ensemble of only one type of nanotube in an aqueous environment. This makes any claim of intrinsic behavior of ensembles very dubious, since variables like catalyst concentration, chirality distribution, amorphous graphite content, multiwall content, and length distribution are very different sample to sample. Despite these caveats, remarkable progress has been made in the last few years towards achieving single chirality samples and metal-enrichment [65-68].

Utilizing and modifying Arnold’s procedure of density gradient ultracentrifugation (DGU) for suspended SWNTs in aqueous solutions [66,67], we (primarily Erik Haroz, myself, Tianhe Yang, and Benjamin Lu) have been able to obtain results for both bundling reduction, as well as metallic-enrichment, for HiPco nanotubes. I will first briefly describe how bundling reduction was performed and measured, before moving towards the important results obtained in the area of metal enrichment.

3.5.1 Bundling Reduction

The DGU experimentation first began as a way to reduce bundling in our nanotube samples. Through van der Waal’s interactions are somewhat weak on a per unit length basis, they add up to a very strong binding force for nanotubes, whose average length in solution is anywhere from 100-600 nm, depending on sonication conditions. Traditionally, nanotube spectroscopists have used O’Connell’s procedure to individualize SWNTs [69]. Despite huge improvements in photoluminescent (PL) yield, these samples are heterogeneous environments, which are composed of multiple different chiralities each with different spec-
The DGU method using density differences between species to spatially separate and segregate them. Typically, one creates a density gradient using iodixanol within the centrifuge tube to highlight the differences in buoyant densities of the species. Spatial separation on the basis of these differences in density are possible if the aqueous samples are ultracentrifugated for a substantial period of time (usually 12 to 18 hours) at high forces (typically on the order of 250,000 g's for DGU purposes).

When a uniform iodixanol gradient is used, SWNTs can be separated according to bundling order. Since a typical nanotube in solution has range of densities (1.11-1.17 g/cm$^3$ [66]), the addition or subtraction of a nanotube within a bundle can cause the bundle unit to be more or less density than its neighbors. More significantly, though, is the aqueous and surfactant layer that surrounds the nanotube. This water surfactant layer is different for bundles than for single tubes. Therefore, as more tubes are added to a SWNT bundle, the density of the entire unit (water, surfactant, and tubes) changes.

The change of density with increasing number of nanotubes was utilized by the DGU process to extract bundle reduced fractions. We looked at normalized photoluminescence (PL) for each extracted aqueous fraction. Photoluminescence occurs when optically excited electrons radiatively decay; it only occurs for materials with band gaps. The PL is normalized to the absorption spectra of each extracted aqueous layer to account for the differences in concentration. To normalize, the average of seven absorption peaks was taken to avoid any chirality selectivity that may have been caused by the DGU process.
As can be seen in Fig. 3.21, the normalized PL intensity decreases as the fraction becomes denser (the higher the layer number, the larger the fraction density). PL is being used to measure bundling, which is an indirect way of probing aggregation. Still, the conceptual model that we followed says that bundles do not fluoresce as strongly as individual nanotubes due to the presence of metallic nanotubes in the bundle, since metallic SWNTs provide a nonradiative relaxation mechanism [70]. That a bundle would have such a metal-like SWNT is based on the probability that one-third of a typical SWNT ensemble is composed of metal SWNTs; for HiPco, this is a very safe assumption [68].

Figure 3.20: Absorption of different layers extracted from an iodixanol gradient. Data taken by T. Yang.

The major source of error in Fig. 3.21 is due to the normalization step, which estimates average concentration, thus concealing the dependence of PL on the photon-electron coupling constant at a given frequency. A better method would be to normalize a full pho-
toluminescent excitation (PLE) map by the absorption spectrum. In this way, the entire semiconducting PL yield as a function of layer depth could be precisely measured.

![Photoluminescence spectrum from different DGU layers](image)

**Figure 3.21:** Normalized photoluminescence from different DGU layers. Data taken by T. Yang.

The main problem with our bundling reduction technique is the very low mass yield of SWNTs in each aqueous layer. For the top layers, the concentration of nanotubes is extremely low. The shear fact that we are dealing with concentrations at least an order of magnitude below that of a typical decant may account for the increased normalized PL, since bundling amount should roughly be proportional to concentration.

Our work fits the conclusions reached by Crochet et al. [70], which saw the PL yield decrease as a function of depth within a DGU gradient. They also reached similar conclusions
concerning the bundling environment of the nanotubes. As a figure of merit, the reported PL quantum yield (how much power is radiated per power unit absorbed) is of the order of 0.1% to 1.0%, which is still an order of magnitude below that of single tube PL quantum yields, which has been reported to be 7% [71].

3.5.2 Metallic Enrichment

To improve our ability to observe CESR in nanotubes, we began the process of metallic enrichment of aqueous SWNT solutions. As such, the ability to metal-enrich SWNTs via the DGU method was developed. This approach for ESR was abandoned because the mass yield was too low (on the order of 10–100 µg). The samples were so well-enriched, though, that we were able to perform in-depth characterization on them, which I will now present. Much of this work was carried out by Erik Hároz, who kindly supplied much of the following data. I will very briefly describe these exciting results, which is currently being submitted for publication.

Two samples were produced from HiPco SWNTs: a typical decant prepared using the procedure from O'Connell et al. [69] and a DGU metal-enriched sample made following the method outlined in Yanagi et al. [72]. For both samples, a series of spectroscopic experiments were performed. First, absorption spectra were taken to show the presence of individual nanotubes. Those spectra, which are shown in Fig. 3.23, demonstrate that several optical transitions have been removed by the DGU process. Further, it is clear that only transitions between 450 nm and 550 nm remain for the DGU sample. This is where most metallic optical transitions exist for the types of chiralites in HiPco nanotubes [73].

To determine what semiconductors were in each sample, we performed photolumines-
Figure 3.22: Metal-enriched fraction (left) as compared to starting decant solution (right). Picture taken by E. Hároz.

cence excitation (PLE) spectroscopy. A PLE map is created by exciting a sample at a given photonic energy and measuring the photoluminescence (PL) that results. Because of non-radiative decay from various sources, the PL is lower in energy than the excitation. Typically in SWNTs, one sees PL from the first conduction band to the first valence band, which is the so-called $E_{11}$ transition; this occurs in the NIR wavelength range.

Because a band gap is needed for photonic relaxation, PLE cannot be used to observe metals. Due to measurements by other researchers, the PLE spectrum from nanotubes can be used a tool to determine chirality assignments [73]. In our work, the PLE maps of the as-produced HiPco decant and the DGU enriched sample are strikingly different (see Fig. 3.24). In the decant sample, the plethora of peaks indicates that several semiconducting SWNTs are present; this spectrum is also demonstrative of the individuality of the SWNTs in solution. For the DGU sample, though, no peaks are present. Because of the absorption spectrum in Fig. 3.23, bundling can be eliminated as the reason for the lack of PLE struc-
ture. It is apparent that metallic SWNTs can create this type of PLE map. Thus, we can be confident that the DGU procedure has played a substantial role in altering the chirality distribution of the sample.

Figure 3.23: Optical absorption spectra for as-produced (red curve) HiPco nanotubes and metallic-enriched (blue curve) HiPco nanotubes in solution. Spectra taken by E. Hároz.

What remains unclear, though, is how metal-enriched our sample has become. Several authors have estimated a SWNT metallicity of >90% on the basis of a background subtracted integration of the absorption spectra [67, 72, 74, 75]. The problem with this method is that the background of a typical SWNT absorption spectra is very much uncertain, both in functional form and origin [75, 76]. Further, even if the metallicity can be reasonably
estimated from this method, one cannot be sure of the \((n,m)\) indices in a given enriched sample, since the metals are not being probed by PLE and absorption peaks are too convoluted to extracted reasonable numbers. Another pressing question is whether or not we are enriching all metals equally or just certain chiralities; this would conceivably give researchers the ability to tease out the mechanism of enrichment, which is still unknown.

To examine the precise chirality distribution in the DGU enriched sample, Erik Hároz went to Los Alamos National Laboratory (LANL) to perform tunable resonant Raman scattering (RRS) spectroscopy. This technique examines the Raman shifts of nanotubes as a function of excitation frequency, in much the same way as PLE does with PL [73, 77, 78]. RRS has the advantage of exciting an electron to an electronic state, instead of a virtual state, which greatly increases the Raman intensity [79]. Hence, the absorption spectrum in Fig. 3.23 provides the wavelengths that we excite at, while the radial breathing modes (RBMs) are
Figure 3.25: RRS spectrum of as-produced HiPco nanotubes in solution (left) and metallic-enriched HiPco nanotubes in solution (right). The inset of Family 27 \((2n + m = 27)\) has been magnified by 1.5 for clarity. The semiconducting chiralities, labeled in black, are gone in the metallic-enriched spectrum due to DGU. Data taken by E. Hároz in S. Doorn’s laboratory at Los Alamos National Laboratory.

what we probe. RBMs are radial contractions and expansions of SWNT diameter with an angular frequency, \(\omega_{RBM}\), proportional to \(1/d_t\), where \(d_t\) is the SWNT diameter. An empirically derived formula for the RBM frequency is

\[
\omega_{RBM} = \frac{c_1}{d_t} + c_2,
\]

where \(c_1 = 215 \pm 2 \text{ cm}^{-1}\text{nm}\) and \(c_2 = 18 \pm 2 \text{ cm}^{-1}\) [78]. The interpretation of \(c_2\) is somewhat in dispute, but it can be considered as a fitting parameter to account for various surfactant, tube-tube, and other interactions [78].

The Raman excitation range used were (with the sources in parentheses): 440-500 nm (frequency doubled continuous wave Ti:Sapphire), 514 nm (Argon laser line), 562-615 nm
(Kiton Red and Rhodamine 6G dyes), and 695-850 nm (continuous wave Ti:Sapphire). Excitation power was maintained at roughly 25 mW, though, due to various efficiencies of the different sources, each spectra was normalized for incident power. Spectra were collected using a CCD mounted on a triple monochromator with a 5 minute collection time. 4-acetamidophenol was used as a frequency calibration standard.

The multitude of tunable laser sources allowed for RRS spectra to be taken for the as-produced HiPco sample and the metal-enriched sample. Figure 3.25 shows the dramatic effect that metallic enrichment has on the RRS profile. Here, several peaks have disappeared because of the enrichment process, while only the metallic and narrow gap semiconductors remain. Within a given $2n + m$ family (where $n$ and $m$ are the chirality indices) those with a chiral angle below 19° are suppressed, while those with a chiral angle above this cutoff angle are relatively enhanced. Because all the chiralities are being probed, tunable RRS is the only way to observe the changes in the metal to semiconductor SWNT ratio on the ensemble scale.

The relative metal to semiconductor population changes can be seen more clearly in Fig. 3.26, where Raman excitation profiles (REPs) of each of the identified chiralities in Family 27 at resonance have been plotted. A REP is generated by taking a slice at a given Raman shift value (in our case, the center RBM shift value) and seeing it varies as a function of excitation frequency (or, equivalently, energy). We can numerically fit the REPs to the Raman intensity equation:

$$I_{Raman}^{fit} = \frac{NM_{e-o}^4M_{e-ph}^2}{([E_{laser} - E_{ii}]^2 + \frac{1}{4} \gamma^2) ([E_{laser} - E_{ii} - \hbar\omega_{ph}]^2 + \frac{1}{4} \gamma^2)}.$$  

(3.18)
Here, $N$ is the relative population of a given $(n,m)$ species, $M_{e-o}$ is the exciton-photon coupling matrix element, $M_{e-ph}$ is the exciton-phonon coupling matrix element, $E_{laser}$ is the excitation energy, $E_{ii}$ is the optical transition energy, $\gamma$ is the electronic broadening factor, and $\hbar\omega_{ph}$ is the phonon energy. A pre-factor, $g$, accounting for experimental gain is omitted due to our use of the calibration standard. We fit the REPs at resonance ($E_{laser} = E_{ii}$), which simplifies both our fitting and interpretation. The fitting only allowed for us to obtain $\hbar\omega_{ph}$.
\( y, \) and \( A, \) where \( A = N M_{e-o}^4 M_{e-ph}^2 \), since the matrix elements are unknown. To account for this, we took theoretical predictions from Jiang et al. [80] to normalize the matrix elements dependence on chiral angle. Those predictions are given in Raman intensity per unit length, so we needed to make the assumption that there was no chirality-dependent length sorting in the sample; this assumption seems very reasonable. By using a given phonon energy and the electronic broadening factor that Jiang et al. used (60 meV), we could back calculate a theoretical \( N_{\text{theory}} \), which would contain the matrix elements. From this, the relative experimental populations could be correctly obtained. Taking the matrix elements into account is extremely critical, since the intensity per unit length for a given chirality in an \( 2n + m \) family decreases as the chiral angle increases; this is due to the relative strengths of the exciton-photon and exciton-phonon couplings [80]. Because armchair SWNTs have the largest chiral angle (30°), performing tunable RRS spectroscopy on armchairs in unsorted nanotubes is very difficult, since their signal is small compared to peaks from other chiralities, as can be seen in Fig. 3.27.

Our relative population results for the two families we examined convincingly demonstrate metallic-enrichment. For Family 27, we began with the following relative populations: for the (9,9), 36%, (10,7) 34%, (11,5) 11%, and (12,3) 18%. After enrichment, the populations became 52%, 46%, 2%, and 0%, respectively, with the 0% being a signifier that we could not experimentally detect the signal coming from the (12,3) in the enriched sample. A similar story bears out for Family 30, whose as-produced relative populations were: (10,10) 40%, (11,8) 16%, (12,6) 22%, (13,4) 19%, and (14,2) 11%. Metallic-enrichment altered those relative populations to 46%, 27%, 27%, 0%, and 0%, respectively. This shift to metallic SWNTs is consistent with our expectations, since previous reports had claimed an increase in metallic species. Yet, this is the first time a true breakdown of relative pop-
Figure 3.27: Raman spectra for the as-produced (left) and metal-enriched (right) HiPco solutions at excitations wavelengths corresponding to the resonances of the armchair species \((6,6)\) through \((11,11)\). The \((6,6)\) and \((7,7)\) are fully resolved without any interference from other chiralities; this is the first time such Raman spectra for armchair species have been obtained. Data taken by E. Hároz in S. Doorn’s laboratory at Los Alamos National Laboratory.

Simulations of a given chirality has ever been obtained. The substantial suppression of the low angle chirality species was not expected. It seems as though a cutoff angle exists for the DGU process, which suggests that some sort of steric or positional mating of the surfactant to large chiral angle SWNTs is occurring. Any full-fledged mechanism hypothesis would need more data, but our results could spur research into this sort of experimental vein.
3.6 ESR Future Work

Future work on the ESR project can be divided into two different time ranges: short and long. For the former, the ESR on the annealed samples must be retaken so that more densely mapped curves can be plotted. The temperature dependence of the spin susceptibility, for instance, is still not understood yet.

Along with retaking the ESR data, I will also show how annealing affects the temperature dependent conductivity of nanotube powders. This crucial experiment will provide a second method for demonstrating how electron movement is altered by removing oxygen. This would be a direct verification of the quasi-1D VRH model obtained via ESR. In addition, conductivity measurements will allow calculations of the skin depth, providing a check to the ESR measurements.

The long term goal is to obtain spin resonance on a single nanotube. This would resolve a number of problems that ensembles of nanotubes have, such as the presence of ferromagnetic catalysts, the inability to control the sample geometry with respect to the static field, tube-tube contacts and related tunneling, and other adsorbed molecules affecting/disturbing the resonance. It would seem that the only way to fully realize spin-charge separation would be to proceed along this path, since the 1-D character of the nanotubes would in no way be comprised by extrinsic factors.
Chapter 4

Strongly AC-Driven Electrons in Carbon Nanotubes

In this chapter, I will describe the Franz-Keldysh effect (FKE) and dynamic Franz-Keldysh effect (DFKE) in semiconductors, as well as describe nonlinear optical processes in SWNTs. The DFKE is not a well-explored phenomena, unlike the perturbative regime (weak as compared to the lattice potential) or multi-photon absorption behavior (strong as compared to the lattice potential); the DFKE is situated in between these two extremes. It occurs when the lattice potential and the optical potential are of the same order of magnitude, setting up a rich interplay between the two terms of the system Hamiltonian. Also included in this chapter is the successful development of polymer hosts SWNTs to be used in for pump-probe spectroscopy experiments in the mid- and far-infrared spectral regions.

4.1 Background

The DFKE is a nonlinear, non-perturbative, coherent photo-induced phenomenon seen in semiconductor structures, such as bulk GaAs [82] and quantum wells [81]. The DFKE lies in between the Franz-Keldysh effect and multi-photon absorption (MPA). The different physical regimes (FKE, DFKE, and MPA) can be characterized by a dimensionless parameter, $\gamma$, which is defined as [81, 83]

$$\gamma = \frac{U_p}{\hbar \omega},$$

where $U_p$ is the ponderomotive potential and $\hbar \omega$ is the far-infrared photon energy. The ponderomotive potential is the average kinetic energy of a particle with a mass $m$ and
Figure 4.1: The interplay between the ponderomotive potential and the AC electric field can be partitioned into different physical regions, marked by values of $\gamma$ [81].

charge $e$ in an AC electric field $E = E_0 \cos \omega t$ [82, 83]:

$$U_p = \frac{e^2 E_0^2}{4m\omega^2}.$$  \hspace{1cm} (4.2)

When $\gamma \sim 1$, one is in the DFKE regime, which is difficult to experimentally study due to the requirements that $\omega$ must be in the far-infrared ($> 5\mu\text{m}$) and $E_0$ must be large (1-10 kV/cm) for a typical semiconducting sample [81]. The other regions of $\gamma$ are given in Fig. 4.1. When $\gamma \gg 1$, one is in the DC FKE regime, while for $\gamma \ll 1$, multi-photon effects are present. A back-of-the-envelope calculation will suffice to see where my experimental parameters fall in this scheme. The far-infrared pump beam I used had an incident average
power of 0.130 W with a pulse repetition rate of roughly 13 MHz and a pulse width of 20 ps focused through a 100 μm pinhole. This means that a given pulse had 10 nJ worth of energy and a incident power per pulse of 6.37 MW/cm². A quick calculation gives $E_0$ to be 69.3 kV/cm, which is fairly high given the number for $E_0$ quoted from Nordstrom et al. If the effective mass of the electrons in SWNTs is assumed to be 0.1$m^*$, then $U_p = 7.35 \times 10^{-21}$ J and $\gamma = 3.25$, which is of the order of 1. As such, my experiment is directly in the DFKE regime, depending of course on the assumption of the effective mass of the electron in a SWNT (which is chirality dependent to first order). Interestingly enough, $\gamma$ should be able to be tuned by changing the incident power and wavelength, especially since the average max power available at 88 μm from the FEL I used was 9 W and the available FEL wavelengths stretched over one order of magnitude. Thus, I had plenty of dynamic range for both variables.

### 4.1.1 Franz-Keldysh Effect

The Franz-Keldysh Effect (FKE) occurs when a low frequency, strong electric field modifies the band structure of a semiconductor. By probing near the band gap with a weak optical beam, one can resolve these changes. Qualitatively, the FKE is closely related to the Stark effect, where an electric field is used to shift the energy states in an atom [84]. The major difference between the two effects is that the Stark effect shifts atom-like discrete states, whereas the FKE alters the continuum in a semiconductor.

If an electric field, $F$, is applied to a bulk semiconductor, a potential energy term will be added to the Schrödinger equation for a free carrier [85]:

$$\left(-\frac{1}{2m} \frac{\partial^2}{\partial z^2} + eFz\right) \phi(z) = \varepsilon \phi(z),$$

(4.3)
where $\phi$ is the envelope of the wavefunction, $z$ is the direction of the applied field and is equal to the electron-hole separation, $z_e - z_h$, and $m_r$ is the reduced effective mass ($\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}$). Equation 4.3 can be solved exactly for $\phi(z)$ to give a functional dependence of an Airy function [85, 86]

$$\phi(z, \varepsilon) = Ai \left( \frac{z - \varepsilon / eF}{z_0} \right) = Ai \left( \frac{eFz - \varepsilon}{\varepsilon_0} \right) \quad (4.4)$$

where $Ai$ is the Airy function, $z_0 = \left( \frac{\hbar^2}{2m_r eF} \right)^{1/3}$ is a length scale and $\varepsilon_0 = \left[ \frac{\langle \varepsilon \rangle^2}{2m_r} \right]^{1/3} = eFz_0$ is an energy scale. The Airy functional dependence produces an exponential "leakage" of the wavefunction into the forbidden band gap, in addition to producing an oscillatory character of the wavefunction in the allowed region of the bands, as seen in Fig. 4.2.

Figure 4.2: When an electric field, $F$, is applied to a semiconductor, both the conduction band and valence band are tilted by $eFz$. The Airy-like wavefunction in this diagram shows oscillatory behavior in the band and an exponential decay into the band gap. The penetration into the band gap increases the tunneling rate between the valence and conduction bands [85].

Using $\phi(z, E)$ from Eq. 4.4, one can calculate the resulting electroabsorption spectrum for free carriers [86]

$$\alpha(\omega) = \frac{\alpha_0 m_r f^{1/3}}{2\pi \hbar^2} \left\{ -\varepsilon Ai^2(\varepsilon) + [Ai'(\varepsilon)]^2 \right\}, \quad (4.5)$$
where \( \alpha_b = \frac{8n^2|d_{cv}|^2\omega}{n_b c} \), \( d_{cv} \) is the interband dipole matrix element, \( n_b \) is the refractive index, \( f = eF \frac{2m_r}{\hbar^2} \), and \( \epsilon = \frac{2m_r(E_g - \hbar\omega)}{\hbar^2} \). The spectrum of this function shows three main features: one, there is absorption below the band gap; two, oscillations occur above the band gap; and three, the oscillations become smaller the farther one goes above the band gap. The FKE refers to all three of these main features. The sub-gap absorption tail created by the presence of the electric field is known as the Franz-Keldysh tail, which can be found by taking the asymptotic form of the Airy function, \( \text{Ai}(x) \), as \( x \to 0 \) [86]:

\[
\alpha(\omega) = \frac{\alpha_b}{32\pi^2 E_g \hbar\omega} \exp \left\{ -\frac{4}{3f} \left( \frac{2m_r(E_g - \hbar\omega)}{\hbar^2} \right)^{3/2} \right\}.
\] (4.6)

As can be seen, the absorption tail is strongly dependent on \( F \). FKE is often viewed as a photon-assisted tunneling process from the valence to the conduction band. Thus, as the electric potential is increased, the penetration into the band gap is increased causing a larger probability of overlap between the electron and hole wavefunctions.

Figure 4.3 : Calculated density of states for electrons in GaAs for a field strength of \( F = 5 \text{ MV/m} \) as a function of \( \epsilon = E - eFz \). The thin curve represents typical free electron behavior, while the thick curve describes the effect of \( F \). The units of \( n(E, z) \) are eV\(^{-1}\)nm\(^{-d}\), where \( d \) is the dimensionality [85].
All of the above has been for the 3-D case, so what about 1-D? Without going into details, I will simply sketch out the argument for how dimensionality will affect the FKE. First note that optical absorption is a probe of the density of states. In 1-D, the presence of an electric field produces a highly oscillatory density of states, \( n_{1D} \) [85]:

\[
n_{1D}^{(F)}(E,z) = \frac{2}{\hbar} \sqrt{\frac{2m_r}{\varepsilon_0}} \text{Ai}^2 \left( -\frac{E - eFz}{\varepsilon_0} \right).
\] (4.7)

The density of states subjected to the presence of a strong DC electric field is shown in Fig. 4.3. What is immediately clear from the figure is that the oscillatory behavior is greatest for 1-D. The difference that the strong electric field makes in the 1-D case is also striking. Therefore, one can expect increasingly larger changes in the optical spectrum as dimensionality is decreased.

### 4.1.2 DFKE

Deviations from the FKE are expected when the applied field frequencies are on the same order as those at which the carriers transverse the Brillouin zone [87], which is when the DFKE becomes important. Calculating the exact form of the DFKE is a complex undertaking that has already been done by Yacoby in 1968 [87]. I will only sketch out his argument to provide contextualization for the relevant experimental phenomena that I attempted to observe. In all cases, it should be kept in mind that \( \hbar \omega \) is the pump photon energy (field that modifies the electron potential) and that \( \hbar \Omega \) is the probe photon energy (field that probes the transitions from valence to conduction bands).

I am looking to find the transition rate from \( \psi_r \) to \( \psi_c \) caused by \( \hbar \Omega \) in the presence of a strong light field, \( \hbar \omega \). The photon energy of the strong field pump is set so that it is far
below the minimum energy gap, $\Delta \varepsilon_{\text{min}}$ [87]:

$$\hbar \omega \ll \Delta \varepsilon_{\text{min}},$$  \hspace{1cm} (4.8)

Here $n$ is the number of photons involved in the valence to conduction band transition. When a uniform electric field is applied to a periodic lattice, one can use Houston wavefunctions to describe the electrons. Equation 4.8 allows the Houston wavefunction for a given band, $L$, to be calculated for a time varying vector potential, $A = A_0 e^{i\omega t}$ [87]

$$\psi_L \equiv \varphi_L \left( \frac{K_0 - eA}{\hbar} \right) e^{iK_0 R} \exp \left[ -\frac{i}{\hbar} \int \varepsilon_L \left( K_0 - \frac{eA}{\hbar} \right) dt \right],$$  \hspace{1cm} (4.9)

where $K_0$ is the momentum in the zero field case, $R$ is the basis lattice vector, $\varphi_L$ is the Bloch function of the $L^{th}$ band, and $\varepsilon_L$ is the energy eigenvalue of the $L^{th}$ band. Importantly, Yacoby notes that the condition given in Eq. 4.8 allows one to consider $\varphi(K - eA/\hbar)$ independent of time.

With the modified Houston wavefunction, the transition rate and current can both be calculated. The total transition rate is defined by Yacoby as [87]:

$$T = \frac{V}{4\pi^3} \int T(K_0) d^3K_0.$$  \hspace{1cm} (4.10)

From Eq. 4.10, one can explicitly find the total transition rate (see Eq. (38) in Yacoby [87]). The explicit form of the total transition rate is a complicated equation, which is highly specific to a given dimensionality, lattice, and valence-to-conduction state coupling. However, the main features of the DFKE are easily extracted: (1) an absorption tail below the band gap; (2) a blue shifting of the absorption edge; (3) oscillations above the band gap energy; (4) generation of sidebands that are even harmonics of $\omega$. These effects are most visible when $U_p \sim \hbar \omega$. 
An example of the type of changes in the differential transmission ($\frac{\Delta T}{T}$) in gallium arsenide (GaAs) is shown in Fig. 4.4. In that figure, it is evident that below band gap absorption is occurring, as well as the blue-shift of the band edge. This shift, which is proportional to $U_p$, is the extra energy the lattice electrons have due to the presence of the field. Thus, DFKE is not simply a photon-assisted phenomena, but rather an interplay between the lattice potential and the field potential.

4.1.3 Relevant Literature on Nonlinear Optical Behavior in SWNTs

Both theoretical and experimental studies have pointed to large nonlinearity coefficients in semiconducting nanotubes. The enhancement can be attributed to the band structure of nanotubes, which provides a large joint density of states due to the 1-D nature of the nan-

![Graph showing theoretical fit and experimental data for differential transmission.](image)

Figure 4.4: Theoretical fit from Yacoby's theory (with modifications for multiple reflections in the sample) to experimental data taken on 3-D GaAs [82].
otube. Except for these works, hardly any studies of nonlinear (outside of second and third harmonic generation) or non-perturbative behavior have been published. A few exceptions to this statement are recent publications on the optical (or AC) Stark effect [88] and the FKE [89]. In both cases, the effects that they observe are unusually large, as compared to typical materials. Theoretical work on the FKE in nanotubes has also been done [90], which showed that the expected FK oscillations are large. Besides these studies, this sub-field remains relatively untouched, both theoretically and experimentally.

4.2 Methods

The Methods section will contain my work on polymer hosts, since this is first step in the DFKE experiment. The polymer project is a self-contained unit: introduction, background, experimental observations, and discussion. Two different polymers, carboxymethylcellulose and t-carrageenan, were developed for use with mid- and far-infrared studies. There are advantages and disadvantages to using either one, but both display relatively good polymer formation and low absorbance in key wavelength regimes. I conclude the Methods section with my results from generating supercontinuum whitelight from a photonic crystal fiber and the experimental setup for the DFKE measurements.

4.2.1 Polymer Development

Many optical properties of SWNTs require them to be well-separated from one another (i.e. individualized), as seen, for instance, in the work of Bachilo et al. [73]. Individualization can be achieved easily in aqueous solutions using the method described in O'Connell et al. [69]. In order to investigate individualized SWNT ensembles optically at low temperatures, however, some sort of host must be employed to maintain this individualization in a solid form. Typically, researchers use polymers to create a matrix to accomplish this.
By mixing a polymer aqueous solution with a nanotube decant, one can form a film upon drying. If mixed correctly, the individualization can be maintained in this quasi-dry solid.

Unfortunately, only a few polymer hosts for nanotube solutions have been developed for use with nanotubes. Four polymers are in common use for optical spectroscopy: poly(acrylic acid) [PAA] [91], poly(vinyl alcohol) [PVA] [92], poly (vinylpyrrolidone) [PVP] [92], and poly(maleic acid/octyl vinyl) [PMAOVE] [93]. In addition, a few researchers use carboxymethylcellulose [CMC] for terahertz spectroscopy [94–96]. Recent reports have demonstrated that polymers can be used to separate/enrich certain chiralities, as well as reduce the optical absorption baseline [97].

**Polymer Criteria**

There were three main criteria for the polymer development sub-project: (1) any host must maintain the individualization of the nanotubes from the liquid to the solid (gel) stage; (2) in order to use an aqueous decant, the polymer had to be water soluble; and (3) the matrix had to be transparent in the optical region (400 nm–1.4 μm) and either the mid-infrared (MIR) regime (specifically, 3–6 μm) or the far-infrared (FIR) regime (λ > 25 μm). The first two requirements are essentially unavoidable, while the third could be fulfilled by multiple means. We found that one polymer could not satisfy all elements of the last criterion, so two polymers were developed to access specific spectral regions: CMC for FIR applications and t-carrageenan for the MIR spectral range. In the subsequent sub-sections, I explore the properties and spectra that make both polymers strong candidates for SWNT hosts for use with MIR and FIR spectroscopy.
4.2.2 Carboxymethylcellulose

Experiments in the FIR wavelength region suffer from water absorption lines and vibrational energy resonances that dot the absorption landscape. As Fig. 4.5 shows, small amounts of water (even in air) greatly hinder the transmission of light from 30 μm to 300 μm. In addition, for applications such as THz spectroscopy, the electric fields that are being produced are weak, so great care is taken to avoid sources of absorption. Thus, the choice of polymer matrix is a strong factor in experimental design when working with FIR spectroscopy.

![Figure 4.5: Computed absorption coefficient of water as a function of wavelength [98].](image)

CMC has previously been used in THz spectroscopy of SWNTs [94–96]. Thus, it seemed reasonable to employ this polymer for FIR experiments. CMC is a water soluble cellulose derivative that has found use as a food thickner and as a flocculating agent [99, 100]. It
is this latter application that may raise eyebrows amongst the nanotube community, since conceivably the point of the polymer host is to avoid flocculation. This may explain why good individualization of the nanotubes was not observed once the films solidified. We have since moved away from using this polymer in the lab.

![Molecular structure of sodium carboxymethyl cellulose](image)

Figure 4.6: Molecular structure of sodium carboxymethyl cellulose [100].

Structurally, CMC is defined by a repeating, modified cellulose unit, as seen in Fig. 4.6. The number of units, given in Dalton (a molecular weight measure), is critical to the polymer properties. As the chain length increases, for instance, viscosity also increases. This in turn affects how the polymeric chains interact with one another and at what concentration they become coiled [99]. The largest molecular weights show gelation at much lower CMC concentrations than smaller molecular weight chains since the larger, longer chains interpenetrate one another more easily, causing an entangled, gelatinous state [99]. Figure 4.7 shows a rudimentary sketch of the different critical concentration junctures of CMC. It is only when the concentration exceeds a certain value [part (d)] that a gel forms. Be-
fore that, a series of concentration-dependent phenomena occur as dictated by the polymer chain length and density.

Figure 4.7: CMC chain conformations at the four different critical concentrations [99]: (a) mean chain distance is equal to persistence length; (b) overlap between large, elongated chains begins to occur; (c) coiled chains start to overlap; (d) coil overlap becomes dense enough so that a gel begins to form.

4.2.3 i-carrageenan

Carrageenases are a class of natural polysaccharides that are derived from Red Seaweeds (Rhodophyceae) [101–103]. Seven different carrageenases have been found, each differentiated by the location and degree of sulfate substitution on the polymer unit [102]. Only three varieties, however, are extensively used: κ-carrageenan, i-carrageenan, and λ-carrageenan (Fig. 4.8). Here, I have listed the polymers in order of gel strength, with κ- and i-carrageenan both forming thermoresversible gels [102, 104, 105] and λ-carrageenan not being able to reach gelation [102, 103]. Though it is the strongest gel, κ-carrageenan is not a good choice for optical spectroscopy because it has turbidity when dry. There is a
large body of research that suggests that the use of a potassium (K$^+$), sodium (Na$^+$), or calcium (Ca$^{2+}$) ions strengthens carrageenan gels and changes the sol-gel transition dynamics [104, 106]. Therefore, one can use weaker, but optically clear, carrageenases and strengthen them through ion additives.

Figure 4.8: The three major carrageenan structures: kappa ($\kappa$), iota ($\iota$), and lambda ($\lambda$) [103]. The differences between the three are given by the number and positioning of the sulfate groups on the repeating structural unit of the polymer.

t-carrageenan was originally developed to be used in an ultrafast spectroscopic study of excitonic dynamics in carbon nanotubes that used an optical pump beam and a MIR probe beam. The optical pump would excite at the $E_{22}$ of a given chirality (we typically use (6,5) because of its prevalence in CoMoCAT nanotubes). These excited electrons, which quickly form into excitons, would then non-radiatively relax to the $1g$ excitonic state, which is a dark (non-light emitting) state. This quasi-equilibrated state could then be probed by a MIR transition to the $2u$ exciton state. Thus, we could utilize the excitonic internal degrees of
freedom to examine the properties of the dark 1g state.

The observation that t-carrageenan has a fairly large and clean MIR window where the 1g to 2u transition should occur made it an ideal candidate for use with this MIR application. In addition, its excellent transparency in the optical region allows it to be used with a variety of other optical phenomena, such as photoluminescence excitation spectroscopy.

4.2.4 Polymer Results

The results for both polymers indicate that they can be used for FIR applications. Yet, t-carrageenan individualized SWNTs considerably better than CMC, while have superior optical clarity. CMC can be used if robust films are necessary, given its inherent flexibility and toughness. CMC also has the advantage that it is much easier to make than t-carrageenan, which not only is difficult to produce, but it is also very fragile.

Carboxymethylcellulose Results

By far, CMC is the easiest polymer to work with that I tested. CMC typically yields an optically clear, mechanically robust film that easily and homogenously mixes with SWNT decants. In addition, CMC has good transmission in the FIR region. The absorbance, for example, beyond \( \approx 25 \mu m \) is below 0.75 absorbance units, which allows CMC to be used for FIR experiments. Tellingly, the absorbance does not spike at known water absorption lines, which leads me to believe that the water content is not significantly high. A useful experiment would be to test the FIR absorption at a variety of film water contents to put quantitative bounds on the effect of water in the optical spectra. It is due to the ease and speed of making these films, and the transparency in the optical and FIR regions, that we chose to use CMC for the DFKE experiment.
However, grave problems with CMC occur when one considers a more thorough examination of their drying properties. In all observed cases, the individualization of the SWNTs in solution substantially decreases via the CMC solidification process. Upon drying, the films often appear blotchy and segregated, unlike the homogeneity of the aqueous stage. Figure 4.9 is a telling statement of this behavior. Originally, I started out with a (6, 5) density gradient ultracentrifugation (DGU) enriched sample in solution, where a relatively well-resolved peak structure can be seen. To remove the iodixanol inherently left, I proceeded to dialyze the fraction with a surfactant bath. The absorption spectra of this iodixanol-free sample is shown in Fig. 4.9. This solution was then mixed with CMC to form a film (see Appendix B for more details), whose absorption profile is displayed on the same figure. It is clear that the absorption peaks are broadened and less defined, which indicates that the degree
of bundling has increased. Certain peaks, such as those at 459 nm, 509 nm, 655 nm, 922 nm, and 1133 nm, are almost fully suppressed, pointing to the loss of SWNT individuality.

Figure 4.10: Pictorial representation of CMC showing carboxymethyl groups extending from the cellulose backbone [100]. Even in the dried state, water can move between stacked CMC chains because of the separation caused by these extensions.

This lack of individualization impacted the optical resonance that I was primarily interested in for the DFKE experiment, which was the $E_{11}$ of the (6,5) nanotube (this is located at 982 nm in my aqueous spectra). Upon immersion in the polymer, this peak broadens and red-shifts to 1000 nm. The nanotube peaks red-shift in a polymer host, which can either be due to the strain placed upon the nanotubes by the matrix [92, 97] and/or through the bundling of the nanotubes. Looking at Fig. 4.10, it may be that the separation between the CMC chains allows a substantial amount of rebundling to occur, especially if the nanotubes are merely lying next to the polymer chains, instead of having them be wrapped around the SWNTs. By having such wide gaps between the CMC chains, the SWNTs may be moved...
together as water molecules leave due to the drying process; this may account for the random blotches of SWNT aggregates that we see in the dry films. At the same time, the CMC chains may still form a stable polymer matrix that is flexible and durable, which is what has been observed.

1-carrageenan Results

In contrast to CMC, 1-carrageenan is a difficult polymer to work with, but has excellent individualization-maintaining properties. Films made from carrageenan tend to be mechanically brittle, if not fragile. Yet, when produced correctly, they are transparent in the optical, MIR, and FIR regions, as can be seen from Fig. 4.14. The MIR window extends from 3.6 μm to 5.6 μm, with strong absorption resonances beginning at 6 μm and continuing out to 25 μm. Starting at 25 μm and extending to 100 μm, the absorbance of 1-carrageenan continuously decreases. This downward trend seems to imply that 1-carrageenan may also be a very strong candidate for FIR applications. However, it is difficult to compare CMC with 1-carrageenan, since both absorbance plots were not normalized for thickness. In an upcoming series of measurements, this parameter will be closely measured to resolve this problem.

Strikingly, the individualization of nanotubes in 1-carrageenan is very well maintained. Figs. 4.12 and 4.13 showcase how well the peak structure remains after immersion in the polymer host. Specifically, I highlight the so-called quartet [four closely spaced peaks representing the $E_{11}$ transitions of the (8,3), (6,5), (7,5), and (10,2) nanotubes] in Fig. 4.12 to show how small resonances can be distinguished in 1-carrageenan. It should be noted that the quartet is often obliterated in poorly prepared solution samples; to have it observed in a polymer host is rare. One strong possibility for the excellent SWNT individualization-
Figure 4.11: Infrared absorption spectrum of a free standing CMC (90 kDa) film. Low absorbance can be seen in some parts of the MIR regime (below 3 μm and 4-6 μm) and in the FIR region (above 20 μm).

Maintaining behavior is that the i-carrageenan polymeric chains form a helical structure upon gelation [101, 102, 107]. This helicity is similar to DNA, which has been shown to be a good wrapping geometry for nanotubes [65].

t-carrageenan is an excellent choice for optical spectroscopy. Consistently, it produces optical absorption spectra that are similar to spectra seen in SWNT solutions. The trouble with t-carrageenan is in its preparation and mechanical stability. With regard to the former, making carrageenan films is difficult, since small errors in heating and casting produce less than optimal films. Still, this is an experimental problem that can be fixed in the near future. Film integrity, on the other hand, is a much harder quandary to resolve. The fragility of t-carrageenan films becomes a true quagmire when low temperature thermal cycling is
considered. The stresses placed upon the film can be relieved by using crystalline quartz or sapphire substrate to mechanically support the film. Future experiments will look at adding κ-carrageenan to the mixture to strengthen the film. Another option is to add K⁺, Na⁺, or Ca²⁺ cations to improve the film integrity.

Two important points should be briefly mentioned about all polymer films. First, any water remaining in the films will turn to ice upon cooling down to 4 K. While this may be obvious, it is not clear what effect the ice has on the mechanical integrity of the film, nor is it obvious how microscopic nature of the SWNT-SWNT interactions is altered, (changes in reaggregation, inter-tube distances, or coiling). The freezing and melting of water that surrounds and interacts with both the nanotubes and the polymer chains is an important

Figure 4.12: Absorption spectrum of HiPco in solution and immersed in t-carrageenan. In this figure, the so-called quartet [(8,3), (6,5), (7,5), and (10,2)] are labeled, showing that even in a polymer matrix, these hard to see peaks can be observed.
thing to examine if these films are going to be used for scientific claims.

Secondly, it must be noted that the thermal conductivities of any polymer host will be low. Although there are no numbers about the low temperature thermal behavior of CMC or \( \tau \)-carrageenan, we can estimate their thermal conductivities from polymers such as PMMA, whose temperature dependent thermal conductivity is given in Fig. 4.15. As can be seen, the thermal conductivity, \( \kappa \), drops from roughly 0.2 W/m-K at 300 K to below 0.02 W/m-K at 1 K. In comparison, a metals have much higher thermal conductivities, especially at low temperatures. For example, copper has a thermal conductivity exceeding \( 1.6 \times 10^4 \) W/m-K at 4 K. The difference of six orders of magnitude is a direct manifestation of the fact that we are using semi-amorphous insulators. Some relief from this problem can be gained by playing with the geometries of the film. Yet, for optical transmission spectroscopies,
the film will need to be placed on a portion of the copper cold finger where a hole exists; this will force heat transmission to take place through the film, where the extremely low thermal conductivity will play a large role in thermal equilibration. It should be noted that the presence of nanotubes will substantially improve the thermal behavior of the polymer films. Thus, increasing the nanotube density becomes important not just for increasing the optical density of our sample, but also for its thermal conductivity.

4.2.5 Whitelight Supercontinuum Generation

The other major development for the DFKE project was whitelight generation from a photonic crystal fiber. In essence, by confining ultra short optical pulses in specific geometries,
Figure 4.15: Temperature dependence of the thermal conductivity of PMMA from 400 mK to 300 K [108]. The y-axis, which is difficult to read, has units of $10^3$ erg/sec-cm-K. PMMA, like other polymers, has a decreasing thermal conductivity with decreasing temperature. Thus, for both CMC and t-carrageenan, low temperature equilibration will be a serious concern.

Highly nonlinear phenomena can produce a relatively flat spectral output extending from the optical to NIR wavelength range. In this way, the coherence and temporal pulse spacing will be the same as a regular Ti:Sapphire laser output, while the spectral content is broadened by roughly an order of magnitude. What is typically lost is pulse width and pulse shape due to the dispersion in the fiber. Even “dispersionless” fibers will still have this problem, since the dispersion-free frequency zone is easily exceeded by either the bandwidth of the incoming laser (up to 50 nm with $\lambda_0 = 800$ nm) or by the whitelight itself propagating in the fiber after its creation.
Supercontinuum generation was first demonstrated by Alfano [109] using picosecond pulses focused on various types of crystals. Although no one mechanism can fully explain this effect, current literature has attributed frequency broadening to self-phase modulation, parametric four wave mixing, Raman processes, and soliton fission [110].

As an example of how self-phase modulation can cause frequency broadening, consider a model example of an ultrafast pulse propagating through a material like sapphire, where $n_2 = 5 \times 10^{-4}$ and $n$, the index of refraction, is defined as

$$n = n_0 + n_2 I(t),$$

(4.11)

where $n_0$ is the intensity independent index of refraction and $n_2$ is the second-order nonlinear index of refraction. An ultrafast pulse can be modeled as $E(t) = E_0 e^{-(t-a)^2/2\sigma^2} e^{i(\omega_0 t - kx)}$ or as $E(t) = \text{sech}^2 \left( \frac{t}{\tau} \right) e^{i(\omega_0 t - kx)}$. Taking a centrosymmetric crystal (such that $\mathbf{r} \rightarrow -\mathbf{r}$ under translation) all even powers of the electrical susceptibility tensor, $\chi$, are zero. Under large driving fields, the second largest contribution to the index of refraction is of order $\chi^{(3)}$.

Differentiating Eq. 4.11 with respect to time gives

$$\frac{dn}{dt} = n_2 \frac{dI}{dt} + I \frac{dn_2}{dt}.$$  

(4.12)

It is within the time-dependent phase, $\phi(t) = \omega_0 t - \frac{2\pi}{\lambda_0 c}$, that the importance of $n$ emerges, since the time derivative of $\phi(t)$ equals $\omega(t)$. If $\frac{dn_2}{dt}$ is ignored, then $\omega(t)$ becomes a function of $I(t)$:

$$\omega(t) = \frac{d\phi}{dt} = \omega_0 - \frac{2\pi}{\lambda_0 c} \left( n_2 \frac{dI}{dt} \right).$$  

(4.13)

Thus, the higher the intensity and the shorter the pulses, the larger the spread of frequencies [111]. The same rule can be roughly applied to the photonic crystal fibers (PCF) that I used to generate whitelight in the experiment.
4.2.6 Experiment and Detection Scheme

The output of a free-electron laser (FEL) producing 20 ps pulses centered at 88 µm with a power of 130 mW was used as the pump beam. This wavelength was chosen for two reasons: one, it is situated in a water-absorption-free region (see Fig. 4.5) and two, the DFKE is strongest for long wavelengths. The repetition time of the FEL was roughly 13 ns, and I synchronized a Ti:Sapphire oscillator to that frequency, so that temporal spacing between the FEL and Ti:Sapphire pulses did not change. Unfortunately, I did not have access to a good pulse picker, so that for every one FEL pulse, there were six oscillator pulses. Thus, my SNR was reduced by a factor of six.

The Ti:Sapphire beam was used to generate white light, which acted as a probe pulse. The probe power was measured to be 40-50 mW exiting the fiber and 10-20 mW at the sample. This power corresponded to a ≈ 10:1 pump to probe power ratio. I used a 50 µm pinhole to spatially overlap the pump and probe beams. A superlattice detector was employed to get temporal overlap \((t = 0)\). The superlattice detector allowed us to view both the FIR signal and the optical signal at the same time, which allowed us to obtain temporal overlap \((t = 0)\) to within 200 ps, which was the RC time of the detector.

To obtain exact temporal overlap, I attempted to use the whitelight as the pump beam and the FEL as probe on a piece of GaAs. I hoped to observe free carrier absorption, since as \(\lambda_{probe}\) became larger, the free carrier absorption effect is augmented. Unfortunately, with a weak pump beam and no pulse picker to avoid the six-fold SNR decrease, no evidence of free carrier absorption on GaAs was seen. Thus, \(t = 0\) was known only to within a 200 ps window.
A LN2 cooled Si CCD with a four-channel fiber optic adapter was used for the experiment. Unfortunately, circumstances prevented us from using more than one channel. In the original setup (Fig. 4.16), each channel was utilized to take in light from a slightly different path: raw white-light, white-light through a reference film, whitelight through the DGU-enriched film, and whitelight through the pump influenced DGU-enriched film. In this configuration, at each pump-probe delay, the full gamut of information would be gathered in one collection period, with the raw whitelight beam being used to normalize out the frequency and intensity fluctuations of the other channels. Knowing the pump-probe pulse
overlap \( t = 0 \), also known as time zero) would then allow the normalized change in trans-
misson, \( \Delta T \), to be plotted as a function of frequency and pump-probe time delay. From
this multi-dimensional data space, I hoped to see a change in the band edge absorption for
the \((6,5)\) nanotube beginning at time zero.

Figure 4.17 : Picture of the actual setup with the FEL path (red line) crossing with the
whitelight (white line) at the sample (blue box). The delay stage motion changes the rel-
ative delay between pump pulses and probe pulses (motion denoted by yellow line). Un-
fortunately, due to circumstances, only one whitelight channel was utilized in the actual
experiment.

However, for this experimental run, there was only one working fiber optic channel. To
compensate for this obvious lack of information, a four step process was used: (1) raw
whitelight scan, (2) whitelight transmission through the sample, (3) FEL pump/whitelight
probe transmission through the sample, and (4) raw whitelight scan. For each case, I mea-
sured the whitelight probe using the Si CCD; what changed is what the light was passing
through. Whenever step (3) is reached, a DFKE-situation may be present, which would
change the absorption of the whitelight making it different than in step (2). Steps (1) and
(4) are necessary to adjust/monitor the frequency and intensity changes of the whitelight,
which is not very stable due to incomplete focusing, pointing stability, and laser fluctuations.

4.3 DFKE Results

Although the experiment was not completely successful, much was gathered from the results obtained. The results section is divided into two sub-sections: the first about supercontinuum whitelight, and the second devoted to the DFKE experimental results.

4.3.1 Supercontinuum Whitelight Generation Results

The first major success of this experiment was observing whitelight supercontinuum generation from a PCF. The setup was prototyped at Rice University using a Kapteyn-Murnane (KM) 800 nm Ti:Sapphire oscillator laser with an ≈80 MHz repetition rate. The emitted laser pulses were estimated to have a bandwidth of 40 nm and a pulse width of 80 fs; these numbers, especially the pulse width, are most likely different from the pulses entering into the PCF, though, this was not measured. Larger pulse widths decrease the peak electric field, which limits the intensity and breadth of the supercontinuum. The typical Ti:Sapphire laser incident power on the PCF was 150 mW.

The system was used at the Forschungszentrum Dresden-Rossendorf (FZD) in Dresden, Germany. The Ti:Sapphire oscillator there was set to produce incident PCF powers of roughly 300 mW. The pulse characteristics were basically the same as those seen with the KM at Rice. A typical output of the PCF after passing through the entire system is shown in Fig. 4.18. What is striking about this figure is three-fold: bandwidth, stability, and spectral density. In terms of bandwidth, the spectrum at the sample had spectral density from 550 nm to 1050 nm. It should be noted that this spectrum includes reflection off of gold
mirrors; because of our use of gold, the reflection curve is limited to wavelengths above 500 nm. This 500 nm bandwidth is one order of magnitude greater than the incoming pulse bandwidth. The group velocity dispersion (GVD) within the PCF changes the shape of the pulse, which causes it to broaden. The GVD is defined as the derivative of the group velocity, \( v_g \), with respect to the wavelength, where the group velocity is given by [110]

\[
\frac{1}{v_g} = \left. \frac{dk}{d\omega} \right|_{\omega_c},
\]

(4.14)

where \( k = \frac{2\pi}{\lambda} \) and \( \omega_c \) is the carrier frequency. The pulse will broaden because the presence of GVD will alter the pulse shape, deviating it from optimum. I estimated the pulse width to be on the order of picoseconds, along with a frequency chirp. To date, neither chirp nor 

Figure 4.18: Whitelight taken at two different times spaced roughly five minutes apart. Fluctuations varied on the order of seconds to minutes depending on how well coupled the fiber was with the laser light.
pulse width measurements have not been performed. These measurements will be made in the next several months.

Spectral density is a significant problem in this experiment. As can be seen, the spectrum is not flat, which indicates that true supercontinuum generation is not quite being achieved. The fact that true supercontinuum generation is not occurring can be seen by looking at the coupling efficiency into the PCF, which is defined simply as

$$\Gamma = \frac{\text{Power}_{\text{out}}}{\text{Power}_{\text{in}}}.$$  \hspace{1cm} (4.15)

A typical power output seen at from the PCF at FZD was 50 mW, making our coupling efficiency $\approx 17\%$, which is roughly a factor of two below what can be achieved with proper coupling.

This non-optimal coupling into the PCF resulted in not only a highly varying spectral density, but also in poor spectral stability. By spectral stability, I mean how the spectral density changes as a function of time. Indeed, as shown in Fig. 4.18, the whitelight probe at the sample varies as a function of time, where the difference between time 1 and 2 is roughly five minutes. This large variation in the probe intensity and frequency distribution immediately raises questions about whether or not meaningful information can be extracted from $\frac{\Delta \Gamma}{\delta t}$. This point will be revisited in the next section.

Still, the bandwidth achieved with the whitelight generator was enough to perform the experiment. Specifically, the two peaks I targeted were the $E_{11}$ and $E_{22}$ of the $(6,5)$ nanotube, whose resonances (in the CMC film) occurred at 1000 nm and 580 nm, respectively. The whitelight spectra clearly shows that spectral bandwidth was produced both above and below these wavelengths, which is crucial for observing the DFKE. Without information
about how the semiconductor absorbs energies above and below the band gap, we will not be able to observe two major features of the DFKE: below band gap absorption and oscillations above the band gap.

4.3.2 DFKE Results

As described in the theory section above, I am looking for a change in the transmission of the sample in the presence of a strong, coherent, FIR pump beam. Specifically, I am attempting to observe three key signatures of the DFKE: below band gap absorption, oscillations in the absorption above the band edge, and a blue-shift of the band edge. If those are observed at a given wavelength, then we can proceed to examine wavelength, power, and polarization dependence to confirm the phenomena.

Two main resonances, one at 1000 nm and the other at 580 nm, were monitored to see if any changes in the transmission were detected. In Figs. 4.19 and 4.20, I plot $\Delta T$ as a function of wavelength and time delay. The time delay was done every 10 ps, because I was essentially scanning for pump-probe overlap. Because the pump pulse was roughly 20 ps long, a 10 ps step size was justifiable. Yet, because I did not have exact knowledge of $t = 0$, my job was made considerably more difficult.

It was critical to look at the frequency dependence of the change in transmission because I was looking for changes both above and below the band gap energy. Whitelight fluctuations could be substantial (above 10%), which affected our calculations of differential transmission. The fluctuations were especially problematic around 700 to 950 nm, where the intensity of the whitelight was largest. In the plots, I have removed this frequency range to focus only on the two band gaps in question.
Figure 4.19: $\Delta I/T$ as a function of pump-probe delay time from 550 nm to 750 nm. If the DFKE were present, changes such as below band gap absorption and oscillations above the band gap, should be evident. The band gap for the E$_{22}$ resonance for this sample is at 580 nm.

Immediately apparent is that around both 1000 nm and 580 nm, no change in normalized transmission is seen. If the DFKE were present, significant changes would be apparent around these frequencies. The fact that the curves are relatively flat for these regions of the spectrum implies that nothing is being observed.

4.4 Future Work

Several easy changes could be made to greatly improve the DFKE experiment for a future attempt. A better polymer matrix could be employed to enhance SWNT individuality and
Figure 4.20: $\Delta T/T$ as a function of pump-probe delay time from 850 nm to 1075 nm. $E_{11}$ is at 1000 nm for this sample. Thus, the DFKE, if present, should be evident at or near 1000 nm.

to withstand the high FIR pulses generated by the FEL. Also, a pulse picker could be used to improve the SNR of our experiment by a factor of six. Establishing the multi-beam detection scheme for normalizing the whitelight beam would also greatly enhance our detection ability. All of these changes will be incorporated into my next attempt at this experiment in 2010.
Chapter 5

Conclusions

This thesis set out to examine electron dynamics of ensembles of SWNTs by using a variety of experimental methods. Primarily, I focused on how spin resonance probed the hopping behavior in annealed nanotubes. I observe that the hopping frequency is due to the energetic barriers that exist between nanotubes; these barriers are lowered due to the presence of oxygen molecules absorbed to the nanotubes. Upon removing the oxygen, tube-tube movement of electrons becomes hindered, resulting in variable range hopping as mode of electron conduction. From the motional narrowing of the linewidth, a hopping frequency of $\approx 32.5$ GHz can be estimated. My data shows the first evidence of motional narrowing seen in nanotubes. In addition, the hopping frequency is the first time such a number has been obtained for SWNTs.

Further, the ESR data reveals that annealing the powder nanotube samples produces a measurable drop in the $g$-factor of $0.0007 \pm 0.0001$. This downward shift may be related to the removal of oxygen. The $g$-factor I observed has little temperature dependence, staying constant at $2.0025 \pm 0.0001$ for the measured temperature range of 4 K to 300 K. Its closeness to the free electron value of 2.0023 is inline with other carbonaceous materials.

Unexpectedly, the absence of oxygen facilitates a two orders of magnitude rise in the spin susceptibility from the non-annealed sample. My data shows that the annealed spin susceptibility was of the order of $10^{-6}$ emu/g, which is roughly three orders of magnitude larger
than previous reports [27]. One hypothesis, related to observations in 1-D polymer chains, is that the oxygen is acting as a fast spin relaxor. Once removed, the spin population that had been previously been undetectable (due to their short phase coherence times) adds to the spin population that is longer-lived.

The ESR results demonstrate several very important features that differ significantly from previous studies. The ESR data I collected from the annealed powder is the first observation of a motional narrowed ESR linewidth in nanotubes. The quasi-1D VRH due to oxygen removal is also unique to this thesis. Even more surprising is that the absence of oxygen in the sample increases the spin susceptibility by roughly two orders of magnitude. Taken together, the ESR results point to the dual role of oxygen in SWNTs: both as a facilitator of electron movement between nanotubes and as a spin decohering presence.

The conductivity of the nanotube films was also measured. The temperature dependence of a typical decant film showed a slowly rising sheet resistance as temperature decreased. This behavior agrees with previous reports in the literature, as well as with the ESR data. In conjunction with both the conductivity and ESR projects, I presented our efforts to develop metal-enriched solutions using a DGU process. Metal-enriched solutions were produced in ensemble form and analyzed using tunable RRS, which all the species of nanotubes to be observed. These experimental results represent the first full ensemble characterization of a DGU metal-enriched sample. It is also the only study that conclusively and quantitatively say that the percentage of metals has increased due to the DGU process.

In Chapter 4, I discussed two important steps with regard to the observation of the DFKE. The first was the experimental developments of t-carrageenan for optical, MIR, and FIR
work, and the second was creating supercontinuum whitelight from a PCF using an ultrafast pulsed Ti:Sapphire laser. The experimental detection of the DFKE was also demonstrated, although not using the full four beam normalization technique. Though more work needs to be done, the work shown in Chapter 4 represents my first attempt to observe the DFKE in nanotubes.
Bibliography


Appendix A

How to Extract $\chi$ from ESR Data

The Dysonian derivative is defined as:

$$\frac{d\chi}{dH} = A \frac{\cos(\varphi)}{\Delta H^2} \left\{ \frac{-2y + (1 - y^2) \tan(\varphi)}{(1 + y^2)^2} \right\}$$  \hspace{1cm} (A.1)

The transverse spin susceptibility, $\chi$, is composed of both absorption and dispersion:

$$\chi = \chi'' \cos(\varphi) + \chi' \sin(\varphi),$$ \hspace{1cm} (A.2)

where the mixing ratio, $\alpha$, is defined as $\alpha \equiv \tan(\varphi)$. For small, $\alpha$, the asymmetry ratio, $A/B$, can be taken as $A/B \approx 1 + \alpha$. The mixing of the absorption and dispersion components greatly influences the Dysonian lineshape.

I would like to determine spin susceptibility from a lineshape that has components of absorption and dispersion. To do this, I will first integrate Eq. A.1 with respect to $H$ to obtain $\chi$. After switching variables from $H$ to $y$, where $y = \frac{H-H_0}{\Delta H}$, I obtain:

$$\chi = \frac{A}{\Delta H} \left\{ \left( \frac{1}{1 + y^2} \right) \cos(\varphi) \right\} + \left\{ \left( \frac{y}{(1 + y^2)^{3/2}} \right) \sin(\varphi) \right\}$$ \hspace{1cm} (A.3)

It can be immediately seen that Eqns. A.2 and A.3 produce a correspondence to the real and imaginary parts of $\chi$. One could go further and observe that the Dysonian lineshape has been separated into an absorption (Lorentzian) and a dispersion curve. Thus, one can write:

$$\chi''(y) = \frac{A}{\Delta H} \left\{ \frac{\cos \varphi}{1 + y^2} \right\}, \chi'(y) = \frac{A}{\Delta H} \left\{ \frac{y \times \sin \varphi}{1 + y^2} \right\}$$ \hspace{1cm} (A.4)
I will use Eq. A.4 later to calculate the static spin susceptibility.

Integrating with respect to \( y \) gives:

\[
\chi''(Y_{\text{upper}} - Y_{\text{lower}}) = \frac{A}{\Delta H} \left[ \tan^{-1}(Y_{\text{upper}}) - \tan^{-1}(Y_{\text{lower}}) \right] \tag{A.5}
\]

\[
\chi'(Y_{\text{upper}} - Y_{\text{lower}}) = \frac{A}{\Delta H} \frac{1}{2} \ln \left( \frac{1 + Y_{\text{upper}}^2}{1 + Y_{\text{lower}}^2} \right) \tag{A.6}
\]

If the magnitude of \( Y_{\text{upper}} \) is the same as \(-Y_{\text{lower}}\), then Eq. A.6 is 0, while Eq. A.5 is symmetric about 0. In other words, the imaginary part of the spin susceptibility does not contribute to the double integrated ESR lineshape. Therefore, upon double integration, the real part of the spin susceptibility \( (\chi'') \) is completely recovered.

The absorbative part of the rf susceptibility, \( \chi'' \), can be related to the spin susceptibility, \( \chi_s \), by the Bloch equations [52]:

\[
\chi''(\omega) = \frac{\chi_s \omega_0 T_2}{1 + (\omega - \omega_0)^2 T_2^2} \tag{A.7}
\]

At resonance, Eq. A.7 can be reduced to:

\[
\chi''(\omega_0) = \frac{\chi_s \omega_0 T_2}{2} \tag{A.8}
\]

The Bloch formulation can be used in an unmodified form for the Dysonian lineshape, since the absorbative part of the Dysonian is Lorentzian. For each lineshape I take with the ESR spectrometer, I fit with Eq. A.1, which allows me to obtain \( \chi'' \). Using Eqs. A.8 and A.4, and relation \( \Delta H = \frac{2}{\sqrt{3}} T_2 \), I obtain:

\[
\chi_s = 3\sqrt{3} \frac{A \cos \phi}{\omega_0 \Delta H^2} \tag{A.9}
\]
The static spin susceptibility is the quantity I seek. But thus far, I have only shown how to get relative spin susceptibilities through fitting.

In order to give the double integrated lineshape real units, a standard reference is needed such as CuSO$_4$. Various schemes and equations have been used to find spin susceptibility using a reference. One example is from Wertz and Bolton [53]

\[
[S\text{ample}] = \frac{A_x R_x (scan_x)^2 G_{std} M_{std} g_{std} [S(S+1)]_{std}}{A_{std} R_{std} (scan_{std})^2 G_{x} M_{x} g_{x} [S(S+1)]_{x}}, \quad (A.10)
\]

where $A$ indicates area under the absorption curve, $R$ is the degeneracy factor (related to hyperfine splitting), $scan$ is the point density per unit gauss (gauss/pts), $G$ is the gain of the receiver, $M$ is the modulation amplitude, $g$ is the $g$-factor of the species, and the brackets indicate concentration of the sample and standard. For most of these factors (such as $M$ and $G$), the standard and the sample values are exact. A few things are important to keep in mind for actual use of this formula. One, the sample and reference should be run in the exact same container/cavity conditions. This is to keep the cavity $Q$ roughly the same for both. Second, the powers (i.e. $H_1$ field) should be the same; if not, one can normalize the fields by $P^{1/2}$. And lastly, the temperatures should be the same. If one is running a temperature dependent scan, then the standard should be done as often as possible.

Similarly, one can examine the spin susceptibility from the detection end, where the voltage signal, $V_S$, is the integral of the recorded ESR signal and can be expressed as [54]:

\[
V_S = \chi'' \eta Q \sqrt{P Z_0}.
\]

(A.11)

Here, $Q$ is the quality factor of the cavity, $P$ is the incident microwave power, and $Z_0$ is the impedance equivalent of the unloaded cavity. $\eta$ is the filling factor, which can roughly be approximated as $\approx \frac{2V_S}{V_C}$ for a TE$_{102}$ cavity [53].
Both Eq. A.10 and Eq. A.11 should give the same spin susceptibility if a reference is used and I have been careful about the definitions of $\chi''$. A generalized expression for the number of probed spins, $N_x$, can be derived by taking elements of both equations. Since $V_s \propto \chi''$, I can define the integrated (with respect to the magnetic field) signal area, $A$, as:

$$A = CN,$$

where $C$ accounts for all other experimental parameters and is proportional to $Q$. Therefore, if all things are equivalent between the sample and the reference, I can write:

$$N_x = \frac{A_x Q_{std}}{A_{std} Q_x} [std] V_{std} N_A.$$  \hfill (A.13)

To extract $\chi_s$ in terms of emu/g (mass susceptibility), I first convert to magnetization by multiplying by $g\mu_B$. Next, I divide by the center field, $H_0$ to get dimensionless $\chi_s$, before dividing by the mass density, $\rho$, to get our final quantity. Therefore, I have:

$$\chi_s(emu/g) = \left( \frac{A_x Q_{std}}{A_{std} Q_x} [std] V_{std} N_A \right) \frac{g\mu_B}{H_0 \rho}.$$  \hfill (A.14)

Lastly, one of the most important and confusing parts of any calculation of spin susceptibility is the use of cgs units. Below, I give a table of the related quantities, their units, and the subsequent conversion to SI.
Table A.1: Terms and Units for Magnetostatics [112].

<table>
<thead>
<tr>
<th>Term</th>
<th>Symbol</th>
<th>CGS Unit</th>
<th>Conversion Factor</th>
<th>SI Unit</th>
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<td>Oe</td>
<td>$10^3/4\pi$</td>
<td>A/m</td>
</tr>
<tr>
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<td>G</td>
<td>$10^{-4}$</td>
<td>T, Wb/m²</td>
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<td>$10^{-3}$</td>
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<td>A/m</td>
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<td>A-m²/kg</td>
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<td>Dimensionless</td>
</tr>
<tr>
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<td>cm³/g</td>
<td>$4\pi*10^{-3}$</td>
<td>m³/kg</td>
</tr>
</tbody>
</table>
Appendix B

Polymer Methodology

Producing both CMC and ι-carrageenan is difficult without a set procedure. Here, I describe how ι-carrageenan is made. The procedure for 90 kDa CMC is very similar, though not exactly the same, to the one given in this Appendix.

ι-carrageenan was procured in a powder form from Sigma-Aldrich (C4014–5G Type V). Depending on the application, a 0.5% w/v to 2.5% w/v solution of ι-carrageenan in 2 mL of 1% w/v H₂O:Sodium Cholate is used. It is necessary that a sodium cholate (SC) surfactant is utilized; in fact, other surfactant systems, such as sodium deoxycholate (SDOC), turn the solution white, resulting in an opaque film. The opacity due to surfactant systems may be related to the pH of the solution.

Though carrageenases are water soluble, their solubility in water is highly environment-dependent. Typically, to create a gel, researchers have exceeded the gelation set point, and then allowed the solution to cold-gel set [101]. The use of ethanol, irradiation, and counter ions (usually K⁺ and Na⁺) are all used to change the gelation temperature. For my purposes, I typically heat the 1% surfactant solution to about 60° C before adding the carrageenan powder. Upon addition of the powder, the solution was stirred and allowed to rise to 65° C. At this stage, the solution is fully mixed and very clear. No bubbles and/or discoloration was seen. The solution is then allowed to cool to 55° C, whereupon a solution (decant) of nanotubes is added. The surfactant system of both the nanotubes and the poly-
mer solution should be the same, such that the addition of the decant does not dilute the surfactant concentration of the entire ensemble. The volume of the nanotube decant was set so that it was the same as the carrageenan solution. In other words, 50% of the liquid was nanotube decant and 50% was t-carrageenan by volume.

The solution is only kept at 55° C for two minutes, to avoid disrupting the micelle structure surrounding the nanotubes. This point is critical since the micelles are highly temperature dependent; destroying their nanotube wrapping because the temperature is too high quickly leads to re-bundling. The solution is then transferred to circular teflon or aluminum molds which are sitting on a clear transparency.

I have experimented with allowing the gels to simply cool (which takes roughly 48 hours) and with keeping them at 30° C for the entire drying period (about 36 hours), both methods seem equally effective. It seems as though controlling the relative humidity, not temperature, is the largest determinant about how quickly the gels dry. Relative humidity control also seems to impact film roughness. Typically, the circular molds are removed after 24 hours of drying to avoid the polymers adhering to the walls of the mold. Upon solidification, the polymer films are separated from the transparency using a razor blade.