SYNTHESIS OF CARBON MATERIALS VIA THE COLD COMPRESSION OF
AROMATIC MOLECULES AND CARBON NANOSTRUCTURES

A Dissertation in
Chemistry
by
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ABSTRACT

Carbon’s ability for catenation makes it a remarkable element and allows for many interesting and surprising properties and structures. Carbon can exist in one of its two thermodynamically stable bulk crystals, graphite or diamond, one of its several nanostructures: fullerene, nanotube, or graphene, or as an amorphous material with a mixed bonding pattern. Carbon also has an ability to bond heteroatoms such as hydrogen which can increase its properties and structures even further. Pressure has been shown to be able to drastically change the bonding in and structure of carbon based materials.

In this dissertation I will present how pressure can be used to synthesize new amorphous hydrogenated carbons and how a battery of analytical techniques can be used to elicit the microstructure of the carbon networks. This microstructure can then be related back to the reaction conditions and more importantly the starting small molecule. This work has been expanded to looking for a molecular analogue to the cold compressed graphite system by investigating the high pressure stability and reactivity of 2-D polycyclic aromatic hydrocarbons.

This work was followed by discovering the failure of Single Walled Carbon Nanotubes at high static pressures. When the tubes fail they transform into nano-graphitic polyhedra. It has been found that metallic tubes preferentially collapse, leaving the semiconducting tubes intact for the most part.

Finally, the most influential work performed in my dissertation has been related to the kinetically controlled solid state reaction of molecular benzene to form diamond nanothreads. These nanothreads pack into hexagonal bundles without axial order. A combination of Raman spectroscopy, x-ray and neutron scattering, transmission electron microscopy, and first principles calculations were performed to confirm their existence.

The three data chapters in this dissertation are enhanced by an introduction to carbon based materials and high pressure chemistry in chapter 1, an overview of the advanced and sometimes
unconventional characterization techniques used throughout the dissertation in chapter 2, and some concluding remarks and future directions for this research in chapter 6.
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EPIGRAPH

“…perhaps the pressure of the air might have an interest in more phenomena than men have hitherto thought.”

--Touching the Spring of Air (1660)
Sir Robert Boyle
1 Introduction to Carbon Based Materials and High Pressure Chemistry

1.1 History of Carbon Based Materials

Throughout human history carbon has played a central role in each and every technological advance. Beginning in ancient times, charcoal was used for the reduction of metal ores such as copper, zinc, and tin which lead to the Bronze Age\(^1\). The use of coal drove the industrial revolution powering not only steam engines but also providing electricity for entire cities\(^2\)-\(^4\). Combustible carbon based fluids, such as gasoline, revolutionized transportation again by fueling automobiles, ships, and airplanes\(^5\). Carbon materials even took our world into the nuclear age with Enrico Fermi’s graphite reactor at the Chicago Pile which exhibited the first man made self-sustaining nuclear reaction\(^6\),\(^7\). The discovery and exploitation of carbon based polymers has had a profound effect of how we lived through the second half of the 20\(^{th}\) century and into today\(^8\). With advancements in polymer science, the controlled synthesis of amorphous carbons\(^9\)-\(^13\), and the unique and amazing properties that carbon has been shown to possess at the nanoscale\(^14\)-\(^18\), carbon promises to play a key role in many of our future technologies\(^19\)-\(^22\).

A main reason that carbon has played such a key role in so many technological revolutions is that carbon can bond in several different ways, depending on the hybridization of the atomic orbitals, and can readily form bonds with many different elements. As a result the material’s physical, electronic, optical, and mechanical properties can change drastically depending on the type of bonding present and what other elements carbon is bonded to. Here I will focus on materials that are either purely carbon in nature or contain only carbon and hydrogen. Even with the limitation of merely two elements these carbon materials can have properties that range from being very mechanically soft and having electrical conductivity
similar to that of a metal to being the hardest known material on Earth that is highly insulating.

This dissertation will focus on how pressure affects the hybridization of the atomic orbitals of carbon and how new and interesting materials can be synthesized from the high pressure reaction of simple carbon precursors. This chapter will provide an introduction to carbon materials of interest, how high pressure is generated and how it subsequently affects chemical systems, and end with a description of the deceivingly complex carbon phase diagram.

1.1.1 Crystalline Carbons: Graphite and Diamond

Graphite is the thermodynamically stable form of carbon at standard temperature and pressure (STP)\textsuperscript{23}. Graphite consists of carbon atoms that have sp\textsuperscript{2} hybridized atomic orbitals, meaning that each carbon is bonded to three other carbon atoms. This type of bonding results in the formation of carbon sheets that stack in an ABAB hexagonal lattice, space group symmetry P6\textsubscript{3}/mmc\textsuperscript{24}. The individual layers are separated by 3.4 angstroms and held together with Van der Waals (VdW) bonds. The crystal structure of graphite can be seen in figure 1-1a.

Because of its structure, graphite has many interesting properties. The electrons within each layer of graphene, are fully delocalized. These delocalized electrons act as a “sea of electrons” much like those of a metal\textsuperscript{25,26}. Because of this graphite has metal-like conductivity along both the a and b axes, parallel to the graphene sheets, of the crystal structure. However, due the large amount of free space between adjacent layers of graphene, electrons do not flow freely along the c axis, orthogonal to the graphene planes, resulting in an insulating material. Also with its metallic nature, the optical constants of graphite cause it
to be highly reflective to a large range of wavelengths\textsuperscript{27-29}. In addition to the electrical and optical properties, graphite’s crystal structure lends itself to interesting mechanical properties as well. The weak VdW interactions between layers of graphite make graphite very soft. This property has led many to use graphite as a solid state lubricant.

The second crystalline phase of carbon is that if diamond. Diamond is only metastable at STP, but as will be discussed later, there is a massive kinetic barrier that separates diamond and graphite. This kinetic barrier is what prevents diamond gemstones, such as those found in jewelry, tools, and optical windows, from spontaneously decomposing into graphite. Diamond consists of carbon that has sp\textsuperscript{3} hybridized atomic orbitals, resulting in each carbon atom being bound to four other carbon atoms in a tetrahedral coordination. The local sp\textsuperscript{3} bonding present in diamond results in a high symmetry cubic crystal structure, space group Fd-3m\textsuperscript{30}, on the macro scale. The crystal structure can be seen in figure 1-1b.

Like graphite, diamond’s electronic optical and mechanical properties are governed by its structure. The sp\textsuperscript{3} bonding that is present in diamond results in the electrons being highly localized in between adjacent carbon atoms. These localized electrons cannot move throughout the material resulting in diamond being highly insulating\textsuperscript{31}. However the covalent
bonding allows for very high thermal conductivity\textsuperscript{32,33}. Additionally, the sp\textsuperscript{3} bonding allows for only sigma bonds to exist within the material. The \(\sigma\rightarrow\sigma^*\) electrical transition is very large in diamond, roughly 5.5 eV\textsuperscript{34}, making diamond very transparent through a large wavelength region. The 5.5 eV band gap sets the high energy absorption edge for diamond. The fundamental phonon frequency as well as multiphonon absorption typically set the low end for the transparency window for materials. Diamond has a fundamental vibrational absorption at 1332 cm\(^{-1}\) or 7.5 micrometers\textsuperscript{35}, however this is IR inactive. Because of this diamond is transparent far into the far-IR. Only a small absorption in the region of roughly 5 micrometers is observed due to two phonon absorption. The large transparency window for diamond is determined directly by the local bonding and global crystal structure. Because the diamond lattice is made up of a single crosslinked covalent network of carbon atoms that are densely packed, diamond is very stiff. The stiffness of the covalent bonds in the diamond lattice results in diamond being the hardest known material.

1.1.2 Amorphous Carbons

One thing that makes carbon such a remarkable element is its ability towards catenation. As was shown in the discussion of diamond and graphite, the local bonding that exists in carbon can drastically change the resulting material’s properties. In addition to the two crystalline forms of carbon, which have only a single type of carbon coordination, metastable carbon materials can exist that have sp, sp\textsuperscript{2}, and sp\textsuperscript{3} bonding present. By combining the local bonding, and by adding heteroatoms such as hydrogen, one can tune the properties of these amorphous carbons from those that are close to graphite to those that more resemble diamond. Figure 1-2 is a ternary phase diagram of amorphous carbons showing the different types of carbon based on sp\textsuperscript{2} content and hydrogen content\textsuperscript{36}. 
Traditionally amorphous carbons have been formed via two routes. First, pyrolysis of carbon containing molecules has been a common route to synthesis carbon materials that are high in sp$^2$ content$^{37,38}$. For example, furfural alcohol is a common starting compound to make nanostructured, graphite-like, carbon materials such as zeolite template carbons$^{39}$. In this process furfural alcohol, which is a liquid at STP, is infiltrated into a porous template, such as a zeolite, and then heated to high temperature.

The alcohol decomposes into a highly sp$^2$ hybridized graphite-like amorphous carbon. The zeolite can be removed by etching with HF. A second, more common approach to synthesizing amorphous carbon is chemical vapor deposition (CVD) and plasma enhanced CVD (PE-CVD)$^{40-42}$. In this type of reaction a gas mixture, typically methane and hydrogen, is introduced to a substrate at either a high enough temperature to decompose or decompose with the assistance of a plasma. Depending on the gas mixture, temperature, and plasma conditions many types of amorphous carbons can be produced. It is with a PE-CVD technique that diamond-like amorphous carbon is deposited.

Figure 1-2: Ternary phase diagram showing the different types of amorphous hydrogenated carbons. Taken from Ferrari et. al. (Reference 36)
Chapter 3 of this dissertation will present on a series of amorphous carbons that have been synthesized by a third technique. These amorphous hydrogenated carbon have been synthesized through the high pressure polymerization of polycyclic aromatic hydrocarbons.

1.1.3 Nanocarbons

While intercalated graphite was the material of interest in carbon chemistry throughout the 1970’s and early 1980’s, in 1985 the groups of Smalley and Kroto discovered that you could recover small carbon nanoparticles from the arc discharge of graphite. When put through a mass spectrometer they discovered that these carbon nanoparticles were in fact C\textsubscript{60} fullerene. From their discovery of C\textsubscript{60} in 1985 nanostructured carbons have become the new material of interest. When carbon is scaled down to the nanoscale, it has many interesting properties and when these properties become better understood and more easily exploitable, nanocarbons will be at the center of many technologies of the future.

It was not long after the discovery by Kroto and Smalley in 1985, that it was discovered that if you were to stretch a C\textsubscript{60} fullerene in one dimension that you could form carbon nanotubes. The first multiwalled carbon nanotubes were discovered by Iijima in 1991. By 1993, Iijima and Bethune were able to synthesize single walled carbon nanotubes (SWNT). These single walled carbon nanotubes it was found could be semiconducting or metallic and come in a variety of different diameters based on how the graphene sheets were rolled. In addition to the electrical properties these sp\textsuperscript{2} carbon nanotubes have amazing mechanical properties. Theoretical calculations show that SWNTs have a tensile strength of almost 1 TPa.
These theoretical mechanical properties are difficult to realize because most SWNTs form hexagonally packed bundles of tubes with varying chirality. Chapter 4 of this dissertation explores the high pressure transformation of these SWNT bundles.

![Atomistic representations of different known carbon nanomaterials and how they relate to hybridization and dimensionality.](image)

Figure 1-3: Atomistic representations of different known carbon nanomaterials and how they relate to hybridization and dimensionality. Note the lack of an sp\(^3\) 1-D material. This new type of material has been discovered and will be presented in Chapter 5.

It was known that the chirality of SWNTs was determined by how the direction that the graphene sheet was rolled. However, at the time of the discovery of the SWNT, individual graphene sheets had not yet been discovered. In 2004, Geim and Novoselov, discovered that with standard Scotch tape, graphite could be thinned down via mechanical exfoliation to a single atomic layer\(^\text{18}\). The resulting material had amazing electrical properties including ballistic electron transport. It was also amazingly strong, with a Young’s modulus of 1 TPa. For their discovery Geim and Novoselov were awarded the Nobel Prize in physics in 2010. Since their discovery a lot of research has gone into the fabrication of graphene on a
larger scale than that afforded by mechanical exfoliation. The reduction of exfoliated graphene oxide is one route, but this results in a highly disordered product\textsuperscript{50,51}. The more promising route to large scale graphene synthesis has been through CVD\textsuperscript{52}.

Until now the focus of carbon nanomaterials has been focused on sp\textsuperscript{2} carbon networks. However, as can be seen in figure 1-3 there are suitable sp\textsuperscript{3} analogues to these sp\textsuperscript{2} networks. The main challenge of extended sp\textsuperscript{3} bonding down to the nanoscale is the problem of highly reactive dangling bonds. The dangling bonds present in these materials must be capped, typically by hydrogen or a halogen. The sp\textsuperscript{3} analogue to C\textsubscript{60} is a class of sp\textsuperscript{3} carbon compounds known as diamondoids\textsuperscript{53}. Diamondoids are found in nature, within oil and natural gas wells, and are cage-like structures. The origin of diamondoids is currently unknown from a mechanistic standpoint, but the most common diamondoid, adamantane, is readily available commercially. Graphane is a theoretical analogue to the sp\textsuperscript{2} carbon sheet graphene. Experimental attempts to synthesize graphane have typically consisted of exposing a graphene sheet to hydrogen plasma, but full coverage has not yet been achieved\textsuperscript{54}. Full coverage of fluorinated graphene has been achieved\textsuperscript{55}. The resulting material has been shown to be highly insulating. Chapter 5 of this thesis will present on a new carbon material that could be considered an sp\textsuperscript{3} analogue to SWNTs.

1.2 Using Pressure as a Variable

As chemists, we typically look to the free energy of a system or more specifically the change in free energy of a system to determine whether a reaction will occur. The free energy equation has three variables that can be readily tuned:
\[ \Delta G = -S\Delta T + V\Delta P + \sum_{i=1}^{k} \mu_i \Delta N_i \]  (Equation 1)

The temperature, T, and the number of molecules of a certain species, N, are the two variables that have traditionally been exploited by chemists to alter the free energy, G, of a system. However, pressure, P, is a term that can also be changed, and in our laboratory pressure can be tuned by such a large margin that its effect of the free energy of a system is orders of magnitude that of temperatures typically available in our lab. Figure 1-4 shows that the free energy of a hydrogen molecule can be altered much more with pressure than with temperature.

![Figure 1-4: Shows the change in free energy of a hydrogen molecule with pressure-temperature conditions easily achievable in the lab. Note the order of magnitude difference in free energy that is achieved from the highest achievable pressure with respect to temperature.](image)

In the Badding lab we can generate pressures upwards of 100 GPa, these are pressures typical in the mantle of the Earth, with the use of diamond anvil cells (DAC). At these pressures
many new and interesting chemical reactions become possible and it opens the door to forming new materials.

1.2.1. Generating High Pressure

In the experiments presented throughout this dissertation, a DAC has been utilized to generate the high pressures needed. The main exception to this is Chapter 5, where a Paris-Edinburgh (PE) cell was utilized to generate high pressure. The DAC is based on an opposed anvil technique pioneered by Percy Bridgman\textsuperscript{56}. Bridgman was awarded the Nobel Prize in physics in 1946 for his work on high pressure physics\textsuperscript{57}. Many of his ideas on generating extreme pressures are still utilized today, like his opposed anvil design. In Bridgman’s experiments he utilized tungsten carbide (WC) as opposed to diamond which limited his maximum pressures to only a few GPa. In the late 1950’s the first DAC was created at the National Bureau of Standards\textsuperscript{58}. This cell was updated through the years to where the modern standard DAC has the following parts that can reach pressures of several Mbar\textsuperscript{59-61}. Single crystal diamond is used for the anvil material. As stated earlier, diamond is the hardest known material which allows for ultrahigh pressures to be achieved. The large transparency window of diamond also allows for a myriad of in situ characterization techniques to be utilized. These characterization techniques will be discussed in greater detail in chapter 2. A hard backing plate is used to support the diamond and align the diamonds in the cell. This is typically WC or cubic-boron nitride (c-BN). A pressure generating mechanism is needed to raise and control the pressure of the DAC. The two most common ways to do this include the use of Bellville washers which can be stacked to create a tunable spring which can then be compressed with a bolt or a gas membrane. The gas membrane is an expandable metal membrane that pushes the two diamonds together with a controlled amount of input gas
pressure. The fourth necessary component is the gasket. The gasket is a metallic disk that goes in between the two opposed anvils. The gasket serves two purposes. The first is as the sample chamber; a hole is drilled, either mechanically or laser cut, through the center of the gasket. The second role the gasket plays is that it provides radial support to the diamond anvils preventing failure of the anvils at the edges \(^6^2\).

![Diagram of a cross section of a diamond anvil cell.](image)

**Figure 1-5**: Schematic representation of a cross section of a diamond anvil cell. Also shown are how different characterization techniques can be applied to the small sample chamber within the metal gasket.

Typically hard metals such as steel or rhenium are used as the gasket material, however, Chapters 2 and 5 describe an experiment where a beryllium gasket with c-BN inserts were used for an advanced x-ray technique. A schematic of a DAC can be seen in figure 1-5.

Pressure within the DAC is monitored in situ via the shift in the fluorescence of ruby \(R_1\) line \(^6^3\). Ruby has an intense doublet in the fluorescence spectrum around 694 nm that is
caused by the spin orbit coupling after the d-orbitals of the Cr\(^{3+}\) ion is split by the crystal field of the Al\(_2\)O\(_3\) host lattice. As pressure is increased in the sample chamber, the peak position of the ruby fluorescence lines red shift. This shift in peak position has been calibrated against the known equations of state (EoS) of several metals.

As stated earlier, Chapter 5 deals with a different type of high pressure cell than the standard DAC. The PE cell is a large volume press\(^{64}\). Where the standard DAC has a sample volume of 8.75 x 10\(^{-5}\) mm\(^3\), the PE cell has a volume of .17 mm\(^3\). This large volume press was developed mainly for in situ neutron diffraction purposes. Since neutron beams have a much lower flux than synchrotron x-ray sources, and the neutron scattering cross section is much lower than that of x-rays a large sample volume is needed to measure the sample.

An image of the PE cell can be seen in figure 1-6a. Because of the increased sample size the PE cell is much larger than a standard DAC and cannot generate pressures comparable to those of a DAC. The pressure in a PE cell is limited to a maximum of about 25 GPa.

The anvil design in the PE cell is much more complicated than that of the DAC. To gain in increase in volume yet retain stability the anvils are polycrystalline diamond (PCD) that are in the shape of a double toroid\(^{65}\). A schematic of the PE cell anvil geometry can be seen in
figure 1-6b. The double toroid PCD is retained by a WC ring which is then fretted into a hardened steel binding ring. The steel binding ring provides extra radial support to the anvil. There are then two backing plates for each anvil: the first is a WC plate with a steel binding ring and the second is a hardened steel plate. This entire anvil assembly is then driven by a hydraulic oil pump. For our experiments we utilized encapsulated metal gaskets to hold our sample and again provide radial support to the PCD anvils. The pressure of the PE cell needs to be measured by either an internal calibrant such as gold for diffraction experiments or indirectly via a precalibrated pressure-load curve.

1.2.2. Effect of Pressure on Chemical Systems

As shown previously, pressure has a drastic effect on the free energy of a system. Pressure not only changes thermodynamic variables such as free energy, but it can also drastically alter the mechanical, optical, and electrical properties of a material. A way of thinking about adding pressure to a system is by adding density to a system. At high pressure liquids and gases both freeze at room temperature. Percy Bridgman found in the early 1900’s that at just below 1 GPa, water freezes at room temperature, into a phase now known as Ice VI\textsuperscript{66}. When his initial paper on this was published he got many letters and inquiries from fruit and vegetable companies about his new “room temperature ice” in hopes that they could decrease their refrigeration costs\textsuperscript{67}. These types of phase transitions were completely unexpected, like many things that occur at high pressure.

The phase diagram of water has done nothing but get more complex now that pressure has been taken into account. Before Bridgman’s discovery of Ice VI it was thought that water consisted of only 3 phases, a liquid phase, the Ice I phase, and a gas phase. Since then there has been extensive research on the seemingly simple H\textsubscript{2}O system, and now there are 14 known crystal structures and two amorphous phases of ice\textsuperscript{66,68-73}. The phase diagram
for ice can be seen in figure 1-7\textsuperscript{74}. The Ice X phase, is an ionic crystal where the protons sit an equal distance from two adjacent oxygen atoms. It is unknown what proton belongs to which oxygen atoms. To this day new research is still being done to elicit the structure of water at high pressure\textsuperscript{75}. 

What may be even more surprising than liquids freezing at room temperature, is that gasses also freeze at room temperature and high pressures. One of the most studied systems at high pressure is that of hydrogen. Theoretical predictions suggested in the 1960’s that hydrogen would become a monoatomic metal at high pressure\textsuperscript{76-78}. Since then the experimental search for metallic hydrogen has been an intense field of high pressure research\textsuperscript{79,80}. There are now four known solid phases of hydrogen, with Phase IV being discovered only over the past two years\textsuperscript{81-84}. The phase IV crystal structure of hydrogen can be seen in figure 1-8\textsuperscript{82}. Although there have been some claims to metallization, no definitive proof has yet been found that would suggest the hydrogen has become fully metallic\textsuperscript{85}. The newest experiments are being performed at pressures well over 200 GPa. When metallic
hydrogen is finally experimentally observed it will be a monumental breakthrough for the fundamental physics community.

Even in the solid state pressure can drastically change a system. Silicon is a semiconductor that exists in the Fd-3m space group. It has the same crystal structure as diamond with each silicon atom tetrahedrally coordinated to four other silicon atoms. However, when pressure is applied to silicon some interesting things occur. With only moderate high pressure, less than 10 GPa, the conductivity of the silicon increases with pressure. At above 12 GPa, silicon goes through a solid-solid phase transition to the $\beta$-tin phase\textsuperscript{86}. In this high pressure phase the silicon has metallic conduction and the silicon atoms are now octahedrally coordinated. Like the aforementioned hydrogen, all systems will eventually become metallic at high enough pressure.

Small molecules go through drastic transitions at high pressure. The most important transformation is that of high pressure polymerization. At high pressure when isolated molecules get pushed close enough to one another, any unsaturated bonds within them will increase their coordination number\textsuperscript{87}. Much work has been done on CN type molecules in an

![Figure 1-8: Atomistic representation of the hydrogen IV crystal structure. Even a very simple diatomic molecule can form complex guest-host crystal structures. This structure has been proposed from Raman and IR spectroscopy along with first principles calculations. Taken from reference 82.](image-url)
attempt to make the theoretically ultrahard phase of cubic-carbon nitride (c-CN)$^{88-90}$. In addition to cyano molecules a lot of work has been done on the effect of pressure on aromatic molecules$^{91}$. Chapters 3 and 5 will go into great detail on the effect of pressure on these systems.

1.3 Introduction to the Carbon Phase Diagram

Figure 1-9 is the deceivingly simple carbon phase diagram deduced by Bundy et.al.$^{92}$ There are merely three thermodynamically stable phases of carbon present in the phase diagram: graphite, diamond, and liquid carbon.

![Carbon Phase Diagram](image)

Figure 1-9: The phase diagram of carbon as of 1994. The two notes of importance are the positive slope between the graphite to diamond transition as well as the positive slope of the diamond melting curve. The dotted line indicates room temperature. The dashed line indicates experimental observations where sp$^2$ carbon has been transformed to diamond.

However, it is well known that there are a myriad of other metastable carbon phases, many of which were discussed earlier. In addition to the metastable forms of carbon that are not shown on the phase diagram, the actual transition from graphite to diamond is not as straightforward as would be expected from the phase diagram, which is based on thermodynamics. This is because many carbon transformations are kinetically driven reactions. Between the
two thermodynamic potential wells of graphite and diamond lies an enormous kinetic barrier. It is this kinetic barrier that separates graphite from diamond that will be discussed in the conclusion of this chapter.

1.3.1 Direct Transformation from Graphite to Diamond

As stated above, the direct transformation from graphite to diamond looks to be simple and straightforward based on the phase diagram of carbon. According to the phase diagram diamond becomes the thermodynamically stable phase of carbon at room temperature at a pressure of less than 2 GPa. However, just as diamond gemstones will not spontaneously transform to graphite on your ring, graphite needs a large thermal energy to push the transformation to diamond. Herein lies a problem. The graphite-diamond phase equilibrium line has a positive slope. This positive slope is due to the positive thermal expansion coefficient of graphite.

Bridgman worked to try and determine where the thermodynamic boundary between diamond and graphite existed by exposing diamond to high pressures and trying to determine at what temperature the diamond will no longer graphitize\textsuperscript{93}. At that P-T condition it is determined that you are then in the diamond thermodynamic stability region. Until the mid 1950’s no reliable graphite to diamond transitions were observed\textsuperscript{94,97}.

1.3.2 Synthetic Diamond

Diamond was first synthesized by a group at General Electric in 1955 using a high pressure high temperature belt apparatus. They transformed carbonaceous material to diamond at pressures in excess of 9 GPa and temperatures near 3000 K\textsuperscript{98}. Bundy et. al. were also the first to directly convert graphite to diamond at 13 GPa and 3300 K in 1966\textsuperscript{99}. Over the course of decades the HP-HT synthesis of diamond has been applied to many different
types of carbonaceous material. Additionally a myriad of metal catalysts have been used to try and lower the P-T conditions necessary to facilitate diamond growth.

Since this discovery there have been two goals of synthetic diamond that have gained great attention that I will focus on. The first is a chemical vapor deposition of single crystal ultrapure diamonds with a high growth rate. This method has drastically reduced the cost and difficulty of synthesizing large diamond samples that hindered the HP-HT techniques. A second goal is to expand the HP-HT technique of diamond synthesis to form diamonds with interesting microstructure. For instance HP-HT synthesis has been used to create both nanopolycrystalline and nanoporous diamonds. Figure 1-10 shows images of both the CVD diamond grown at the Geophysical Laboratory of the Carnegie Institution for Science and the nanodiamond grown in a multianvil press by the Irifune group in Japan.

![Figure 1-10: (Left) Nano-polycrystalline diamond synthesized from a polycrystalline graphite rod. (Taken from reference 103). (Right) High quality multi-carat single crystal diamonds grown from a MPCVD reactor by collaborators at the Geophysical lab. Image courtesy of Carnegie Institution for Science](image)

There are currently three techniques used to synthesize diamond via a CVD approach\(^\text{100}\). The first is a hot-filament CVD, where a heated wire is used to create a plasma that diamond is deposited from. This technique has drawbacks in that it has a fairly low
growth rate, can only form polycrystalline samples, and often has contamination issues from the filament. The second method is a arc jet torch CVD which results in much higher growth rates with a high carbon conversion efficiency, but it has not been thoroughly controlled enough to create high quality single crystal diamonds. The third technique used to synthesize diamond is a microwave plasma CVD (MPCVD) system. In this method high the crystallinity can easily be tuned from polycrystalline to single crystal. Also since it is a low pressure technique, the chemical impurities can be removed. Recent advances in MPCVD have been able to grow large, high purity single crystals of type IIa quality.

To synthesize nanodiamond which has mechanical properties in excess of single crystal diamond, Irifune used a polycrystalline graphite rod as starting material\textsuperscript{101-103}. His group then placed the rod into a multianvil press, an updated system to the belt apparatus pioneered at General Electric in the 1950’s. The synthetic conditions were pressures of 12-25 GPa and temperatures between 2300 and 2500 K. When the samples were recovered transmission electron microscopy was used to determine that the diamond was nanocrystalline in nature. Further work has suggested that the microstructure of the nanodiamond, texture as Irifune refers to it, is highly dependent on the crystallinity of the starting graphite rod.

Nanoporous diamond has been synthesized by Zhang et. al. from a template microporous carbon starting material\textsuperscript{104}. The microporous carbon is template from a zeolite and then the inorganic zeolite is removed by an acid etch. What makes this reaction so intriguing is the mild reaction conditions for the transformation from a graphitic starting material to diamond. A multianvil press similar to the one used by Irifune was used in this synthesis. The microporous carbon was pressurized to 21 GPa and heated to only 1300 K,
which was enough to have complete conversion to diamond. TEM micrographs and BET isotherms were used to verify the nanoporous nature of the resulting diamond material.

It has been shown that although the phase diagram of carbon appears very simple when compared to other systems, the ability of carbon to form kinetically stable intermediates and be kinetically stable well into the thermodynamic stability regime of other phases makes the study of carbon very interesting.

1.4 Goals on the Dissertation

The goals put forth in this dissertation are to synthesize and characterize new forms of carbon found through the high pressure reaction of small molecules and carbon nanostructures. A large range of characterization techniques, some seldom used in the past for high pressure work, have been utilized to elicit the structure of both crystalline and amorphous forms of carbon. These new materials have the potential to address needs such as the formation and failure of lightweight, high strength composites.
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2 Characterization Techniques

The ability to characterize both *in situ* and *ex situ* carbon based samples at high pressure is a nontrivial analytical problem. Sample sizes are small, low Z, and often times contained within large experimental equipment. Throughout my graduate career I have modified traditional analytical methods to suit the needs of the high pressure experiments. This chapter will focus on the theoretical background of several of the most used analytical techniques for the experiments in chapters 3-5 and how they are modified to work with samples either at high pressure or recovered from high pressure.

2.1. Vibrational Spectroscopy

When discussing the motion of molecules it is important to think about how many degrees of freedom (DoF) a molecule has and subsequently how these motions can be measured. A molecule in the gas phase has 3*N degrees of freedom of motion, where N is the number of atoms. Three of those DoF are taken by the molecules translational motion, in the x, y, and z directions. Typically 3 more DoF are taken by the rotation of the molecule. However, if the molecule is linear there are only two rotations because the rotation axis parallel to the molecule is degenerate because there is no change in orientation as it rotates. This results in the following equation for determining the number of normal vibrational modes in a molecule:

\[
\text{Number of vibrations} = 3N - 6 \quad \text{(For non-linear molecules)}
\]

\[
\text{Number of vibrations} = 3N - 5 \quad \text{(For linear molecules)}
\]
For example, carbon dioxide, CO$_2$ has 4 vibrations, two of which are degenerate. (figure 2-1a). The two degenerate modes consist of the in plane and out of plane bending modes. A non-linear molecule such as dichloromethane will have 9 vibrational modes (figure 2-1b). Now that we know how many vibrations are to be expected we need to determine a way to measure them.

![Diagram of vibrational modes for CO$_2$ and CH$_2$Cl$_2$](image)

Figure 2-11: Atomistic representation of the different vibrational modes for CO$_2$ and CH$_2$Cl$_2$. The O-C-O bending mode is doubly degenerate which is why there are only 3 modes shown for CO$_2$ instead of the calculated 4.
When light interacts with matter it can do one of four things: reflect, transmit, absorb, or scatter. By measuring how light interacts with small molecules we can determine the vibrations that are present. Molecular vibrations typically have an energy that resides within the mid-infrared region of the electromagnetic spectrum. Therefore, a common technique to probe molecular vibrations is infrared absorption. A second way to measure molecular vibrations is through Raman scattering. In Raman scattering light is scattered by the molecular vibrations and the light that has lost or gained energy relative to probe beam is collected. This energy difference is due to the incident beam causing a molecular vibration (resulting in a Stokes shift) or a molecular vibration adding energy to the incident beam (resulting in an anti-Stokes shift) Due to selection rules, these two techniques are complementary and can give a great deal of information about the material under study. The two techniques will be described in greater detail and how they can be adapted to in situ high pressure experiments will be discussed².

2.1.1. Raman Spectroscopy

When a photon, typically visible light, from a laser source impinges on a sample the vibrations within that sample can inelastically scatter the light. Only about 1 in 1,000,000 incident photons are inelastically scattered, whereas the rest are elastically scattered (Rayleigh scattering) so Raman is generally a weak technique³. Raman scattering can most easily be explained through the energy diagram in figure 2-2. Although the electron is excited to an imaginary state, this state does still have a finite lifetime and as will be observed can cause the Raman spectrum to broaden due to lifetime effects.
An electron is excited from its ground state to a very short lived imaginary state. This state can be either within the band gap (HOMO-LUMO gap for small molecules) or above the band gap. Then when the electron recombines in the ground state it goes into either a higher or lower lying vibrational state than where it started. The energy difference that is observed is equal to the strength of the vibration probed. The molecular vibration can either detract or add energy to the incident photon. However for a photon to gain energy upon scattering, it requires the molecule to begin in an excited vibrational state. If we investigate the vibrational partition function it becomes evident that at room temperature a very small number of molecules are present in an electronic excited state.

\[ \varepsilon_n = \left( n + \frac{1}{2} \right) \hbar \nu \]  \hspace{1cm} (Equation 2.1)

\[ q_{vib}(T) = \sum_n e^{-\beta \varepsilon_n} \]  \hspace{1cm} (Equation 2.2)

\[ f_n = \frac{e^{-\beta \hbar \nu (n+\frac{1}{2})}}{q_{vib}} \]  \hspace{1cm} (Equation 2.3)
Equation 2.1 is the standard harmonic oscillator equation which will give the spacing between vibrational energy levels. Equation 2.2 is the vibrational partition function which is the total vibration energy of a system as a function of temperature; $T$. Equation 2.3 can be used to calculate the population of excited vibrational states. It can easily be calculated that the number of molecules in excited vibrational states decreases exponentially\(^4\). This barrier gets higher as the vibration increases in energy. Therefore anti-stokes Raman is a much weaker measurement than measuring Stokes Raman, especially as you move away from the laser line.

Raman has been shown to be able to determine changes in the stoichiometry of ternary II-VI semiconducting optical fibers. 488 nm Raman was utilized in figure 2-3 to gain an understanding of the transition between ZnS to ZnSe through a $\text{ZnS}_x\text{Se}_{1-x}$ intermediate. The changes in the longitudinal and transverse optical (LO and TO) modes in the ZnSSe alloys with respect to the pure ZnS and ZnSe materials shows evidence of alloying and not just a mixture of two distinct and chemically different phases.

![Figure 2-3: 488 nm Raman of ZnS, ZnSe, and two ternary structures of ZnS$_x$Se$_{1-x}$. Raman is good probe of stoichiometry of solid structures. Taken from Sparks et.al.\(^5\)](image)
Energy of the vibration is not the only important aspect of Raman spectroscopy. Raman has very distinct selection rules, which makes it a great compliment to infrared absorption. The only vibrational modes that will cause Raman scattering are vibrations that result in a change in polarizability. This means for a mode to be Raman active there needs to be a change in the deformation of the electron cloud surrounding a bond with respect to its normal mode of vibration. This means that simple diatomic stretches such as C-C and H-H are very strong in Raman spectroscopy. An additional symmetry argument can be made using polarized Raman spectroscopy. By using a laser of known polarization and rotating an analyzer in the collection optics, the symmetry of a vibration or the orientation of macromolecules can be determined. If a molecule has totally symmetric modes, such as the C-H stretching or a radial breathing mode in cyclohexane, the Raman intensity of light collected with the same polarization as the laser will be drastically different than the Raman intensity collected with a polarization 90° to the incident polarization. Totally symmetric modes will scatter the light, while retaining the polarization of the incident laser. Therefore, when collecting Raman scattered light at 90° to the incident polarization, the totally symmetric modes will be much lower in intensity than the non-totally symmetric modes.

\[
Depolarization Ratio = \frac{I_{\perp}}{I_{\|}} \quad \text{(Equation 2.4)}
\]

Non-totally symmetric modes will have a depolarization ratio equal to 0.75. Totally symmetric modes will have a depolarization ratio \(0 < \text{Depolarization Ratio} > 0.75\).

The Raman performed in our lab has all been micro-Raman spectroscopy. Figure 2-4 shows the standard diagram of a Raman spectrometer.
As stated beforehand, only roughly 1 in 1,000,000 incident photons are Raman scattered. Because of this spectrometers require a very tight notch or long pass filter or multiple spectrometers to reject nearly all the Rayleigh scattered light. After the rejection filter is the option to include an analyzer to perform polarized Raman. The light is then dispersed off of a grating and focused onto a CCD detector. Although Raman scattering happens equally in $360^\circ$, we are only able to collect light that is backscattered through our microscope objective. The amount of light collected a microscope objective is exponentially proportional to the numerical aperture of the objective used.

$$NA = n \sin \theta$$  \hspace{1cm} (Equation 2.5)

The problem that is run into when performing Raman spectroscopy in a diamond anvil cell is that a long working distance objective is required. Typical DACs require a working distance
of at least 1 inch. Under normal circumstances, NA and working distance are inversely proportional. Therefore ULWD objectives are required for in situ DAC work. Because of this, we are typically limited in both magnification ($20\times$) and NA (0.35). This limitation in NA not only affects the overall intensity of the signal, but it can also cause problems with confocality. If Raman bands of interest lie near the first order diamond mode they can easily be obscured or covered up by the diamond signal because much of the light being collected by the spectrometer is coming from light being scattered by the diamond. In order to avoid as much signal from the diamond as possible, we often place a confocal pinhole into the collection optics (figure 2-5). Since this pinhole is in the same focal plane as the sample, only light that is focused at the sample will be allowed to pass through the pinhole. This cuts down drastically on the amount of collected Raman scattering generated from the diamond anvils. Throughout this dissertation, both in situ and ex situ Raman spectroscopy will be central to the characterization of the materials.

![Confocal Pinhole Diagram](image)

**Figure 2-5:** The collection optics for a confocal Raman spectroscopy. The most important part is that the confocal pinhole is in the same focal plane as the sample. This allows for only light focused at the sample to be sent through the spectrometer adding very selective z-resolution.
2.1.2. Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is very similar to Raman spectroscopy in that they both measure the vibrational modes. However, they differ in three very specific ways: the light-matter interaction, instrumentation, and selection rules\textsuperscript{10}.

Light can interact with matter in any of three different ways (figure 2-6): absorption/transmission, reflection, or scattering. As discussed above, Raman spectroscopy relies on the process of inelastic scattering. In FT-IR sample absorption is relied upon to measure the vibrational spectrum. As was shown in figure 2-2 the difference in energy levels for molecular vibrations is very small and therefore a different light source is necessary than that employed in Raman scattering.

![Figure 2-6: Different photon-matter interactions are expressed. Transmission/absorption where a beam of light is attenuated as it passes through a sample (Does not change the energy). A beam can be reflected at the same angle that it is incident upon the surface with equal energy. A beam can be scattered equally in 360° and can either be of equal energy (Rayleigh scattering) or a different energy (inelastic scattering).](image)

Instead of a monochromatic visible laser which typically has an energy ranging from 1.6-5 eV, FT-IR relies on the broadband emission from a glowbar. This glowbar emits continuous radiation from approximately 2-50 micrometers. This energy range is well suited to measure molecular vibrations which typically have energies between 400 and 4000 wavenumbers, or 2.5-25 μm.
The selection rules for having an IR active mode are different from those of Raman scattering. In order for a vibrational mode to be IR active it must have a change in dipole moment with respect to the normal mode.

\[ I_{IR} = \frac{\partial \mu}{\partial N} \]  \hspace{1cm} (Equation 2.6)

\[ I_{Raman} = \frac{\partial \alpha}{\partial N} \]  \hspace{1cm} (Equation 2.7)

Where \( \mu \) is the dipole moment, \( \alpha \) is the polarizability, and \( N \) is the normal mode of vibration. Because Raman and FT-IR have different selection rules, they can be very complementary techniques. For instance, FT-IR is very sensitive to functional groups such as C-H and C-O but cannot observe C-C and C=C symmetric stretches whereas Raman spectroscopy is very sensitive to the homonuclear symmetric stretches and less sensitive to different functional groups.

It can be difficult to perform FT-IR in a DAC because the beam waist of the standard FT-IR beam is typically an order of magnitude larger than that of a standard sample within a DAC. Because of this a Bruker Hyperion 3000 FT-IR microscope\(^{11}\) was utilized to perform both in situ and ex situ FT-IR analyses.
Figure 2-7: Beam path of the FT-IR microscope used for the analyses in this dissertation. All measurements were made in transmission mode (orange path).

The beampath for the micro-FT-IR can be seen in figure 2-7. Due to a wide bandwidth of energy needed to perform FT-IR standard, refraction based lenses cannot be used to focus the IR beam into the sample within the DAC. This is because the refractive index of material changes with wavelength. Therefore if you were to try and focus a beam that contained wavelengths of 2.5, 5, and 10 μm through a singlet lens, they would focus at three different points (figure 2-8a). Additionally it is difficult to find a material that has a uniform transparency region for all the wavelengths of interest. Because of this, reflecting objectives are used as both condensing and collecting objectives. Since reflection is not dependent on the refractive index of the material and is not wavelength dependent, all the wavelengths of light within the polychromatic beam will be focused at the same point (figure 2-8b)

12. The reflecting objectives have a long working distance, 1 inch, which makes them suitable for in situ DAC work. FT-IR has been utilized throughout this dissertation to compliment the Raman scattering work.
2.2. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging technique where a high energy beam of electrons are transmitted through a very thin sample, typically less than 100 nm. The electrons are generated from either a heated filament tungsten or LaB$_6$, or a field emission gun and accelerated under vacuum through a column via a potential difference. A standard TEM column can be seen in figure 2-9. The electrons are focused throughout the column via a series of magnetic lenses. As they pass through the sample an image is created on either a phosphor plate or CCD camera. By using the de Broglie equation you can extract the wavelength of the electrons based on the accelerating voltage (equation 2.9) of the instrument. However, to get the true wavelength a relativistic correction needs to be taken into account (equation 2.10). By ignoring the relativistic correction the wavelength of the electron is overestimated, especially at higher accelerating voltages$^{13}$.

$$\lambda = \sqrt{\frac{h^2}{2meV}} = \frac{1.23 \text{ nm}}{\sqrt{V}} \quad \text{(Equation 2.9)}$$
\[ \lambda = \sqrt{\frac{h^2 c^2}{eV(2m_0 c^2 + eV)}} \]  

(Equation 2.10)

Because of the small wavelengths used for this technique, sub-angstrom spatial resolution is achievable with TEM. TEM has proven to be a powerful technique throughout this dissertation in gaining a deep understanding of the microstructure of carbon based and other inorganic materials.

Figure 2-9: Ray diagram of a standard transmission electron microscope. (a) Shows the top of the column form the emission source to the sample while (b) shows the collection optics from the specimen to the CCD.

2.2.1. Brightfield Imaging

Brightfield imaging is the standard technique utilized during the TEM analyses for this dissertation. Brightfield TEM is the direct imaging of the electrons that pass through the sample without filtering with respect to energy. The magnification available to in the standard brightfield TEM technique range from several $100 \times$ to $1.5$ million $\times$. Figure 2-10 exhibits several Brightfield optical micrographs of glassy carbon recovered from $50$ GPa
without a pressure transmitting medium, CaCO₃ impurities on a carbon sample, and silica nanoparticles dispersed onto a copper grid.

The contrast that is observed in Brightfield imaging is formed by absorption of electrons through the sample. This absorption can be formed most commonly by two reasons. The first is that there could be a Z-contrast between different parts of the sample. This would require the sample to the heterogeneous with respect to elemental makeup. Higher z-elements will appear darker than light elements. A second source of this contrast is from varying thickness within the sample. Thicker parts of the sample will appear darker than thinner parts, even if the sample is homogeneous in its elemental makeup.

2.2.2. Selected Area Electron Diffraction

In addition to performing simple imaging, the electron microscope can also perform diffraction experiments. If the electron beam is tightly focused onto the sample, the electrons will diffract as they pass through the sample. As is seen in standard x-ray diffraction, polycrystalline samples will exhibit well defined sharp rings about the central direct beam. A single crystal will exhibit discrete spots corresponding to the Bragg plane that is oriented
normal to the electron beam. Amorphous samples will consist of broad rings about the direct beam. Figure 2-11 contains electron diffraction images of an amorphous sample.

![Figure 2-11: Electron diffraction of an amorphous carbon. No discrete Bragg peaks are observed, only diffuse scattering.](image)

By utilizing the condenser systems present on the TEM, you can easily select very small areas of your sample on which to perform diffraction.

Through standard analysis techniques the patterns can be indexed much the same way x-ray diffraction patterns can. Throughout this dissertation SAED has been utilized only for sample and impurity identification.

2.2.3. Energy Filtered Transmission Electron Microscopy

When an electron passes through a sample it can inelastically scatter off of the electron clouds of the sample. Because of the high energy of the accelerated electron, it typically interacts with core electrons rather than valence electrons. With a spectrometer system the electrons of different energies can be filtered out and imaged.

The change in energy based on the core electrons is very element specific and can be used as a tool of elemental identification. If a CCD camera is mounted at the output of the
spectrometer it is possible to make an element specific image. Figure 2-12 is an EFTEM image of silica nanoparticles coated in silicon.

![Oxygen Map](image1.png) ![Silicon Map](image2.png)

**Figure 2-12**: EFTEM micrographs of silica nanoparticles coated in silicon via an HPCVD process.

You can see both the silicon map which is bright everywhere. When the spectrometer is set to measure the oxygen atoms though, only the silica nanoparticles are bright. This verifies that the nanoparticles are silica and they are surrounded by silicon. No silica exists beyond the edges of the nanoparticles.

### 2.2.4. Electron Energy Loss Spectroscopy

Similar to EFTEM, electron energy loss spectroscopy (EELS) is an element specific technique that relies on the fact that electrons can be inelastically scattered from the core electrons of the atoms within the sample.

More specifically than the EFTEM though, EELS can give information on the local bonding environment of carbon based materials. There are three peaks of interest within the EELS spectrum of carbon based materials. The first peak is at low energy and is not actually
element specific. The peak between 20 and 50 eV is called the plasmon peak and gives information of the overall electron density of the sample. If the sample thickness is known the plasmon peak position and intensity can be used to determine the density of the carbon sample. The second two peaks of interest are in the 280-300 eV energy loss range. This two peak system corresponds to the $\pi \rightarrow \pi^*$ and the $\sigma \rightarrow \sigma^*$ transition. Figure 2-13 shows the carbon K-edge region of the EELS spectrum of pristine glassy carbon and glassy carbon recovered from 50 GPa with and without pressure transmitting medium. When comparing samples this is a powerful technique to determine relative $sp^2$ to $sp^3$ content of your materials. However, with careful measurement of a 100% $sp^2$ standard quantitative $sp^2$ to $sp^3$ ratios can be garnered from the EELS spectrum of the carbon K edge. For the work done in this dissertation, qualitative measurements comparing the carbon K-edge were performed.

2.3. X-Ray Diffraction

X-ray diffraction (XRD) is a technique which can give the exact atom positions within a solid crystal. XRD can typically be divided into two categories, single crystal XRD
and powder-XRD (PXRD). X-ray scattering can also give information about the local bonding environment within disordered materials through the pair distribution function (PDF). The diffraction work performed in this dissertation will focus on PXRD and PDF analysis.

X-rays can interact with matter in any of three main ways. The most common way is through coherent scattering, wherein the incident beam has the same energy as the scattered beam. Coherent x-ray scattering, using the kinematic model where the beam is allowed to scatter only once before exiting the material, is what we consider when discussing x-ray diffraction. Two other ways that x-rays can interact with a material are incoherent scattering and absorption. In incoherent scattering the scattered beam has lost energy from interacting with the electron cloud of the material. This can be taken advantage of to perform x-ray spectroscopy as is described in both sections 2.3.3 and in chapter 4. Due to their high energy, x-rays are typically absorbed by core electrons within a material. The resulting fluorescence can be used for elemental identification.

![Figure 2-14: Nanometer resolution X-ray fluorescence map of an indium-gallium nanowire at 270 K. Discrete phase separation into pure gallium droplets, roughly 100 nm in diameter are observed (circles) within the In-Ga alloy.](image)

Figure 2-14 shows a high resolution x-ray fluorescence map of 150 nm Ga-In nanowire cooled to 250 K measured at Sector 26 of the Advanced Photon Source at Argonne National...
Laboratory. The map clearly shows regions where gallium is highly concentrated within the wire. Most of the work performed in this dissertation deals with coherent x-ray scattering.

When an x-ray diffracts off of a 1-D array of electrons that are spaced periodically the resultant wave is a discontinuous function with maxima that correspond to where constructive interference occurs. In between the maxima there exist small ripples from where the interference waves do not completely wash each other out. In standard PXRD these ripples may not exist because as the number of points (atoms) increase towards infinity the diffraction lines become very narrow delta functions. These ripples or diffuse scattering become important when dealing with complex disordered materials or nanomaterials. The position of the diffraction lines are governed by the periodicity of the spaced electrons and related by the phase angle, \( \varphi \).

\[
\varphi = 4\pi \frac{a \sin^2 \theta}{\lambda} \quad \text{(Equation 2.11)}
\]

When moving from individual electrons to clusters of electrons like those found in atoms there becomes a drastic importance to the intensity of the diffracted beam with respect to the angle that it is diffracted. This is because the scattered wavefront differs in phase angle because it can scatter from electrons located in different energy levels and therefore different positions. This results in a Gaussian decay in the intensity of the scattered beam with increasing angle. This is known as the atomic scattering factor, \( f \), and can be observed in figure 2-15. Since x-rays are scattered by the electron cloud of atoms the intensity of a diffracted beam is proportional to the number electrons present in the material. Therefore,
heavy elements since as metals are going to scatter x-rays much better than a light element like carbon, this also renders hydrogen nearly invisible to x-rays.

Moving from a 1-D lattice of electrons to a 3-D lattice of atoms we must take into account not only the discontinuous scattering function from the phase angle but also the intensity decay that comes from the atomic scattering factor. The atomic scattering factor must also be modified if we are to have more than one atom in the unit cell. To average over the entire unit cell we should use the structure factor F. Since we wish to observe diffraction planes within a lattice it is easier to think in terms of (hkl) as opposed to phase angle. Therefore the intensity of a diffracted beam is can be found in equation 2.12.

$$I(hkl) \propto F^2(hkl) \frac{\sin^2 \theta_1 \sin \theta_2 \sin \theta_3}{\sin^2 \sin \theta_2 \sin \theta_3}$$

(Equation 2.12)

This discontinuous intensity equation is only non-zero at specific hkl points. These hkl points are referred to as Miller planes. These are crystallographic planes of atoms within a crystal related by a repeating symmetry. The Miller planes can be thought of as a series of
mirrors that will diffract only at a set \( \theta \) for a given wavelength depending on their spacing, \( d \). This can be explained by Bragg’s law:

\[
n\lambda = 2d \sin \theta \quad \text{(Equation 2.13)}
\]

By using the peak intensities and peak positions for a given diffraction pattern the atomic positions can be determined for a given crystal. However, in this dissertation perfect crystals cannot always be obtained. Bragg’s law and the PXRD breaks down when disorder in introduced to the system or if the crystal size is reduced to the nanoscale. To overcome this obstacle, a PDF analysis was used to determine local bonding environments.

When performing a PDF analysis we will treat both the Bragg peaks and the diffuse scattering equally. To do this effectively it requires that we are able to scan a wide range of Q space. Figure 2-16 shows a schematic of how to interpret Q space and equation 2.14 relates the momentum transfer vector, Q, to Bragg’s law.

\[
Q = \frac{4\pi \sin \theta}{\lambda} \quad \text{Equation 2.14}
\]

With X-rays the main way to cover a large enough section of Q space to generate a high quality PDF is to use large 2-D area detectors and high energy x-rays (80-115 keV) that are only available at advanced synchrotron sources. Section 2.3.2 will explain two such beamlines where experiments were performed. The results of these experiments can be found in chapter 5.
When performing a total scattering experiment one needs to generate the total scattering structure function which is a normalized scattering intensity from the sample. To get this normalized intensity the structure factor as well as any background scattering must be taken into account.

![Diagram of momentum transfer vector](image)

**Figure 2-16**: Q, the momentum transfer vector is the resultant vector between the direct transmitted beam and the diffracted beam. It can easily be related the angle of diffraction by equation 2.14. It is important to use Q with synchrotron x-ray diffraction because the wavelength can be tuned easily and therefore the 2θ for the same Bragg plane at different incident beam wavelengths will differ making it difficult to compare experiments.

This can result in a highly noisy spectrum at high Q. As stated earlier, the atomic form factor for x-rays drops off as a Gaussian function as you go to higher Q. Therefore during normalization, the counts are typically small at the highest values of Q, along with a small form factor. Therefore when the normalization occurs, \( \frac{1}{f} \), it results in dividing by a very small number. At high Q the value of S(Q) will approach unity. Since the total scattering structure function exists in reciprocal space and the PDF is a real space atom-atom pairwise correlation, the two terms are related by a Fourier-Transform. The PDF, G(r), can be found in equations 2.15 and 2.16.
\[ G(r) = \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} F(Q) \sin(qr) \, dQ \]  \hspace{1cm} \text{(Equation 2.15)}

\[ G(r) = 4\pi r [\rho(r) - \rho_0] \]  \hspace{1cm} \text{(Equation 2.16)}

F(Q) is equal to Q[S(Q)-1]. It can be seen from equations 2.15 and 2.16 that the number density of the sample is important in generating a quantitative PDF. Additionally since the integral in equation 2.15 does not cover all space but is limited by experimental design, the resolution of the PDF is finite and determined by the value of \( \frac{2\pi}{Q_{\text{max}}} \). Additionally, the chosen cutoff in the S(Q) of where to perform the FT is very important. The cutoff should be chosen at a point where the S(Q) is equal to unity. If it is not then the resulting PDF will have ripples around each peak due to performing a FT on a partial top-hat function\(^{20}\).

When the experiment is planned and performed properly with adequate background subtractions and normalization, along with a signal to a high \( Q_{\text{max}} \), the PDF analysis can be a very powerful technique in determining the local atomic structure for amorphous solids, liquids, and nanomaterials. The PDFgetX2 program was used to convert from the S(Q) to G(r)\(^{21}\).

2.3.1. High Resolution Angle Dispersive X-Ray Diffraction at 16-ID-B Beamline at the Advanced Photon Source

Sector 16 of the Advanced Photon Source at Argonne National Laboratory is dedicated to research performed at high pressure and therefore specially equipped to deal with DACs. Beamline 16-ID-B in particular is specially designed to perform very high resolution PXRD studies within DACs of low Z materials. More information on the HPCAT beamline can be found in the following reference\(^{22}\).
The reason that 16-ID-B is well suited for performing high resolution PXRD of low Z elements within a DAC is due to its construction. Since the beamline was built specifically for DACs the motion control for DAC alignment has been optimized. The x-ray energy can be tuned from 26-37 keV with a maximum flux of $5 \times 10^{10}$ photons per second at the sample. The x-ray energy is high enough that there is minimal absorption or attenuation of the beam as it passes through the diamond anvils, but low enough as to not cause detrimental Compton scattering. With the use of Kilpatrick-Baez (KB) mirrors the x-ray beam can be focused to a $5 \times 5 \, \mu m$ spot size. This spot size is much smaller than the typical gasket hole used in our experiments, therefore parasitic signal from coherent scattering of the typically heavy metal (Rhenium or Tungsten) gasket can easily be avoided.

A large 2-D area detector was used for all the experiments. The MAR 345 CCD detector is a circular detector with a $100 \times 100 \, \mu m$ pixel size. The detector can be moved as to maximize the resolution needed. Data is processed using established software, Fit2D, which integrates the 2-D CCD image to a 1-D diffraction pattern.

Data collected on 16-ID-B will be presented in Chapters 3, 4, and 5.

2.3.2. High Energy Angle Dispersive X-Ray Diffraction at 11-ID-C and 6-ID-D Beamlines at the Advanced Photon Source

High energy angle dispersive X-ray diffraction was performed both within a newly developed large volume DAC (LVDAC) on beamline 6-ID-D and on samples recovered from the LVDAC$^{23}$ (6-ID-D) and the Paris-Edinburgh cell (11-ID-C and 6-ID-D) with the goal of obtaining high resolution pair distribution functions. Additional information about performing high energy x-ray diffraction at the Advanced Photon Source can be found here$^{24}$.

These beamlines have been constructed to perform total scattering experiments out to high momentum transfer vector, $Q_{\text{max}}$. They have energies that range from 70-130 keV on 6-
ID-D and a set energy of 111 keV on 111-ID-C. Both beamlines utilize a large 2-D Perkin-Elmer CCD area detector in order to maximize their coverage in Q. The detector is placed very close to the sample in order to reach the highest $Q_{\text{max}}$. However because of the high energy, resolution is much lower on these measurements than those performed at 16-ID-B. A second drawback, specifically when performing in situ studies is that because the beam has such high energy, it cannot be focused. This means we have a beam size that ranges from $\sim 300 \mu\text{m} \times 300\mu\text{m}$ to $1 \text{ mm} \times 1 \text{ mm}$. Another drawback that is found with the high energy beamlines is that because Compton scattering scales with x-ray energy, at these very high energies both air scattering and Compton scattering from the DAC cause major problems in background subtraction. Very careful background measurements must be taken in order to generate a reliable total scattering structure function and subsequent PDF.

The in situ study was performed at 6-ID-D and will be described in detail in Chapter 5. The ex situ measurements performed at 11-ID-C will also be described in Chapter 5.

### 2.3.3. Inelastic X-Ray Scattering at 16-ID-D Beamline at the Advanced Photon Source

Like 16-ID-B, 16-ID-D is a beamline specifically set up for high pressure DAC experiments. For these experiments a panoramic DAC is required with a special type of gasket. This experimental set up will be described in detail in Chapter 4. Inelastic x-ray scattering gives much the same information as EELS performed within the TEM, however this has the advantage of being done in situ.

A diagram of the 16-ID-D beamline can be seen in figure 2-17. This spectroscopic technique has an x-ray beam pass through the carbon sample. Some photons are scattered by the electron cloud and lose energy corresponding to the carbon K-edge, roughly 285 eV. The photons are dispersed on a Si (111) analyzer and then sent to the detector. The instrument has
a resolution of about 0.1 eV. As was discussed with EELS the information gathered from this data will allow for a determination of the sp\(^2\) to sp\(^3\) ratio and how that changes within a carbon sample with the application of pressure.

Figure 2-17: A) Is a schematic of the 16-ID-D beam path from the storage ring through the sample to the detector. B) is an optical image showing how the beam goes through the gasket of the panoramic DAC and then there are small slits to block out any parasitic scattering from the beam which may have leaked into the diamond anvils. Due to the small nature of our sample and the needed high resolution a single channel Si (555) analyzer was used instead of the array of analyzers. (Courtesy of Dr. Paul Chow, HPCAT)

2.4. Neutron Diffraction

Neutron diffraction is very similar to x-ray diffraction in the sense that the physics of diffraction are the same. Neutrons still follow Bragg’s law and can be used to determine the crystal structure of materials. There are however three two major differences with neutron diffraction and x-ray diffraction. First, in these experiments the neutrons used are polychromatic. The neutrons are generated by a spallation source where a series of linearly accelerated alpha particles bombard a metallic mercury target. Upon bombardment the mercury target expels neutrons to a series of instruments within the target building. The
wavelength of the neutrons are determined by Equation 2.17 and they follow a standard Maxwell speed distribution. Because of this several calibrations are needed including both a Q space calibration and a time of flight, ToF, calibration. The second major difference between neutron diffraction and x-ray diffraction is the scattering mechanism of the particle. Neutrons have no charge and are therefore not scattered by the electron cloud of an atom. The neutron is scattered by the nuclear strong force present inside the atom’s nucleus. This has a twofold effect. First this makes the atomic scattering cross section for each atom very different from their x-ray atomic form factor. In fact the scattering of neutrons from a hydrogen atom is roughly equal to that observed from a carbon atom. Therefore neutrons can be used to observe the hydrogen atoms that are nearly invisible to x-ray radiation. A second effect that being scattered by the highly localized nucleus rather than the multiple energy levels of the electron cloud is that there is no fall off observed with Q of the atomic form factor in neutron diffraction. This typically allows for a higher signal to noise ratio of the total scattering structure function out to higher $Q_{\text{max}}$.

Sections 2.4.1 and 2.4.2 will describe two different instruments used to measure neutron diffraction at the Spallation Neutron Source at Oak Ridge Nation Laboratory. The data collected from these measurements will be presented in Chapter 5.


The SNAP instrument located within the Spallation Neutron Source at Oak Ridge National Laboratory is set up to perform neutron diffraction experiments at very high pressures. The beamline is set up to hold and manipulate large Paris-Edinburgh cells when they are equipped with a hydraulic oil pump. These cells can reach pressures up to 25
GPa when configured with double toroid sintered diamond anvils. A deeper discussion of the PE cell was given in Chapter 1. One of the most important aspects of performing diffraction at pressure is the use of a TiZr gasket. The TiZr gasket provides zero background because titanium and zirconium both scatter neutrons with the same cross section, but cause them to be scattered 180° out of phase from each other. This results in total destructive interference and results in no signal.

The beamline configuration can be seen in figure 2-18. The neutron beam must be highly collimated to parasitic scattering.

To achieve this hexagonal BN is machined to collimate the beam from the entrance slit to the sample. “Hot neutrons”, those having a higher energy than can be absorbed by the slits must also be minimized to avoid parasitic diffraction or background scattering from air. In order to do this, bags of paraffin wax are stacked around the slits and in the line of site of each of the
two detectors. The SNAP instrument has two detector bays which can be moved to collect both high angle and low angle diffraction. Diffraction experiments performed at SNAP will be discussed in Chapter 5.

2.4.2. Time-of-Flight Energy Dispersive Neutron Diffraction on the Nanoscale Ordered MAterials Diffractometer (NOMAD) Instrument at the Spallation Neutron Source

As stated earlier the lack of a drop of in atomic form factor with Q makes neutron diffraction possible to very high Q values. The NOMAD instrument at the SNS is used to perform total scattering experiments because of its massive detector coverage, and therefore its ability to measure to very high $Q_{\text{max}}$. More information on the NOMAD instrument can be found in the following reference\textsuperscript{27}.

The experiments preformed at NOMAD have much less need for shielding to limit air scatter because the entire beampath from the entrance slits, past the sample, and into the detector bay are under vacuum. The sample is placed within a thin walled silica capillary and an empty capillary is used as a background measurement. Simple background subtractions from secondary scattering and incoherent scattering are taken into account based on previously measured standards such as a polycrystalline nickel pellet (for ToF calibration), vanadium rod (for incoherent/instrument scattering), and single crystal diamond (for Q space calibration). The results obtained from experiments performed on NOMAD are presented in chapter 5.
REFERENCES

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3 High Pressure Stability and Reactivity of Polycyclic Aromatic Hydrocarbons

3.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been under investigation for decades due to their chemical and physical properties\textsuperscript{1-5}. Due to their electronic and crystallographic orientations they have been investigated a lot for potential applications in molecular electronics and liquid crystals\textsuperscript{6}. PAHs are small molecules composed of fused carbon ring systems. They can be either \textit{cata}-condensed where all carbon atoms are edge atoms, or they can be \textit{peri}-condensed where there are carbon atoms that are on the interior of the molecule. Figure 3-1 shows many PAH molecules that will be investigated throughout this chapter. In this chapter the high pressure reactivity of these molecules will be investigated with regards to crystalline graphite.

![PAH molecules]

Figure 3-1: The Clar structures for each PAH studied in this chapter. The aromatic sextet is denoted as a circle within one ring.
3.1.1. Cold Compressed Graphite Transition

As discussed in chapter 1 the transition from graphite to diamond appears to be a simple process based on the thermodynamic phase diagram. However, as stated before, there exists a massive kinetic barrier between the two crystalline phases of carbon wherein the direct transformation of graphite to diamond occurs at roughly 13 GPa and 2000 K. This does not mean that graphite persists at all areas of the phase space though. In the carbon system there exists a metastable phase of carbon that has attracted a great deal of attention for over half a century.

Cold compressed graphite was first discovered in 1962 by Drickamer while studying the change in electrical resistance in highly crystalline graphite. It was then studied by the synthetic diamond pioneer, Francis Bundy and General Electric. This metastable carbon phase, initially attributed to hexagonal diamond, has been classified by the name cold compressed graphite. The high pressure phase is formed when graphite is compressed to between 12 and 18 GPa at room temperature depending on the crystallinity of the starting material. At this point the graphite flake will appear transparent under diascopic illumination if thin enough (Figure 3-2).

![Figure 3-2: Transmitted light optical micrographs of cold compressed graphite. The graphite can clearly be seen as transparent, but the sample is not recoverable to ambient conditions. Taken from Reference 7](image-url)
As shown by Drickamer and other researchers this transparency is accompanied by a drastic increase in the electrical resistance along the a-axis of graphite$^{14-16}$. At ambient pressure graphite has an electrical conductivity similar to that of a metal along its a and b axes$^{17,18}$, but as the crystal undergoes the transition to cold compressed graphite, the electrical resistance increases several orders of magnitude. As the pressure is released back to ambient conditions the cold compressed graphite reverts back to the original graphite with minimal defects, resulting in a slightly smaller grain size. Reports have stated that the cold compressed graphite phase can be quenched to ambient pressure if the temperature is lowered to 77 K$^{13}$. However, upon warming the quenched phase back to room temperature the cold compressed graphite reverts to the original crystal.

Many studies have been performed on cold compressed graphite in an attempt to elicit the structure of the high pressure phase. In addition to the experimental reports on cold compressed graphite, many theoretical papers, proposing different structures, have been published over the years on the subject$^{19-22}$. The fact that the high pressure phase is transparent indicates that there is substantial sp$^3$ bonding present thus opening the optical gap. This hypothesis has been confirmed via in situ inelastic x-ray scattering experiments. Mao et.al. found that at high pressure the $\pi\rightarrow\pi^*$ transition nearly disappeared indicating a massive decrease in the amount of sp$^2$ carbon present$^{23}$. Additionally, Raman spectroscopy of the quenched product indicates a highly disordered carbon, still with sp$^2$ content. Recent powder x-ray diffraction results indicate that the cold compressed graphite phase can be indexed well to the m-Carbon phase$^{24}$ initially proposed by Li et.al.$^{22}$ This m-Carbon phase does not contain any sp$^2$ carbon though, which does not agree with the previous spectroscopic techniques. The latest diffraction study that indexes well to the m-Carbon
structure explains the very sluggish reaction. The structure of cold compressed graphite is still a hotly debated issue\textsuperscript{25}.

As a chemist I was mainly interested not in the structure of cold compressed graphite but with the fact that the activation energy for going from a highly sp\textsuperscript{3} hybridized carbon material to a totally sp\textsuperscript{2} hybridized carbon material was very small. As was seen in the experiment where the cold compressed carbon system was quenched at low temperature, strong carbon-carbon bonds were broken and formed with a change in temperature of only about 200 K. I chose to address this issue from the small molecule perspective and treated graphite as an infinitely large PAH. The rest of the chapter explores why small molecules like PAHs react irreversibly to form amorphous hydrogenated carbons whereas graphite can react reversibly. The end of this chapter along with chapter 6 will leave a hypothesis for a set of small molecules that could be used to gain a deeper understanding of the cold compressed graphite system.

3.1.2. Irreversible Reaction of Small PAHs to Amorphous Hydrogenated Carbon Networks

Small aromatic molecules have been investigated under high pressures for over a century\textsuperscript{26,27}. However, it has only been over the past 50 years that reactions of these molecules have really been investigated thoroughly\textsuperscript{28-34}. It is interesting to look at the reactivity of PAHs from the simple perspective of E. Clar’s aromatic sextet theory. Clar’s aromatic sextet is a graph theory based way of looking at the global aromaticity of PAHs that are composed of fused six-membered rings\textsuperscript{4}. Recent high power computational techniques based on valence bond theory and molecular orbital theory along with graph theory studies such as molecular electrostatic potential topography\textsuperscript{35} and electron density topography
mapping have all shown that Clar’s sextet rule is a very good estimation of a PAH’s global aromaticity and therefore stability.

Clar’s aromatic sextet is defined as a ring having six pi-electrons localized within it and is denoted by a circle. Figure 3-1 shows the Clar structures for many PAHs. The theory states that an aromatic sextet can be diluted down and therefore lose its stability, therefore, according to this theory the stability of a PAH increases by maximizing the number of sextets. It is this idea that only rings that contain a sextet of pi-electrons will be highly stabilized that leads to the differences in reactivity, electronic, and optical properties of many PAH systems.

This chapter will explain reactivity trends in PAHs observed during the room temperature compression of different molecules in a DAC. The reactions were monitored in situ via visible Raman spectroscopy and in some cases angle dispersive XRD. In the case of the acenes the recovered amorphous hydrogenated carbon products were subject to a series of analytical techniques including TEM (with SAED and EELS), FTIR, and multiwavelength Raman spectroscopy. A primer on multiwavelength Raman spectroscopy is also included in this chapter as it is a very powerful analytical tool for analyzing the microstructure of amorphous hydrogenated carbon. The results presented here concerning the acene work have been written into a manuscript awaiting submission while the work on 2-D PAHs is ongoing.

3.2. Irreversible Reaction of Acenes to a-C:H network

Acenes are a class of linearly fused cata-condensed PAHs. Naphthalene is the simplest acene as it is two benzene rings fused together by a single edge. Anthracene is the next member of the acene family containing three rings. As the ring count expands it contains
the molecules of tetracene, pentacene, hexacene, etc… Clar’s aromatic sextet rule fits very well when considering the stability of the acenes. As the number of rings increase the molecules become more and more unstable. This is due to the dilution of the aromatic sextet across all the rings. In an acene molecules there can be only one aromatic sextet \(^{2,3,35,37-39}\). As the ring count increases this aromatic sextet is diluted and by the time you reach the size of pentacene, the molecules begin to react with air at room temperature. Acenes can also readily act as dienes in Diels-Alder cycloadditions when treated with a strong dienophile\(^{40}\). The low aromatic stabilization present in the acenes gives them an almost olefinic character and reactivity.

In addition to the increase in reactivity, the optical properties of the acene molecules change dramatically with increasing length. This can be thought of in terms of the traditional particle in a box. As the acene length, or conjugation length, is increased the box will increase in length as well, lowering the energy between the HOMO and LUMO of the molecule. This decreasing in initial HOMO-LUMO gap with increasing acene length will become important in terms of thinking about the high pressure stability and reactivity of these molecules.

It has been shown previously that pentacene’s conductivity will increase as pressure is applied and at low temperature will become metallic in nature. At ambient pressure pentacene is shown to irreversibly react to form a semiconducting product. This is a direct result of pressure closing the HOMO-LUMO gap of the already small band gap pentacene molecule. Figure 3-3 shows a similar phenomenon occurs with naphthalene in that as pressure in increased on the molecule it begins to absorb more and more visible light finally resulting in an irreversible reaction.
As pressure is applied to the originally transparent naphthalene crystals, the color of the sample changes to a deep red at high pressure, indicating a decrease in the HOMO-LUMO gap. A similar effect is observed for anthracene. Since pentacene starts with such a small optical gap, it is opaque at room temperature, however, as stated before, previous electrical measurements concur a similar effect.

3.2.1. High Pressure Stability and Reactivity

The high pressure stability and reactivity of several acene molecules has been investigated within a DAC at room temperature$^{41,42}$. It was found that each of these molecules react irreversibly at room temperature to form an extended amorphous
hydrogenated carbon product. They react through a series of runaway polymerization reactions based on their starting structure. Polymerization reactions are highly promoted both kinetically and thermodynamically at high pressure due to their large negative activation volumes. Multiwavelength Raman spectroscopy has been used to analyze the final products as to their microstructure. TEM was utilized to determine the crystallinity of the recovered products. FT-IR was used to roughly determine the hydrogen content and sp²/sp³ ratio.

Table 3.1: Reaction threshold pressure for several acene molecules as determined via in situ Raman spectroscopy

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Reaction Threshold Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>50 GPa</td>
</tr>
<tr>
<td>Anthracene</td>
<td>32 GPa</td>
</tr>
<tr>
<td>Pentacene</td>
<td>18 GPa</td>
</tr>
</tbody>
</table>

As per Clar’s sextet rule, it was found that pentacene was the least stable acene studied due to the dilution of its single aromatic sextet over five linearly fused rings. The reactivity observed in pentacene was consistent with previous work on the molecule. Neither anthracene nor naphthalene had been studied to pressures where room temperature polymerization occurs. Naphthalene was determined to be the most stable molecule, not reacting until over 50 GPa of static pressure. Table 3.1 shows the reaction pressure threshold for each of the starting acene molecules.

The reaction was monitored in situ via visible Raman spectroscopy. Figure 3-4 shows Raman spectra collected at 514 nm excitation for naphthalene within a DAC. Raman spectra were collected over a wide range of wavenumber shifts including the region that corresponds to the C-C modes associated with aromatic bonding.
Two strong $a_g$ modes near 1577 cm$^{-1}$ and 1382 cm$^{-1}$ are present among several others in the ambient pressure Raman spectrum of naphthalene. Another peak near 1504 cm$^{-1}$ grows in intensity as the pressure is increased above 5.8 GPa, suggesting that there is a transition to a different crystal packing. The transition is not associated with irreversible reaction, as the Raman spectrum reverts to that of naphthalene until a pressure of 50 GPa is reached. These modes all broaden and shift to high wavenumbers upon compression. This shift to higher wavenumber is expected due to a shortening of the bond. By shortening the bond the force constant associated with the bond is increased and subsequently the vibrational mode shifts to higher wavenumber as per Equation 3.1.
\[ \nu = \frac{\sqrt{k}}{\sqrt{\mu}} \]  

(Equation 3.1)

Where \( \nu \) is the frequency of the vibration, \( k \) is the force constant from Hooke’s law, and \( \mu \) is the reduced mass of the atoms involved in the vibration.

It can be seen that as pressure is increased in the sample, there is a massive increase in the background signal. This background is due to fluorescence of the sample. Fluorescence is a major problem in Raman spectroscopy due to the fact that the quantum efficiency of fluorescence typically measures in the tens of percent on the incident beam whereas only about one in one million incident photons are Raman scattered. The fluorescence associated with the sample here is not necessarily that of the direct HOMO-LUMO transition in naphthalene, but are more likely associated with excimer formation in the crystal structure. Excimer formation is common when studying \( \pi \)-conjugated organic molecules at high pressure because of their propensity to \( \pi-\pi \) at defect sites caused by inhomogeneous stress on the sample\textsuperscript{29,30}. The excimer signal red shifts upon compression, much like the vibrational modes. This is because not only are we pushing the atoms closer together, but we are also compressing the electronic wavefunctions. At the highest pressures observed in the Raman, the peak of the excimer fluorescence blocks any collection of usable Raman signal. Because of this an exact conversion pressure for the naphthalene to amorphous carbon transition could not be determined. However, it was observed that if the pressure was released below 50 GPa the recovered sample would retain the Raman spectrum of molecular naphthalene. If the pressure was released after reaching a maximum pressure of over 50 GPa, the recovered product would retain a high photoluminescence (PL) background when excited with a 514 nm laser. This high PL background with visible excitation wavelengths is consistent with an
amorphous hydrogenated carbon material with a high (almost 50 at%) hydrogen content. Sections 3.2.2. and 3.2.3. discuss the characterization techniques used to determine the microstructure of the recovered polymerized naphthalene product.

Visible Raman spectroscopy was also performed on anthracene and pentacene within a DAC. The excimer fluorescence of anthracene was very intense in the region of interest at very low pressures. As pressure was increased above 15 GPa the excimer fluorescence red shifted enough to be past where Raman measurements were performed and therefore the Raman of anthracene could be obtained above these pressures. Excimer fluorescence was not a problem with the pentacene sample because the low HOMO-LUMO gap of both pentacene and its subsequent excimer were at low enough energy to be beyond the region of interest in the visible Raman spectra. Figure 3-5 shows the in situ visible Raman spectra of anthracene and pentacene.

![Figure 3-13: A) in situ Raman of anthracene. b) in situ Raman of pentacene. At the highest pressures it is evident that the molecular signatures disappear and are replaced by a broad amorphous signature.](image-url)
As with the naphthalene sample the Raman modes red shift and broaden with increasing pressure. The peaks broadened due to a decreased lifetime of the imaginary state created upon Raman excitation. Equations 3.2-3.4 show how collisional deactivation increases the lifetime broadening of the Raman spectra observed at high pressure\(^{45}\).

\[
\delta E = \frac{\hbar}{\tau} \quad \text{(Equation 3.2)}
\]

\[
\delta E_{col} = \frac{\hbar}{\tau_{col}} \quad \text{(Equation 3.3)}
\]

\[
\tau_{col} = \frac{1}{z} \quad \text{(Equation 3.4)}
\]

Where \(\delta E\) is the line width of peak of interest and \(\tau\) is the lifetime of the created excited (imaginary) state. At high pressure there is a higher probability of collisions which leads to a larger \(z\) in equation 3.4. This results in a very small \(\tau_{col}\) which results in a larger energy distribution of the peak.

As the pressure reached 32 GPa in the anthracene sample and 18 GPa in the pentacene sample the Raman modes characteristic of the original small molecules go away. They are replaced by a single broad peak located between 1600 and 1700 cm\(^{-1}\). This peak corresponds to the “G peak” characteristic of amorphous hydrogenated carbon. Again, similar to the naphthalene, if the samples were decompressed before they reached the point of reaction, the Raman spectra of the recovered products would be the same as those of the original acene molecules. Sections 3.2.2. and 3.2.3. will discuss the characterization of the
recovered amorphous hydrogenated carbon materials via a series of techniques including TEM, FT-IR, and multiwavelength Raman spectroscopy.

### 3.2.2. TEM and FT-IR Analysis

TEM as well as SAED were performed on the samples recovered from high pressure to determine crystallinity. EELS was also performed in an attempt to extract a relative sp²/sp³ ratio from the three materials. Optical micrographs were also collected of the recovered products with diascopic illumination in an attempt to relate the sp²/sp³ ratio to the colors observed for each material. FT-IR was performed to analyze the C-H stretching region of the recovered amorphous hydrogenated carbons. This could give a qualitative view of the sp²/sp³ ratio of the final amorphous carbon products.

Figure 3-6 shows the TEM and optical micrographs of the products recovered from the polymerization of the acenes.

![Image of TEM and optical micrographs](image)

**Figure 3-14:** a) The starting acene molecules. b) Transmitted light optical micrographs of the recovered polymerized acenes. Scale bar = 50 μm. c) Bright field TEM micrographs with SAED patterns of the recovered acenes indicating the amorphous nature of the recovered product. Scale bar = 50 nm

The inset in the TEM micrographs is a SAED pattern. The diffuse rings in the SAED pattern confirm that the recovered product is in fact amorphous. The few faint spots in some of the
patterns correspond to a small amount of ruby powder which was used to monitor the pressure in situ. The Brightfield TEM micrographs do not show any characteristic features of crystalline order and are therefore determined to be amorphous. EELS was performed on each of the three samples using the FE-TEM discussed in Chapter 2. Figure 3-7 shows the EELS spectrum of both the first plasmon peak and the carbon K-edge region.

Figure 3-7: EELS spectra of the recovered amorphous hydrogenated carbons. a) shows the plasmon peak which indicates an amorphous carbon. b) shows the carbon K-edge which is used to determine sp²/sp³ ratio.

The first plasmon peak is in the region consistent with amorphous carbons with mixed sp² and sp³ carbon, it is lower than that of diamond but higher than graphite. The carbon K-edge region can be used to determine the sp²/sp³ ratio of an amorphous carbon. Because there was an absence of a 100% sp² hybridize standard on our TEM and because of differences in sample thickness it was not possible to perform a quantitative study on the sp²/sp³ ratio. However, we were able to compare the sp² content between samples based on the relative
peak intensities of the $\pi \rightarrow \pi^*$ transition at 284 eV and the $\sigma \rightarrow \sigma^*$ transition at ~295 eV. As the $\pi \rightarrow \pi^*$ transition decreases the sp$^2$ content decreases$^{48}$. It can be seen from our analysis that the polymerized pentacene has the most sp$^2$ carbon. The EELS analysis seems to indicate that there is roughly equal sp$^2$ carbon in both the polymerized naphthalene and polymerized anthracene samples. This could be explained because it is well established that amorphous carbons with high sp$^3$ carbon content and high hydrogen content are very susceptible to beam damage in the TEM. During the TEM session if the EELS probe was left on the polymerized naphthalene sample for an extended period of time, a visible hole was observed in the sample. The area around this hole was observed to be graphitic with the classic 3.4 Å lattice spacing. Beam damage in the TEM will play an important role later in the dissertation in Chapter 5. Because of this beam damage the EELS data collected for the polymerized naphthalene sample may not be accurate.

The optical micrographs observed indicate that the HOMO-LUMO gap decreases from the polymerized naphthalene to the polymerized anthracene to the lowest gap of the polymerized anthracene. This would indicate that the polymerized naphthalene has the most sp$^3$ carbon whereas the polymerized pentacene has the most sp$^2$ carbon, with the polymerized anthracene having an intermediate sp$^2$/sp$^3$ ratio. This conclusion was reached based on simple MO theory. The gap between the $\sigma \rightarrow \sigma^*$ state is much larger than that of the $\pi \rightarrow \pi^*$ transition. The band gap of an amorphous hydrogenated carbon can be thought of as a mix of high lying $\sigma \rightarrow \sigma^*$ states and low lying $\pi \rightarrow \pi^*$ states where the higher sp2 bonding leads to a smaller band gap. As can be seen in figure 3-6b the polymerized naphthalene has the widest optical gap because it appears orange under diascopic illumination. The polymerized anthracene has a deep red color indicating that it is only transparent to wavelengths at the far
edge of the visible spectrum and into the infrared. The polymerized pentacene sample was opaque to visible radiation. A 750 nm long pass filter was placed in the collection optics so that only near-IR radiation was collected from the bulb. The polymerized pentacene is transparent to radiation in the NIR region of the electromagnetic spectrum. Through this analysis it was determined that the polymerized pentacene had the lowest HOMO-LUMO gap where the polymerized naphthalene had the largest gap.

FT-IR was used to analyze the C-H stretching region of the recovered products. FT-IR is a better technique to look at the C-H modes in the recovered samples because it is more sensitive to the mode of interest and there are no 2\textsuperscript{nd} order Raman bands to interfere with the C-H signal. Figure 3-8 shows the FT-IR spectra of both the starting molecules and recovered amorphous hydrogenated carbon products.

![Figure 3-8: FT-IR of both starting molecule and the final amorphous hydrogenated carbon products. The main difference between the starting and final products are that the final products have a drastic increase in sp$^3$ C-H stretching mode.](image)

The infrared spectra of the polymerized samples at ambient pressure are very different from that of the acene molecules. Absorptions in the region below $\sim 2000$ cm$^{-1}$ are broadened for polymerized naphthalene and anthracene, as might be expected for a
disordered polymer. The absorptions for polymerized pentacene are not broadened as much, suggesting that this material may not be as disordered. New absorptions characteristic of hydrogen bound to sp\(^3\) carbon arise around 2960 cm\(^{-1}\) upon polymerization of all three molecules. The spectra in the C-H stretching region could be fit with multiple peaks, with each individual peak position matching positions previously reported for hydrogenated amorphous carbon\(^{49}\). Each of them could be assigned to hydrogen bound to sp\(^2\) or sp\(^3\) carbon. The sums of the relative integrated intensities of these two groups of peaks can be used to quantitate the proportions of hydrogen bound to the two types of carbon. After integration, the percentage of hydrogen bound to sp\(^3\) sites in each compound was determined to be 70.86\%, 69.33\%, and 35.48\% for polymerized naphthalene, anthracene, and pentacene respectively. This cannot be taken as the exact sp\(^2\)/sp\(^3\) ratio because the FT-IR is probing only carbons bound to hydrogens, not all carbons.

3.2.3. Multiwavelength Raman Analysis

Multiwavelength Raman spectroscopy has proven to be a very powerful tool for characterizing the microstructure of amorphous carbon materials\(^{50-53}\). When discussing multiwavelength Raman spectroscopy there are two very important modes present in amorphous hydrogenated carbon. The first mode is typically located between 1560 and 1620 cm\(^{-1}\) and is called the G peak. The G peak is the C–C stretching mode of an sp\(^2\) hybridized bond. This includes sp\(^2\) bonds located in rings and chains. This mode is the same that is observed in graphite at 1582 cm\(^{-1}\). If you think about graphite there should be a second mode, the ring breathing mode, but because of the symmetry of the graphite crystal, the E\(_{2g}\) mode is symmetry forbidden in graphite\(^{50}\). However, as disorder is introduced to perfect graphite the translational symmetry is broken and the selection rules are relaxed. Because of this, many
disordered carbons also have a peak located between 1300 and 1450 cm\(^{-1}\) which is called the D peak. Although the first order diamond mode is located at 1332 cm\(^{-1}\), the D peak is a disorder peak and corresponds to the sp\(^2\) ring breathing mode. This has been verified because the sp\(^3\) vibrational density of states goes to zero above about 1340 cm\(^{-1}\). Because the D peak can exist above that threshold, it cannot be due to sp\(^3\) carbon\(^{5d}\). The most important thing to remember about both the D and G peaks is that they are both only probes of sp\(^2\) carbon.

Figure 3-9 exhibits the modes corresponding to both the D and G modes.

![Figure 3-9: Eigenmodes for both the D and G peak. Both modes correspond to sp\(^2\) bonding.](image)

By observing how these two modes change in both position (dispersion) and intensity, much can be learned about the microstructure of the amorphous carbon. A third mode of interest is the T peak, the tetrahedral carbon peak. This peak is only visible under DUV excitation. The reason this mode is only visible under DUV excitation is because of the Raman cross section of sp\(^2\) carbon vs sp\(^3\) carbon. As excitation moves more and more to the NIR the sp\(^2\) carbon, in rings, becomes more and more resonantly enhanced. This is because graphite has a zero band
gap. As you decrease the size of the graphene sheet a small gap opens in the band structure. This gap is very small and lies within the NIR region of the electromagnetic spectrum. Because of this NIR laser excitation resonantly enhances the signal swamping out any potential signal from sp\(^3\) carbon. Even in the visible region of electromagnetic spectrum, the sp\(^2\) carbon has a cross section roughly 100 times that of the sp\(^3\) carbon. It is only in the DUV, where you are getting closer to the resonant enhancement of sp\(^3\) carbon, that the Raman cross sections become close to 1:1 between sp\(^2\) and sp\(^3\) carbon. The T peak is located around 1060 cm\(^{-1}\) and is a very broad peak that corresponds to C-C sp\(^3\) bonding. By having sp\(^3\) bonding present in an amorphous hydrogenated carbon sample, it introduces a large degree of topological and structural disorder into the sp\(^2\) carbon network.

The disorder, both whether it is topological or structural and the extent of the disorder can be determined via the multiwavelength Raman spectroscopy technique. Topological disorder results from when the sp\(^2\) carbon ring network is broken. The easiest way to do this is the introduction of sp\(^3\) carbon. If this sp\(^3\) carbon is terminated by hydrogen, though, it typically will not result in much structural disorder. Structural disorder is formed when the disorder results in many of the bonds being strained by having to form bonds at angles far from 109.25° for sp\(^3\) bonding and 120° for sp\(^2\) carbon. This typically results from amorphous carbons that have a high degree of C-C sp\(^3\) bonding and low hydrogen content. In order to probe topological disorder via Raman spectroscopy the dispersion of the G peak needs to be measured. If the G peak shifts in position greatly with excitation wavelength then there is a large degree of topological disorder. Structural disorder is typically determined by the FWHM of the G peak. If the FWHM of the G peak is greater than 100 cm\(^{-1}\) then there is said to be a high degree of structural disorder.
The aforementioned resonant enhancement effect can also give microstructural information about how the sp\(^2\) carbon network is bonded. As was said, sp\(^2\) carbon located in rings is resonantly enhanced as the excitation wavelength approaches the NIR. Therefore the D peak will increase relative to the G as the excitation wavelength changes from the DUV to the NIR. In some cases the D peak is nonexistent in the DUV Raman spectra of disordered carbons. If there exists a large change in the D to G ratio with excitation wavelength it can be thought of as meaning that most of the sp\(^2\) carbon is bound in ring systems and the sp\(^2\) carbon content is high. If there is a high slope of the D to G ratio, but it remains low, it means that there is less sp\(^2\) carbon present, but what is there is located within ring systems. If there is minimal change in the D to G ratio and the value is low it means that there is very little sp\(^2\) content present in the system and what sp\(^2\) carbon is there is located in chains. This type of analysis has been applied to the polymerized acene samples that were recovered from high pressure. In the experiments presented the following excitation wavelengths were utilized: 244 nm, 364 nm, 458 nm, 514 nm, 633 nm, and 785 nm.

Figure 3-10 shows that dispersion of the G mode with excitation wavelength of the polymerized acene products. Topological disorder can be determined by measuring the “G” peak dispersion. The dispersion of the “G” peak is 0.37 cm\(^{-1}\)/nm, 0.08 cm\(^{-1}\)/nm, and 0.05 cm\(^{-1}\)/nm in polymerized naphthalene, anthracene, and pentacene, respectively. This high degree of order in the polymerized pentacene fits well with the sharp peaks observed in the FT-IR spectrum. This indicates that the polymerized naphthalene has a very high degree of topological disorder. This topological disorder is because the ring system has broken and a large degree of sp\(^3\) bonding has formed from the smallest acene molecule.
Figure 3-10: G Peak dispersion versus excitation wavelength. This is a good emasure of the topological disorder of the amorphous hydrogenated carbon.

The structural disorder has been determined to be minimal based on the DUV Raman (Figure 3-11) of each of the recovered samples.

Figure 3-11: DUV Raman spectra of each of the recovered polymerized acenes. The FWHM of the G peak is small indicating a lack of structural disorder.
The FWHM of each sample is roughly 60 cm\(^{-1}\), well below the threshold cutoff for structural disorder. Low incident powers (~100 µW) were maintained on the samples to avoid sample damage. The high energy (5.08 eV) of the UV laser can easily damage carbon samples, especially those with a lot of hydrogen content\(^5\). The DUV Raman of the naphthalene sample also indicates a substantial T peak indicating a fairly large amount of sp\(^{3}\) bonding. The two other samples both show very small T peaks that may or may not be background signal.

As mentioned before the bonding environment of the sp\(^{2}\) carbon can be determined by looking at the relative intensities of the D and G peaks with respect to excitation wavelength. Figure 3-12 shows the D to G ratio versus excitation wavelength for each of the three recovered products.

![Figure 3-12: The change in the D to G ratio with respect to excitation wavelength for each of the recovered products. This can give information on the environment of the sp\(^{2}\) bonding.](image)

It is seen that the polymerized pentacene sample has a high D to G peak ratio along with a high slope with respect to excitation wavelength. This indicates that the polymerized
pentacene sample has a lot of $sp^2$ carbon and that a preponderance of that carbon is bound in large clusters of ring systems. The polymerized anthracene also has a relatively high slope in the D to G ratio with respect to excitation wavelength, but the absolute D to G ratio is lower than that of the pentacene sample. This would indicate that the amount of $sp^2$ present in the polymerized anthracene sample is lower than that of the pentacene sample. However, a preponderance of that $sp^2$ carbon is still located in clusters of rings. There does not appear to be an effect of the excitation wavelength on the D to G ratio of the polymerized naphthalene sample and the absolute D to G ratio is very low. This supports the idea that there is a large degree of $sp^3$ bonding present in the polymerized naphthalene sample and that whatever $sp^2$ carbon remains is located predominantly in chains.

With this analysis we can classify the three products into different types of amorphous hydrogenated carbons. The high topological disorder and low $sp^2$ content in the polymerized naphthalene sample results in it being classified as a polymer-like amorphous hydrogenated carbon. Both the polymerized anthracene and pentacene samples are classified as highly hydrogenated graphite-like amorphous hydrogenated carbons. This is because both exhibit most of their high $sp^2$ bonding in graphitic clusters based on the D to G ratio and both exhibit very low topological disorder. Their carbon structure makes them very similar to nanocrystalline graphite or glassy carbon, except that they still retain a high hydrogen content.

Visible Raman spectroscopy was utilized to estimate the hydrogen content of the three amorphous hydrogenated carbon samples. Figure 3-13 exhibits the 514 nm excitation Raman spectra of the polymerized anthracene and pentacene samples. The polymerized Naphthalene is not shown because the PL background was too high to use this technique.
When hydrogen is incorporated into an amorphous carbon it passivates many non-radiative recombination centers and results in a strong broadband PL background.

![Figure 3-13: 514 nm excitation Raman spectra of the polymerized anthracene and pentacene. The height of the G peak with respect to the slope of the background PL gives a good estimation of hydrogen content.](image)

Equation 3.5 allows the quantification of the hydrogen content of the amorphous hydrogenated carbon via a 514 nm Raman measurement.

\[
H \ [at\%] = 21.7 + 16.6 \log \left( \frac{m}{I(G)} \right) \ [\mu m] \]  
(Equation 3.5)

Where \( m \) is the slope of the PL background between 1050 and 1800 cm\(^{-1}\). From this measurement it was determined that the hydrogen content of the polymerized anthracene and pentacene samples were 37 at\% and 33 at\%, respectively. This indicates a slight loss of hydrogen from the starting material, 42 at\% and 39 at\% for the starting molecules. Because
the PL background overwhelms the Raman signal for the polymerized naphthalene sample at 514 nm excitation it is assumed the hydrogen content is above 40 at%.

3.3. High Pressure Stability and Reactivity of Pyrene, Coronene, and Triphenylene

It has been shown that Clar’s sextet rule for aromatic stability can easily be applied to linear acene molecules, but it is interesting to see what occurs when the PAH extends in two dimensions and reaches something closer to graphite. One thing that Clar’s aromatic sextet does well is to predict global aromaticity trends, but if fails in determining local aromaticity which could more accurately predict reaction points. To more accurately predict local aromaticity, more computationally advanced techniques such as molecular electrostatic potential topography, para-delocalization index, the harmonic oscillator model of aromaticity, and nucleus independent chemical shifts have been developed\textsuperscript{5,56}. These combined with Clar’s aromatic sextet help to describe some preliminary results obtained by studying the 2-D PAHs pyrene, coronene, and triphenylene.

3.3.1. Vibrational Spectroscopic Characterization

Visible Raman spectroscopy was used to try and determine reaction threshold pressures for pyrene and coronene. The \textit{in situ} Raman data collected at 514 nm excitation can be observed in figures 3-14 and 13-15 for pyrene and coronene respectively. The Raman data for pyrene indicates a sluggish transition from its molecular form to an amorphous hydrogenated carbon starting at 19 GPa and completing its transformation above 26 GPa. This transition is at a similar pressure as graphite, but like with the acenes this is an irreversible reaction. According to Clar’s aromatic sextet the pyrene molecule should be more stable than the anthracene molecule, but it appears to react at a lower pressure than expected. This expectation is due to the fact that pyrene has two sextets spread over 4 rings.
Figure 3-14: *in situ* visible Raman spectra of pyrene. At high pressure the molecular modes are replaced by a broad G peak.

Although coronene is typically thought of as a graphite analogue, the Clar diagram (figure 3-1) clearly shows 3 sextets, 1 empty ring, and 3 localized π-bonds. Both Clar diagrams and newer computational techniques expect higher reactivity at these localized bonds. In fact experimental attempts at a high pressure-high temperature hydrogenation of coronene support the idea that the localized bonds have a higher reactivity. This increased reactivity suggests that coronene should react at a similar pressure as graphite or pyrene. This is not the case. From figure 3-14 it can be seen that like pyrene coronene goes through a sluggish transition from its small molecule to an amorphous hydrogenated carbon network. Up to over 42 GPa, Raman modes characteristic of the original coronene molecule can be observed in addition to a growing G peak. This G peak begins to grow in at pressures over 34 GPa. Angle dispersive XRD was also performed on coronene in the DAC.
3.3.2. Angle Dispersive X-ray Diffraction

The angle dispersive XRD performed on coronene indicate that the small molecule exists in a monoclinic crystal system up to the highest pressures measured, over 30 GPa. When the pressure was raised above this point, the Bragg peaks were absorbed into the background. XRD in a DAC of small molecules is difficult due to the high Compton scattering. This Compton scattering could not be overcome and therefore a reaction threshold for Coronene could not be established.

Angle dispersive XRD was also performed on the molecule triphenylene at beamline 16-ID-B at the Advance Photon Source of Argonne National Laboratory. Peaks consistent with triphenylene’s monoclinic structure were observed to upwards of 50 GP, indicating that no chemical transformation had occurred to that pressure. Triphenylene was recovered back to ambient pressure after being exposed to static pressures over 55 GPa. This high degree of
stability exhibited by triphenylene is expected due to the fact that it has only aromatic sextets that are not diluted. It has no preferred reaction points like the acenes, pyrene, or coronene.

3.4. Future Directions

Future experiments should include finding a reaction threshold for the polymerization of triphenylene. Although triphenylene is fully delocalized in the sense that there is no preferred reaction paths, it should still undergo an irreversible polymerization reaction. This is because it is a cata-condensed PAH. It has been established that carbon bonds that form on the edge of a carbon system are much harder to break than those formed from interior carbons. Since triphenylene is cata-condensed it should irreversibly react.

To investigate further the reversible nature of small PAH molecules at high pressures, a fully delocalized para-condensed PAH would need to be synthesized and studied. I have synthesized the molecule peri-hexabenzocoronene which would fulfill this criteria. Figure 3-16 shows the reaction pathway to the large para-condensed PAH.

![Figure 3-16](image)

*Figure 3-16: The reaction pathway used to synthesize peri-hexabenzocoronene. This molecule should act as a good graphite analogue because it is a fully delocalized para-condensed PAH.*

Moving forward it would be best to study the reversible nature of the cold compressed graphite transition from both this small molecule perspective and the crystal perspective. XRD and Raman are powerful tools for this analysis. The work presented here on the acenes has been written into a manuscript and is awaiting submission. More work is needed to
determine the exact reaction thresholds for pyrene, coronene, and triphenylene. It would also be beneficial to investigate the reactivity of perylene as well. Observing how the amorphous hydrogenated carbons products formed from each of these precursors would be a very nice follow up study to the acene work. Future work on HBC will be shown in chapter 6.
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4 High Pressure Transformation of Single Walled Carbon Nanotubes to Graphitic Polyhedra Under Cold Compression

4.1 Introduction

Single walled carbon nanotubes (SWNTs) were first discovered simultaneously in 1993 by Iijima\(^1\) and Bethune\(^2\), merely two years after Iijima’s discovery of the multiwalled carbon nanotube (MWNT)\(^3\). Since then carbon nanotubes have garnered immense attention due to their interesting structure and their amazing materials properties. This chapter will provide a background on the structure of carbon nanotubes along with the two most common synthetic methods. This discussion will be followed by a brief history of the analysis of SWNTs under static compression, both from an experimental and theoretical perspective. In the theoretical community there are competing theories of what occurs to SWNTs at high static pressures. To this point experimental results have been inconclusive. The chapter will end with new experimental results indicating that metallic SWNTs preferentially collapse to form graphitic polyhedra leaving the semiconducting SWNTs more or less intact. These results are being prepared for a manuscript to be submitted.

SWNTs are an interesting allotrope of carbon in that it is a truly one-dimensional (1-D) structure, roughly 1 nanometer (nm) in diameter and tens of micrometers (μm) in length. They are made up of purely sp\(^2\) bonding and can be thought of as being a single graphene sheet, a single covalently bonded layer of graphite, rolled up into a cylinder. How the sheet is rolled, the chirality of the tube, determines the properties associated with the SWNT\(^4\). Figure 4-1 shows how a graphene sheet can be rolled to form a SWNT of certain chirality. The hollow nature and large aspect ratio of the very narrow tube makes SWNTs promising candidates for gas adsorption media\(^5-7\). Because of this SWNTs have been investigated
extensively as potential hydrogen storage substrates. SWNTs can be either semiconducting, typically with a low band gap, or metallic.

This difference in electrical properties is one of the reason that SWNTs have been proposed to be used in many electronic applications. For instance, in metallic SWNTs ballistic electron transport has been demonstrated\(^8,9\). In addition to their impressive electronic properties, SWNTs have been shown to have amazingly strong mechanical properties. Tensile strengths on the order of 1 TPa (roughly 10 million atmospheres) have been determined on isolated SWNTs\(^10,11\). This may be thought of as odd since graphite, an all \(sp^2\) allotrope of carbon is thought of as being very soft (used as a solid state lubricant in some situations). The low mechanical strength of graphite is highly anisotropic. What makes graphite soft is the weak Van der Waals bonding that exists in between graphene sheets. Graphite is actually an
amazingly strong material in the a- and b- directions of the crystalline lattice. Since SWNTs consist of only a single sheet of graphene rolled into a cylinder, the mechanical strength of that graphene sheet is transferred to the SWNT. This high mechanical strength, and very low weight, of SWNTs has been exploited in composite materials\textsuperscript{12,13}.

Large scale synthesis of SWNTs is typically achieved via one of two methods. The first method to synthesize SWNTs was the same that was used to synthesize C\textsubscript{60} fullerene\textsuperscript{14} and MWNTs, the arc discharge method\textsuperscript{15}. In this method carbon soot is collected from graphite electrodes after an arc discharge using more than 100 amps. Within this soot exist SWNTs, MWNTs, C\textsubscript{60}, and amorphous carbon which can be separated from each other. Metal catalysts can be used to increase the yield of SWNTs compared to other products formed during this process such as MWNTs and fullerenes. However, this results in metal impurity contents of between 5 and 35wt\% which can be difficult to remove without severely damaging the SWNT sample. The second method for the large scale production of SWNTs is the laser vapor desorption or laser ablation technique\textsuperscript{16}. In this method a heated graphite target is hit with high powered lasers which vaporize the carbon in the presence of a metal catalyst. This method results in a higher yield than the traditional arc discharge method and does not have the problems associated with metal impurities. The diameter of the SWNTs can also be better controlled in this method than in arc discharge by controlling the temperature of the graphite target. The main impurity that is formed during this type of synthesis is amorphous carbon. This amorphous carbon can easily be disposed if with a peroxide wash. The SWNTs are then annealed at high temperature in an inert atmosphere to remove any defects formed during the peroxide wash. The drawback of pulsed laser vaporization is the prohibitive cost to scale the reactor to a large scale. The tubes used for the
research presented in sections 4.2 and 4.3 were synthesized by Xiaoming Liu via the pulsed laser vaporization method in the laboratory of Peter Eklund at Pennsylvania State University.

When SWNTs are synthesized, either by the arc discharge method or the pulsed laser vaporization method, they rarely exist as isolated tubes. Typically tens to hundreds of individual nanotubes assemble into hexagonally close packed bundles of nanotubes. Within these bundles, tubes of different diameters and chirality exist. Figure 4-2 shows a Brightfield TEM micrograph of bundles of SWNTs.

![Figure 4-2: Brightfield TEM micrograph of the pristine SWNTs synthesized via PLV. The micrographs verify that the tubes are in fact single walled with diameters roughly equal to 1 nm. No metal impurities were observed in the sample.](image)

Because of their long interaction lengths, tens of micrometers, typically weak Van der Waals forces are strong enough to hold these bundles together. Much research has been done to break apart these bundles without destroying the individual tubes so that isolated tubes can be studied. The isolation and separation of SWNTs has a large and fascinating literature but is not the focus of this dissertation, but could prove useful for the continuation of this work along with the work presented in Chapter 5.
The most convenient tools to analyze the structure of SWNTs are Raman spectroscopy, TEM, and X-ray Diffraction. In the Raman spectrum of SWNTs there are two regions of interest. The first is a region between 100 cm\(^{-1}\) and 300 cm\(^{-1}\). The peaks in this region correspond to the radial breathing mode of the tube. This mode can be used to determine the diameter of the tubes that are being investigated\(^{17}\). Figure 4-3a shows a schematic of the RBM for an 8,8 SWNT.

![Schematic of RBM for an 8,8 SWNT](image)

Figure 4-3: a) Atomistic representation of an 8,8 nanotube showing the eigenvectors corresponding to the radial breathing mode. b) Kataura plot relates the excitation wavelength/RBM position to the electronic property and chirality of the SWNT.

One thing to remember when looking at the Raman of SWNTs is that the only tubes that are being observed are ones that are in resonance with the excitation laser. This is why it is very important to perform multiwavelength Raman spectroscopy when analyzing SWNT samples. In addition to learning the diameter of the SWNTs under investigation by equation 4.1\(^{18}\), the electrical properties can be determined.

\[
\omega_r = \frac{223.75}{d_t} \quad \text{(Equation 4.1)}
\]
Figure 4-3b shows a Kataura plot which related the position of the RBM and excitation wavelength to the electrical property of the nanotube\textsuperscript{19}. From this plot it is possible to determine whether the SWNT is metallic or semiconducting. The other Raman active mode in SWNTs is the carbon-carbon symmetric stretching mode\textsuperscript{20,21}. This is the same mode as the $E_{2g}$ mode found in graphite and is thus located at roughly 1590 cm\textsuperscript{-1}. It is slightly higher than the $E_{2g}$ mode in graphite due to the increased strain imparted on the mode due to the curvature of the SWNT.

TEM was the first characterization technique used to verify the presence of both SWNTs and MWNTs. Since then TEM has remained an important analytical tool for the investigation of SWNTs. TEM was used to directly measure the diameter of SWNTs in order to verify the Raman dependence of the RBM with tube diameter. X-ray diffraction, the traditional tool for structural analysis, has actually failed to a degree in characterizing SWNTs\textsuperscript{22,23}. This is because the size of the nanotubes makes the observable Bragg peaks have very low 2θ values. Additionally, the lack of axial order within a bundle of SWNTs, due to differing chirality between tubes, has made structural inversion difficult. However, the trigonal packing of SWNTs into crystalline bundles has been verified through X-ray diffraction. All three of these characterization techniques, as well as \textit{in situ} inelastic x-ray scattering (IXS), were utilized to determine the high pressure transformation of SWNTs.

\textbf{4.1.1 SWNTs Under High Pressure}

Pressure has been used as a tool to investigate many different materials and SWNTs are no different. Some of the first experiments on SWNTs at high pressure were attempts to transform SWNTs to diamond via a high pressure, high temperature synthesis. The thought was that the higher energy per carbon-carbon bond due to curvature of the SWNT would
lower the transition to diamond\textsuperscript{24-26}. The transition of SWNTs to diamond has been determined to be 14.5 GPa and 1800 K\textsuperscript{27}. In addition to the direct transformation to diamond, other high pressure phases of carbon nanotubes have been investigated.

There have been several theoretical papers suggesting novel high pressure phases consisting of crosslinked bundles of SWNTs\textsuperscript{28-30}. These crosslinked structures contain a mixture of sp\textsuperscript{2} and sp\textsuperscript{3} bonding and are considered to be exceptionally hard, rivaling diamond in hardness. There has been one experimental paper that suggests an ultrahard phase of carbon was formed at high pressure from the cold compression of carbon nanotubes to roughly 100 GPa in a DAC\textsuperscript{31}. The phase was hexagonal and recovered to ambient conditions. A structural refinement could not be completed due to the small sample size. They determined the phase to be ultrahard because it caused a ring crack in the diamond anvil. Ring cracks in diamond are formed when the material within the DAC causes the diamond culet to elastically deform. Upon relaxing, the diamond relives the immense strain by cracking. When this occurs it is implied that the material within the DAC is at least as hard as diamond because it is causing the diamond to elastically deform. A second experimental study found another superhard phase of carbon is formed from the compression of SWNTs to 55 GPa\textsuperscript{32,33}. This phase also has a hardness that is comparable to that of diamond however there was minimal structural information on the high pressure phase. These experimental results will be compared to the experimental results found in this dissertation from the cold compression of SWNTs.

Throughout the late 1990’s and early 2000’s, SWNTs at pressure were heavily studied\textsuperscript{34-38}. In these studies it was determined that at roughly 5 GPa the RBM disappears from the Raman spectrum. This is due to the fact that the cross section of the carbon
nanotube is no longer circular. As the tubes within a bundle are pressed closer and closer together the cylindrical tube begins to deform and the cross section become polygonal\textsuperscript{39,40}. As the tube is further compressed the cross section of the tube begins to flatten into an oval and eventually could completely collapse. Raman studies to 30 GPa indicate the resiliency of SWNTs to high pressure in recovering both the RBM and the tangential mode at 1590 cm\textsuperscript{-1} to ambient conditions. These results seem to indicate a nearly fully reversible flattening of the SWNT at high static loads. Nearly is used because many researcher do take note of the much lower intensity of the RBM in the recovered samples relative to the starting material.

It can be seen from a study of the experimental and theoretical literature of SWNTs at high pressure that there exist two distinct differences of opinion about what occurs to the structure of SWNTs. On the one hand, some researchers believe that SWNTs will react with adjacent nanotubes within a bundle to form an ultrahard sp\textsuperscript{3} or mixed sp\textsuperscript{2}/sp\textsuperscript{3} phase of carbon while other researchers believe that SWNTs will collapse under a high enough static load. The following two sections will investigate what occurs to pulsed laser vaporization sample of SWNTs under a large non-hydrostatic load within a DAC. A combination of multiwavelength Raman spectroscopy, TEM, and X-ray diffraction will confirm that metallic SWNTs preferentially collapse into graphitic polyhedra leaving the more structurally resilient semiconducting SWNTs intact.

4.2 \textit{in situ} Characterization of SWNTs under High Pressure

SWNTs synthesized via the pulsed laser vaporization method were loaded into a symmetric DAC equipped with 300 μm culets. The sample chamber was formed by a T301 stainless steel gasket with a roughly 100 μm diameter hole centered between the culets. Type Ia natural diamonds were used with low fluorescence to ensure adequate Raman spectra could
be obtained. The same cell was used for in situ XRD studies. A different panoramic DAC was used for the in situ IXS experiments. In this cell 400 μm culets were used with a c-BN/Be composite gasket.

4.2.1 Multiwavelength Raman Spectroscopy

Raman spectroscopy was performed at 458 nm, 488 nm, 514 nm, 633 nm, and 785 nm excitations. Figure 4-4 shows both the RBM (a) region of the Raman spectra as well as the tangential mode (b) of the pristine SWNTs.

![Raman Spectra](image)

Figure 4-4: Multiwavelength Raman spectra of pristine SWNTs before being loaded into the DAC, a) shows the RBM region and classifies each tube according to its electrical property. The T mode region (b) shows very little disorder, small D peak, in the pristine sample.

As can be seen from figure 4-4a the nanotube diameter has a distribution between 1 and 1.5 nm and contains both semiconducting and metallic tubes. Table 4.1 shows the distribution of SWNTs that can be found within the sample.
<table>
<thead>
<tr>
<th>Excitation Wavelength (nm)</th>
<th>RBM Peak Position (cm$^{-1}$)</th>
<th>Tube Diameter (nm)</th>
<th>Semiconducting or Metallic</th>
</tr>
</thead>
<tbody>
<tr>
<td>458</td>
<td>180.85</td>
<td>1.24</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>458</td>
<td>198.39</td>
<td>1.13</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>488</td>
<td>169.27</td>
<td>1.32</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>488</td>
<td>189.61</td>
<td>1.18</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>488</td>
<td>200.45</td>
<td>1.12</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>514</td>
<td>185.81</td>
<td>1.20</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>514</td>
<td>191.75</td>
<td>1.17</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>633</td>
<td>172.44</td>
<td>1.30</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>633</td>
<td>189.59</td>
<td>1.18</td>
<td>Metallic</td>
</tr>
<tr>
<td>633</td>
<td>199.2</td>
<td>1.12</td>
<td>Metallic</td>
</tr>
<tr>
<td>785</td>
<td>146.93</td>
<td>1.52</td>
<td>Metallic</td>
</tr>
<tr>
<td>785</td>
<td>159.75</td>
<td>1.40</td>
<td>Metallic</td>
</tr>
<tr>
<td>785</td>
<td>194.1</td>
<td>1.15</td>
<td>Semiconducting</td>
</tr>
</tbody>
</table>

Both the RBM and the T modes were followed with pressure at each excitation wavelength. As pressure was increased there was a consistent red shift and peak broadening observed in the sample’s spectra at each wavelength. As was reported in previous papers the RBM does disappear for all excitation wavelengths above 7 GPa. Again, this is due to the fact that the SWNTs have lost their circular cross section due to either flattening or polygonization. At higher pressures several discontinuities in the T peak shift are observed. Between 10 and 20 GPa there seems to be a softening of the T peak observed in all excitation wavelengths other than the 633 nm. The 633 nm excitation seems to plateau in that region and then above 20 GPa even drops a bit in position, indicating some sort of structural transformation. The most drastic change in peak position with pressure can be observed in the 785 nm Raman. Full in situ Raman spectra can be found in the Appendix. Above 30 GPa the peak position of the T peak blueshifts drastically. This shift in peak position has been attributed to the transformation of the SWNTs to graphitic polyhedral. Figure 4-5 shows the change in T peak position with pressure for all excitation wavelengths.
The change in the T peak position with respect to applied pressure at several different excitation energies. The T peak blueshifts to higher frequencies due to the shortening of the C-C bond length.

The reason the graphite has been proposed as the resulting material is because the downshifted peak in the 785 nm Raman spectra falls nearly directly on the line created by Goncharov in his study on the Raman of graphite to 55 GPa. As can be seen in figure 4-6 this transformation is irreversible. The peak remains close to the same decompression curve as the graphite sample studied by Goncharov. Even though there may be some discontinuities observed for the 458 nm, 488 nm, and 514 nm excitation spectra (mode softening between 10 and 20 GPa), the samples were completely recoverable to ambient conditions as will be seen in section 4.3.
Figure 4-6: Change in T peak position with pressure at 785 nm excitation. The dashed line is the experimental line of best fit from Goncharov. The data for the compressed SWNTs falls closely to that line.

Based on the in situ Raman there appears to be two transitions; the first is in the 633 nm spectra at between 10 and 15 GPa where a blue shift in the Raman spectrum is observed. The second is a very drastic transformation observed in the 785 nm spectra where the T mode drops in peak position to fall nearly directly on the compression curve of pristine graphite.

4.2.2 in situ Angle Dispersive X-Ray Diffraction

in situ X-ray diffraction was performed on the SWNT sample synthesized from the PLV method. This experiment was performed at beamline 16-ID-B of the Advanced Photon Source at Argonne National Laboratory. The beam energy was 30.5 keV, $\lambda = 0.406$ Å. The high flux provided by the insertion device instrument allowed for adequate signal to noise even with a low Z sample. However, a high background was present in many of the diffraction patterns due to the large amount of Compton scattering from the diamond anvils.

Figure 4-7 shows the diffraction of the SWNT sample in the DAC.
The Bragg peaks arising from the sample are from the trigonal lattice that the tubes pack into and not from the axial direction of the tubes. It can be seen that as the pressure is increased the Bragg peaks shift to higher Q because the d spacings are being compressed. There are a few peaks indicated by asterisks that arise from either ruby powder which was used a pressure calibrant and the stainless steel gasket. Peaks from the diamond anvil were easily masked due to them being single crystal in nature. As the pressure reaches upwards of 30 GPa, all Bragg peaks are absorbed into the large background. However, upon decompression the Bragg peaks corresponding to the SWNT sample return. This indicates the bundle of SWNTs is structurally resilient up to at least 30 GPa. This is the same pressure that the drastic change in the 785 nm Raman spectrum was observed. No evidence of graphite can be observed within the sample in situ, but a high background is present even to the lowest pressures. XRD has been performed on the recovered sample without the diamond anvils and will be presented in section 4.3.
4.2.3 *in situ* Inelastic X-ray Scattering

Inelastic X-ray scattering is a technique that can be used to monitor the $sp^2/sp^3$ ratio in situ. In this experiment a focused x-ray beam is sent through the gasket and sample. This geometry is required because the large single crystal diamond anvils will cover any signal that comes from the carbonaceous sample. This makes it very important to avoid the diamonds with the x-ray beam. Because of this a special gasket was needed. The gasket was prepared in a way similar to that presented by Wang et al.\textsuperscript{42} In this procedure a composite c-BN/Be gasket was created. Figure 4-8 shows a top down diagram of the gasket used for this experiment.

![Composite, x-ray transparent gasket used for in situ IXS measurements.](image)

Due to the anisotropy present in SWNT samples and the very small amount of sample the data collection was difficult. Because of the poor signal to noise we were unable to decipher any trends in $sp^2$ bonding within the SWNT sample at high pressure. Future work on IXS measurements on the SWNT sample is planned and could prove very useful.

4.3 Characterization of SWNTs Recovered from High Pressure

By removing the SWNT sample from the DAC, it opens new characterization techniques such as TEM and also cuts down drastically on the background for both multiwavelength Raman spectroscopy and X-ray diffraction. The multiwavelength Raman
spectroscopy and TEM were performed on a sample that was recovered from 50 GPa. The Raman was performed on top of one of the diamond anvils because the sample did not stick within the gasket when recovered. Because of this, in several spectra presented here there will be a sharp peak within the D peak. This sharp peak is the diamond anvil beneath the recovered sample. No evidence of diamond formation was observed in either XRD or TEM analysis.

### 4.3.1 Multiwavelength Raman Spectroscopy

Much like what was observed in Chapter 3, multiwavelength Raman spectroscopy has proven to be a powerful technique in helping to discern the microstructure of the recovered SWNTs. Figure 4-10 shows the Raman spectra (both the RBM (a) and T mode (b)) of the SWNT sample recovered from 50 GPa. As can be seen the RBM modes for the 458 nm, 488 nm, and 514 nm excitations remain nearly untouched. This shows the resiliency of the SWNTs that were probed by these wavelengths, which all happen to be semiconducting in nature. The RBMs of the recovered samples measured with 633 nm and 785 nm excitation have changed in several ways. The modes that were classified as metallic have been removed or at least drastically reduced in intensity. This would indicate that these metallic tubes have been destroyed or at least drastically modified in some way.
The second difference between the starting material shown in Figure 4-4 and the recovered material is figure 4-9 is the appearance of a D peak. As was stated earlier the D peak arises when the translational symmetry is broken within graphite or graphene structures. It corresponds to the typically symmetry forbidden $A_2$ mode\textsuperscript{43}. It can be seen that the D peak rises drastically with respect to the G peak as excitation wavelength increases. As was explained in Chapter 3, this rise in D peak intensity indicates that the resulting material is made predominantly of sp\textsuperscript{2} carbon and the preponderance of that sp\textsuperscript{2} carbon is found in ring systems. In addition to the D/G ratio, the D peak dispersion can be used as a gauge to describe topological disorder. D peak dispersion has the inverse effect as G peak dispersion described in Chapter 3. If the D peak disperses greatly with excitation wavelength it typically means that the measured material is highly ordered\textsuperscript{44}. Figure 4-10 shows the D peak dispersion of the recovered SWNT sample.

Figure 4-9: Multiwavelength Raman spectra of SWNTs recovered from 50 GPa. a) shows the change in the RBM, specifically for the 633 nm and 785 nm excitations. b) shows the increase in defects as evidenced by a large D peak around 1330 cm\textsuperscript{-1}. 
The D peak has a dispersion of 0.196 cm$^{-1}$/nm. This high dispersion is typical of highly ordered systems such as nanocrystalline graphite. This high D peak dispersion along with the loss of the RBMs of the metallic nanotubes were the first evidence to support the in situ Raman data that graphite had been formed from the static cold compression of bundled SWNTs.

### 4.3.2 Transmission Electron Microscopy and X-ray Diffraction

There has been no previous study that examines the recovered SWNT samples via TEM. A TEM grid was prepared by wiping the lacey carbon grid across the diamond anvil culet after multiwavelength Raman spectroscopy was performed on the sample.

Figure 4-11 shows several Brightfield TEM micrographs that have small regions of highly graphitic polyhedra. The lattice fringes of the round nanoparticles were measured to be roughly 3.4 Å, the lattice spacing of the c-axis within graphite. These graphitic shells also exhibited SAED patterns consistent with a nanocrystalline graphite material.
The TEM shown here strongly supports both the in situ and recovered multiwavelength Raman spectra indicating a transformation of a small number of SWNTs to graphitic polyhedra. This transformation can be thought of as occurring by SWNTs being compressed to such a degree that the cross sectional area of the tube becomes too strained at the edges of the curve. This high degree of strain within the tubes is relieved by unzipping the tube. The dangling bonds of adjacent broken tubes are joined and they adopt the lowest energy structure. It is well established that spherical particles are preferred because of their limited high energy surface area.

The formation of graphite is also supported by the X-ray diffraction patterns collected on the recovered sample from over 30 GPa. Once the diamond anvils were removed the Compton scattering dropped to such a degree that weak peaks were able to be indexed. The large background observed in figure 4-12 comes from scattering form air.
Figure 4-12: X-ray diffraction pattern of the SWNT sample recovered from 31 GPa. In addition to the peaks corresponding to the pristine nanotubes, new peaks that can be indexed to graphite arise in the pattern. The asterisks indicate ruby powder that was used as a pressure calibrant.

As can be seen the most intense peak corresponding to the initial SWNT sample is retained. Additionally, peaks that can be indexed to graphite can be observed. The peak position of the graphite peaks suggest some residual strain exists in the recovered sample, which is not odd considering the high non-hydrostatic pressure. The asterisks indicate ruby which again was used as an internal pressure calibrant. This is the first time that an x-ray pattern of a recovered sample of SWNTs could be indexed. Previous work on cold compressed nanotubes indicate the recovery of a hexagonal phase which is ultrahard\textsuperscript{31}, but could not index the structure. Our results are consistent with the idea that an ultrahard phase of carbon formed at high pressure and recovered to graphite. If the SWNTs transformed to graphite at pressures above 19 GPa, as is supported by our in situ Raman investigation, then the graphite would exist in the cold compressed graphite phase\textsuperscript{45}. It has been well established that cold compressed graphite has a hardness comparable to that of diamond and reverts back to hexagonal sp\textsuperscript{2} graphite upon decompression. It is hypothesized that when the SWNTs unzip at high pressure to form the graphitic polyhedra that they are in a cold compressed state. This could be why no new
Bragg peaks were observed in situ for the diffraction. This new result that shows that metallic SWNTs break down to form graphitic nanoparticles at high pressure, leaving the semiconducting SWNTs intact is an interesting result and will be investigated further.

4.4 Future Considerations

One of the main investigations that is currently ongoing is to determine the reaction threshold for the conversion of SWNTs to graphitic polyhedra. In this experiment SWNTs are being recovered every 5 GPa to investigate how the Raman spectra and TEM micrographs change with pressure. From this study it will be possible to determine if in addition to electronic properties, if diameter plays any role in the collapse of SWNTs. It would be expected that the larger SWNTs would collapse into these graphitic shells at lower pressures than the smaller tubes.

In addition to studying mixed bundles of SWNTs, it will become important to study the effect of chirality on this transformation. If a sample of SWNTs separated by chirality could be used it may be possible to gain a deeper understanding of the breadown mechanism and thresholds for each tube type. This type of information could prove to be very important because SWNTs are often being considered for ultra high strength applications. Because of this, it is important to have a thorough understanding of the failure mechanisms of these materials.
REFERENCES


5 Synthesis of Sub-nanometer Diamond Threads from the Solid State Polymerization of Benzene

5.1 Introduction to Benzene at Pressure

Benzene, the prototypical aromatic molecule whose basic ring structure was determined by Kekule in 1865\(^1\), has been studied under high pressures for over a century. Percy Bridgman, who won the 1946 Nobel Prize in physics for his contributions to high pressure physics, discovered that a room temperature benzene would freeze and went through a first order, solid-solid, phase transition\(^2,3\). Due to his experimental set up, in situ structural characterization was not available.

More research was performed on benzene in the 1960’s. In 1967 Block discovered that benzene could be polymerized at high pressure, 8 kbar, and high temperature, 800 K\(^4\). The material recovered was dark in color and no structural analysis was performed, however, the color indicates a slightly pyrolyzed sample. Piermarini was able to perform x-ray diffraction of benzene at high pressure throughout the 1960s. He was able to confirm that benzene crystallized in the same structure at high pressure as it did at low temperature. More importantly he was able to solve the crystal structure of the second high pressure phase in benzene that Bridgman had discovered in 1914. He determined the high pressure benzene phase existed as a monoclinic crystal of P2\(_1\)/c symmetry\(^5\). Figure 5-1 shows an atomistic representation of the high pressure benzene phase along each crystallographic axis. He determined that this crystal structure persisted to 25 GPa, at which point the benzene crystal became amorphous.
Throughout the 1980’s and 1990’s further work was performed on benzene using more advanced x-ray diffraction techniques and Raman spectroscopy\textsuperscript{6-11}. From this work a complex phase diagram for benzene was developed with between III and IV phases existing before the point at which benzene becomes amorphous. Many of the high pressure phases were wrongly identified new phases because transitions between benzene phases are sluggish. This means that at many points, two crystalline phases can exist simultaneously, resulting in complex Raman and X-ray patterns that could be easily misconstrued as new phases.

In the 2000’s more work was done by the Bini group to clean up the high pressure phase diagram for benzene created by Cansell\textsuperscript{12-17}. Bini used a combination of X-ray diffraction an infrared spectroscopy. The work from his group determined that there in fact only two high pressure benzene phases before an irreversible polymerization reaction that occurs around 20 GPa at room temperature\textsuperscript{15}. Figure 5-2 shows the phase diagram for benzene created by Bini’s group. In addition to the work done by Bini in studying the solid state polymerization of benzene via FT-IR, Jackson et. al.\textsuperscript{18} was studying the product formed by the high pressure polymerization of benzene by DUV Raman spectroscopy. In this study it was determined that the microstructure of the recovered
material was consistent with that of a polymer-like amorphous hydrogenated carbon that had a high sp$^3$ carbon content.

![Figure 5-2: Phase diagram for benzene developed by Roberto Bini's group\textsuperscript{16}. There are only two crystalline phases at room temperature before polymerization. Black dots are the polymerization pressures for samples that were annealed in the benzene II phase.]

Bini proposed a ring opening type mechanism that began a runaway crosslinking polymerization. He proposed the reaction occurred at defect sites such as excimer sites or grain boundaries\textsuperscript{16,17}. This was supported by the fact that the polymerization occurred at consistently higher pressures when the sample was annealed in the benzene II phase (the black dots in figure 5-2).

At this point only amorphous products have been obtained from the high pressure reaction of benzene. I will show in this chapter that we have used kinetic control, via a slow decompression of the sample, to create an ordered 1-D nanomaterial from a topochemical reaction within the benzene II crystal. By gaining control of this solid state high pressure reaction we have opened a new field of research into both solid state organic chemistry and carbon based nanomaterials.

5.2 Synthesis and Characterization of Diamond Threads

Low-dimensional carbon nanomaterials such as fullerenes\textsuperscript{19}, nanotubes\textsuperscript{20-22}, graphene\textsuperscript{23}, and diamondoids\textsuperscript{24} have attracted great attention because of their symmetry,
extraordinary physical and chemical properties, and potential as building blocks for nanotechnology\textsuperscript{24,25}. As stated above compression-induced polymerization of aromatic molecules such as benzene could provide an alternative route to ordered carbon nanomaterials\textsuperscript{26,27}, but despite almost a century of intensive study\textsuperscript{3-5,11,16} only amorphous reaction products have been observed from high-pressure reaction of benzene\textsuperscript{8,14,17,28} and other aromatic molecules\textsuperscript{29}. Below is reported the recovery to ambient pressure of macroscopic quantities of a novel crystalline one-dimensional sp\textsuperscript{3} carbon nanomaterial formed by high-pressure solid-state reaction of benzene. Slow decompression in a large-volume apparatus helps control the reaction kinetics to yield structural order. X-ray and neutron scattering, Raman spectroscopy, solid state NMR, and transmission electron microscopy combined with first-principles calculations from collaborators within the Crespi group at Penn State reveal the formation of close-packed bundles of sub-nanometer-diameter sp\textsuperscript{3} bonded carbon threads, capped around their circumference with hydrogen. They are crystalline in two dimensions and short-range ordered in the third. These diamond nanothreads promise extraordinary properties such as strength and stiffness higher than that of sp\textsuperscript{2} carbon nanotubes or conventional high-strength polymers\textsuperscript{30}. They may be the first member of a new class of ordered sp\textsuperscript{3} carbon nanomaterials that are synthesized by kinetic control of high-pressure solid-state reactions between aromatic precursors, reactions inaccessible to conventional gas-phase synthesis approaches.

High pressure shifts the balance of intramolecular and intermolecular interactions towards the latter, forcing unsaturated molecules to react to form more saturated dimers, polymers, and extended amorphous networks\textsuperscript{12}. Prior to reaction, small unsaturated
molecules that are gases or liquids typically freeze to form ordered molecular crystals. When atomic displacements are highly constrained by steric hindrance, solid-state reactions under pressure can be topochemical, where the structure of the final product reflects the symmetry of the starting molecular crystal\textsuperscript{16}. This type of reaction is very valuable due to the fact that in a crystalline solid the orientation of the molecules relative to one another is fixed. Pressure can then be used to carefully tune the distances between these molecules, resulting in increased control over the final product. For example, compressed crystals of certain simple unsaturated aliphatic molecules react topochemically at pairs of carbons to form well-known ordered, linear polymers such as crystalline polyethylene\textsuperscript{31} or enantiopure polycyanoacetylene\textsuperscript{32}. Benzene has the potential to polymerize at any of six equivalent carbons. This reactivity has always been found to yield disordered, hydrogenated carbon\textsuperscript{11,16} after compression, apparently because the propagation of reaction through the benzene molecular crystal is not constrained to a single direction or mechanism. The product formed by high-pressure reaction can have a sp\textsuperscript{3} carbon fraction of ~50\%, similar to the polymer-like amorphous carbon produced by plasma deposition\textsuperscript{14}. Reaction products formed by polymerization of benzene at ambient pressure, such as linear and dendritic polymers, involve coupling between benzene rings that remain intact and aromatic\textsuperscript{33}. The high-pressure benzene reaction reported here differs from all of these examples in reacting at all six carbons to produce an extended, one-dimensional, ordered, saturated nanomaterial with a local diamondoid-like structure.

Benzene samples of varying isotopic makeup ($^{12}$CH, $^{12}$CD, $^{13}$CH, and $^{13}$CD) were compressed to 20 GPa at room temperature within a VX3 Paris Edinburgh cell equipped with a pair of double toroid polycrystalline diamond anvil, maintained at this pressure
for one hour, and slowly released to ambient pressure at an average rate of 2 GPa/hr to recover a solid white product with no residual liquid benzene. The sample was contained within either stainless steel, zirconium, or titanium-zirconium alloy encapsulated gaskets. The sample was loaded at low temperature to avoid evaporation of the high vapor pressure benzene. Vapor from the liquid nitrogen was used to avoid water contamination of the sample. The samples were then removed from their gasket materials. No effect of reaction threshold was observed between the four different isotopes and no catalytic effect was observed between the three different gasket materials.

After recovery, dissolution of the sample was not apparent upon exposure to light hydrocarbon organic solvents, indicating that it is not composed primarily of small molecules. Consistent with this observation, the material began to pyrolyze in air at a temperature of 250 °C rather than melting indicative of a high molecular weight. Bright-field transmission electron microscopy (TEM) micrographs of this product consistently exhibit long-range parallel striations suggestive of tubes or threads as seen in Figure 5-3.

Figure 5-3: Brightfield TEM micrographs of diamond nanothreads. Long parallel striations show a periodicity of 6.4 Å.
These parallel striations are consistent across many areas of several samples. Extended sonication in pentane disrupts this regular lattice and reveals, narrow, curved one-dimensional structures that project outward from the sample’s edges, as shown in Figure 5-4.

Figure 5-4: Brightfield TEM micrograph of heavily sonicated nanothread sample. Small isolated threads protrude from the edges of the sample in this image.

The total scattering structure function $S(Q)$ derived from either synchrotron x-ray or neutron diffraction reveals Bragg peaks that reflect the order seen in the TEM. Figure 5-5 shows the x-ray data.

Figure 5-5: Total scattering structure function of diamond nanothreads indexed to a 2-D hexagonal lattice. Reduced pair distribution function, inset, indicates grain size of roughly 15 nm.
The width of the prominent (100) peak, which manifests in the spatial extent of the real-space reduced pair distribution function (PDF) (inset) indicates a crystalline domain size of tens of nanometers, consistent with the TEM imaging. This diffraction is very different from samples decompressed relatively quickly at ~20 GPa/hr in a diamond anvil cell. Those samples did not show any Bragg peaks and were more consistent with the previous reports of benzene polymerizing to form an amorphous hydrogenated carbon. Figure 5-6 shows the total scattering structure function of the polymerized benzene recovered from a traditional DAC experiment.

![Figure 5-6: Total scattering structure function of benzene recovered from a traditional DAC experiment. No Bragg peaks are present due to its amorphous nature.](image)

Our results suggest that decompression that is slower than is typical in a standard diamond anvil cell is critical to retaining well-ordered samples at ambient pressure. In section 5.3 it will be discussed that there is some evidence that reaction begins at high pressure, but the slow decompression is what allows the sample to be retained.

The number of Bragg peaks observed in the S(Q) is too small for structural inversion, but they are consistent with a two-dimensional hexagonal lattice with $a = 6.47$ Å. All of the prominent Bragg peaks (i.e. (100), (200), (310)) can be indexed to this 2D lattice (as can several weaker features), suggesting that the third dimension does not have coherent
long-range order. The relative peak intensities are consistent with a form factor of cylindrically symmetric columns of charge\textsuperscript{34} with geometry consistent with the atomistic model discussed below. The lattice constant is in excellent agreement with the $\sim6.4$ Å spacing between striations seen consistently in multiple high-resolution TEM images: the natural conclusion is to associate the hexagonal lattice with a close-packed bundling of tube- or thread-like structures that are not long-range ordered axially due to some combination of on-thread and inter-thread axial disorder. Similar bundling occurs in $sp^2$ bonded carbon nanotubes\textsuperscript{34}, but with a much larger lattice parameter; (individual $sp^2$ carbon nanotubes within a nanotube bundle are well-ordered axially, although the bundle as a whole is not since it is a heterogeneous mixture of differently-wrapped tubes). This much large lattice parameter is due to their large cross sectional area when compared to the threads discussed here.

![Figure 5-7: Compression of d spacings of diamond nanothreads within a DAC. The compression is compared to the anisotropic compression of graphite and a theoretically predicted tube.](image)

Synchrotron x-ray diffraction measurements on the recovered sample reloaded into a diamond anvil cell were collected as a function of pressure. They reveal that the (100) and (200) peaks shift at a rate consistent with weak van der Waals bonding between the
entities that generate the observed Bragg peaks. Figure 5-7 shows the change in d spacing of the (100) and (200) peaks with pressure compared to the covalently bonded axes (a- and b-) and van der Waals (c) bonded axis in graphite. First-principles modeling also strongly supports this “nanothread” architecture, as described below.

The diffuse scattering that accompanies the Bragg peaks provides the distribution of short-range C–C, C–H (C–D) and H–H (D–D) pairwise correlations\(^{35}\). By Fourier transforming \(S(Q)\), these can be represented in real space as the total pair distribution function \(G(r)\). Figure 5-8 shows the total scattering structure functions measured by both high energy x-rays and neutron diffraction techniques.

![Figure 5-8: Total scattering structure function of diamond nanothreads measured with high energy x-ray and neutron scattering.](image)

In these measurements a \(Q_{\text{max}}\) of 25 \(\text{Å}^{-1}\) was achieved, but a cutoff of 21 \(\text{Å}^{-1}\) was used for blending purposes and signal to noise considerations. Both the intense Bragg peaks (at low Q) and diffuse scattering (at high Q) are clearly apparent in the scattering patterns. Figure 5-9 shows both x-ray and neutron total pair distribution function data for a \(\text{C}_6\text{D}_6\) sample decompressed at 7 GPa/hr. When looking at a carbon hydrogen system it is very important and beneficial to perform total scattering experiments using both neutrons and
x-rays. This is because it makes it easier to determine the partial pair distribution functions (shown as gray outlines in figure 5-9).

![Figure 5-9: Total pair distribution function of diamond nanothreads as measured with x-rays and neutrons. Solid line is the experiment while the dashed line is a theoretical structure shown atomistically in figure 5-11. The gray lines are the partial pair distribution functions.](image)

When doing the x-ray experiment, it will only be sensitive to the carbon atoms in the system. This is because x-rays are scattered from the electron cloud of an atom and hydrogen does not have enough electrons, one, to be detected by x-rays. However, since neutrons are scattered by the nuclear strong force, there is a more complex relation between scattering cross section than the Z number in X-rays. For instance deuterium is very sensitive to neutron diffraction and shows up very strongly. Because of this when performing the simulated pair distribution function we took the following intensity normalizations into effect. D-D interactions made up 50% of the intensity, C-C interactions made up 25% of the intensity, and C-D interactions made up 25% of the intensity.
An analysis of the total pair distribution function yields a nearest-neighbor carbon-carbon distance of 1.52 Å, which is characteristic of dominant sp³ bonding. Coordination numbers extracted from the neutron G(r) using the experimental atomic density of ~0.11 atoms/Å³ (close to the 0.116 atoms/Å³, value obtained from the first-principles calculations described below) are ~0.99 and ~3.2 for nearest-neighbor C–D and C–C respectively, which is consistent with a dominant phase wherein each carbon atom has one hydrogen and three carbon neighbors. The density was determined by pressing the polymerized benzene into a cylindrical pellet and measuring the mass per unit volume. The corresponding second-neighbor C–C coordination number is similarly consistent with a structure of 1:1 C:H stoichiometry dominated by sp³ bonding, with a slight excess carbon coordination which may arise from a few carbon atoms that lose hydrogen and cross-link to adjacent threads. ¹³C solid-state nuclear magnetic resonance confirms predominantly (~80-84%) sp³ content. Figure 5-10 shows the ssNMR spectra with the sp² and sp³ carbon labeled.

![Figure 5-10: ssNMR spectra of two different nanothread samples. Blue corresponds to sp³ carbon whereas red corresponds to sp² carbon. The average sp³ content is 82 at%.

Figure 5-10: ssNMR spectra of two different nanothread samples. Blue corresponds to sp³ carbon whereas red corresponds to sp² carbon. The average sp³ content is 82 at%.}
ssNMR has historically been the go-to technique for determining the sp²/sp³ content for carbon materials. Until this point, the sample sizes obtained from traditional DAC experiments have been too small to perform these measurements. These measurements were performed in single pulse mode with ¹³C isotopically labeled samples on a 300 MHz and 400 MHz instrument. Figure 5-9 also shows a simulated G(r), obtained from a structural model inspired by two predictions reported in the literature for highly stable one-dimensional allotropes of sp³ carbon: an extremely thin (3,0) sp³-bonded carbon ‘nanotube’ terminated by hydrogen and the “polymer I” phase predicted in a first-principles structural optimization of compressed benzene.

*Figure 5-11: An atomistic representation of two theoretically predicted nanothread structures and how they are related by Stone-Wales rotations (left). The resulting atomistic model of our Monte Carlo simulation to form a disordered nanothread used for the simulated G(r) (right).*
As shown in Figure 5-11, these two structures are interrelated by two successive Stones-Wales transformations (i.e. rotations by 90 degrees of a carbon-carbon dimer, in this case with associated hydrogen atoms following along). The best match to the experimental data is a partially disordered structure that introduces a proportion of Stone-Wales transformations into an idealized (3,0) starting point. (The degree of broadening imposed in the model is consistent with a combination of instrumental and thermal broadening plus heterogeneities not explicitly included in the structural model, such as thread endcaps, occasional cross-links, and a small sp² component to the sample). This disordered thread that was created by the aforementioned Monte-Carlo simulation, right side of Figure 5-11, was created by Enshi Xu of the Crespi group. The agreement between theory and experiment in the fine details of the pair distribution function out to the third neighbor shell is excellent. One small feature in the x-ray G(r) is absent in the simulated PDF: a small shoulder just above 2 Å at a distance consistent with a second neighbor around a four-fold ring. Four-fold rings are often associated with particular reaction pathways (e.g. 2π+2π cycloaddition), whereas the simulated spectrum is based on a quasi-equilibrium Monte Carlo model; this feature likely reflects the important role played by reaction kinetics in carbon nanosystems. It has been established that the typically symmetry forbidden [2π+2π] cycloaddition can be promoted at high pressure due to combination of its negative activation volume and the mixing of energy levels which can in effect create the necessary singly occupied molecular orbital (SOMO) for the reaction to proceed without photoexcitation.³⁶ (The amplitude of this feature is consistent with less than one four-fold ring per benzene formula unit). The lack of sp³-derived structure in the pair distribution function beyond 4–5 Å provides an independent
line of evidence that the long-range order seen in diffraction must be transverse to the axis, i.e. in a non-covalently-bonded direction. An isolated nanothread with this degree of axial disorder (and no neighbors to enforce mutual alignment) readily curves and kinks as shown in the rightmost column of figure 5-11, in a manner suggestive of that seen in the sonicated sample of Fig. 5-4. Note that the features in Figure 5-9 arise almost entirely from intra-thread correlations, since inter-thread pairwise correlations will be washed out by different instantiations of disorder on each thread. It is also possible that the absence of overall long-range sp$^3$-derived axial order in the sample reflects the presence of several distinct species of individually axially well-ordered nanothreads – such as the theoretically predicted (3,0)$^{30}$ and polymer I systems$^{26}$, the cycloaddition-derived structure described below, or the recently predicted polytwistane$^{37}$ – their superimposed longer-ranged features in G(r) being washed out by more subtle long-range heterogeneities.

The intensity, polarization, and frequency of Raman-active modes in carbon materials are often very sensitive to structural details and conformation, providing a Raman spectral fingerprint, typically between 500 cm$^{-1}$ and 1500 cm$^{-1}$, for coupled C-C single bonds. The modeling from the Crespi group predicts a Raman-active C-C radial breathing mode for the (3,0) sp$^3$ nanothread, the Polymer I structure, and three other candidate structures that are disordered by Stone-Wales bond rotations, all in the region from 690 to 820 cm$^{-1}$. In addition to the pristine tubes, the position RBM was calculated for the (3,0) ‘nanotube’ at various pressures and found that the frequency shifts from 747 cm$^{-1}$ at ambient pressure to 814 cm$^{-1}$ at 20 GPa. The radial breathing mode of these sp$^3$ structures is at much higher frequencies than similar modes in sp$^2$ carbon nanotubes$^{38}$ because their
diameter is much smaller. A Raman mode is observed for $^{12}$C nanothreads at 805 cm$^{-1}$ in figure 5-12 on a fluorescence background arising from the small amount of hydrogenated sp$^2$ carbon present$^{39}$.

![Figure 5-12: 633 nm Raman spectra of $^{12}$CH and $^{13}$CH diamond nanothreads. Two carbon modes are observed, RBM and flexure mode, with the proper isotope shift. The asterisks in the $^{12}$CH sample are the steel substrate on which the sample was measured.](image)

The slight discrepancy between theoretical calculation and experiment observation could come from structure disorder, local environment strain, or the computational limits of density functional theory. The isotope shift of this mode observed in equivalent measurements on a $^{13}$C sample identifies it as a C-C vibration ($778$ cm$^{-1}$/805 cm$^{-1}$ = 0.967; compared to the square root of the $^{12}$C/$^{13}$C mass ratio, 0.961). The Raman was collected over a wide range of wavenumber shifts at 633 nm excitation. Power was kept below 10 mW as to avoid damage and heating of the sample. A polarization analysis with 785 nm excitation reveals the mode to be polarized and thus totally symmetric, as would be expected for the radial breathing modes of the (3,0) nanotread. The Polymer I nanotread also exhibits a radial breathing mode that is nearly totally symmetric. This mode symmetry severely constrains the possible Raman mode assignments. Modeling
also predicts a depolarized Raman-active flexure mode with optical character in the region of 930 to 990 cm\(^{-1}\), consistent with the observation of a depolarized C-C mode in the Raman spectrum at 1005 cm\(^{-1}\) (within the accuracy of the calculation).

![Polarized Raman spectra of 785 nm excitation for the \(^{13}\)CH sample. The RBM is found to be nearly totally symmetric and the flexure mode is found to be not symmetric.](image)

For the (3,0) nanothread this mode involves tilting of the linked six-fold rings in this structure relative to each other. Unlike the flexure modes of sp\(^2\) nanotubes, which are not Raman active,\(^{40}\) these modes are Raman active with optical character within the primitive unit cell. Raman modes that are totally symmetric, such as the radial breathing modes for the (3,0) ‘nanotube’ and polymer I structure, should exhibit Raman depolarization ratios \((\rho = I_{\text{perpendicular}}/I_{\text{parallel}})\) less than 0.75.\(^{41}\) A depolarization ratio of 0.65 is observed experimentally in figure 5-13 for a \(^{13}\)CH sample under 785 nm excitation. A partially disordered structure derived from both these ideal structures is the best match to the experimental pair distribution functions, but it appears that the totally symmetric character of the radial breathing mode is at least partially preserved (although a heterogeneous mixture of different species of more well-ordered nanothreads could
provide an alternative explanation). The flexure mode is not totally symmetric and is observed to be depolarized with $\rho=0.75$.

The observation of only two modes in the Raman fingerprint region with shifts and polarization properties consistent with our optical spectrum calculations provides further evidence for the synthesis of $sp^3$ nanothreads. Molecular species that have Raman modes in the spectral regions associated with these two modes can be ruled out because they are not observed in mass spectrometry. Table 5.1 shows relevant characteristic frequencies in the spectral region of 750 cm$^{-1}$ to 1100 cm$^{-1}$, part of the single bond C-C spectral fingerprint region, for hydrocarbon vibrations reported in the Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules and also for candidate diamondoid molecules which have multiple adamantane-like cages.$^{42,43}$ The presence of molecules arising from reaction of benzene under pressure and exhibiting these vibrations can be ruled out from several lines of evidence, thus providing further support for the respective assignments of the observed Raman modes at 805 and 1005 cm$^{-1}$ to radial breathing and flexure modes characteristic of $sp^3$ nanothreads. Furthermore, the Raman polarization analyses are inconsistent with the presence of alkane chains, including long-chain alkanes, which would not exhibit totally symmetric modes in the region of 800 cm$^{-1}$. Cyclohexane, benzene, certain diamondoids, and adamantane would exhibit totally symmetric modes, but are not observed in the mass spectrometry experiments or have Raman shifts inconsistent with those observed (e.g., benzene, cyclobutane, larger diamondoids). Moreover benzene and cyclohexane are liquids that would evaporate upon sample recovery. The presence of isopropyl tertiary carbons would require the formation
of methyl groups from benzene, which would require hydrogen shifts that appear unlikely.

Table 5.1 Characteristic Raman Frequencies of Hydrocarbon Vibrations in the Raman Fingerprint Region.\textsuperscript{42,43}

<table>
<thead>
<tr>
<th>Peak Position (cm(^{-1}))</th>
<th>Vibrational Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>837-905</td>
<td>C-C Skeletal stretch in n-Alkanes</td>
</tr>
<tr>
<td>800-900</td>
<td>Longitudinal Acoustic mode in n-Alkanes</td>
</tr>
<tr>
<td>800-810</td>
<td>C-C(CH(_3))(_3) Isopropyl tertiary carbon</td>
</tr>
<tr>
<td>802</td>
<td>Ring breathing of cyclohexane</td>
</tr>
<tr>
<td>1001</td>
<td>Ring breathing of cyclobutane</td>
</tr>
<tr>
<td>992</td>
<td>Ring breathing of benzene</td>
</tr>
<tr>
<td>1040-1100</td>
<td>CCC antisymmetric stretch in n-Alkanes</td>
</tr>
<tr>
<td>800</td>
<td>C-C Stretch in adamantane</td>
</tr>
<tr>
<td>758</td>
<td>C-C Stretch (Cage breathing) in adamantane</td>
</tr>
<tr>
<td>&lt; 758</td>
<td>C-C Stretch (Cage breathing) in larger diamoindoids ,</td>
</tr>
<tr>
<td>950</td>
<td>C-C Stretch in adamantane</td>
</tr>
</tbody>
</table>

Moreover, these carbons would not have the requisite Raman polarization properties. As diamondoid size increases, the cage breathing mode decreases in frequency to values much below that observed at 805 cm\(^{-1}\).\textsuperscript{144} Multiple allotropes of graphane could provide alternative low-enthalpy high-pressure phases with a 1:1 C:H stoichiometry.\textsuperscript{45} However all known variants of graphane are clearly inconsistent with the measured ~6.4 Å lattice spacing observed in TEM and XRD between weakly bonded structural subunits. Figure
5-14 shows several predicated X-ray diffraction patterns for different graphane subunits and compares it to the experimentally derived total scattering structure function.

![X-ray diffraction patterns](image)

Figure 5-14: Simulated x-ray diffraction patterns for 5 crystalline allotropes of graphane compared with the total scattering structure function from the diamond thread samples. Additionally, the inter layer spacings for each of the graphane structures are far shorter than the striations observed in TEM.

Figure 5-15 shows the sumion chromatogram from the GC-MS of the polymerized benzene taken from a hexane extract.

![Sumion chromatogram](image)

Figure 5-15: Total sumion chromatogram of the recovered nanothread sample. Note small oligomers along with several reaction byproducts.
From the total sumion chromatogram it is possible to observe several byproducts of the reaction. The most common byproducts are biphenyl, naphthalene, m- and p-terphenyl, and an unknown high molecular weight molecule with a strong anthracene base ion. Additionally several dimers, trimers, and tetramers are observed. Chromotographs of the individual dimers, trimers, and tetramers suggest three distinct classes of oligomers or nucleation sites. Full chromatographs can be seen in the appendix. This could be from different nucleation sites result in slightly different propagation methods. This lends credence to the observation that we have no Bragg reflections in the axial direction of the threads.

This new material has a fascinating intermediate nanostructure: the carbon threads can be thought of as “thick” polymers or “thin” nanowires. The presence of multiple covalent bonds across their cross-section (three such “strands” can be seen in Figure 5-11) removes them from the realm of traditional polymers (two-stranded ladder polymers are their closest cousins\(^46\)), while the fact that every carbon atom is a surface atom distinguishes them from all known nanowires (e.g., diamond nanowires previously synthesized by CVD methods\(^32\)). The closest relative to this material is a recently published report on the sintering of functionalized congressane molecules within a SWNT to form a diamond nanowire\(^47\), however this was a template growth method. The lack of both a central hollow and local planarity disqualifies the term “nanotube.”

Crystalline polymers are generally ordered both axially and transversely, while other systems with 2-D order and 1-D disorder are typically irregularly stacked layered materials\(^48\), which is a very different structural limit. The term “nanothread” best captures these unique structural features.
5.3 Mechanistic Insights to Thread Formation

Looking at figure 5-1 it is easy to imagine how an array of hexagonally closed packed bundle of threads can form. When the benzene II crystal structure is viewed down the a- and b- axes one can see a slipped stack of benzene molecules arranged in hexagonally packed columns. These hexagonally packed columns also exist in the benzene II structure when viewed along the c-axis, but this seems like a less probable reaction route. This is because C-H bonds from adjacent columns are interdigitating down the column of molecules. This would prevent two molecules in the same column from getting close enough together to undergo a reaction. In situ X-ray diffraction data collected in a new large volume DAC (LVDAC)\textsuperscript{49} at the advanced photon source with high energy x-rays provides evidence for a topochemical reaction that occurs along either the (100) direction of the benzene II crystal structure. Figure 5-16a shows diffraction data of benzene within the LVDAC. Because the LVDAC has polycrystalline diamond seats, instead of the traditional tungsten carbide, they are x-ray transparent and contribute heavily to massive Compton scattering. Because of this Compton scattering, only the most intense peaks were able to be tracked, the (100) reflections. It can be seen that there is a discontinuity in the compression of the (100) reflection in benzene roughly 20 GPa. Figure 5-16b shows the change in the (100) reflection with pressure. Upon decompression the (100) reflection of the benzene II phase shifts in position to become the (100) reflection of the recovered nanothreads. This continuous transition of the (100) reflection in the starting benzene crystal to the recovered nanothread sample indicates that the reaction is topochemical in nature. The discontinuities present in the change in peak position with pressure (Figure 5-
16b) indicate that the reaction begins at high pressure and not upon decompression as was suggested by previous researchers.

Figure 5-16: a) in situ high energy x-ray diffraction following the (100) Bragg Reflection. b) Tracks the change in (100) peak position with pressure. Not the discontinuities in the upload and download curves which could be indications of chemical reaction.

Additionally the peak position of the (100) peak at the lowest pressure achievable in the LVDAC and the peak position of the (100) reflection in the recovered nanothread sample are still a bit different. This could indicate a second reaction that occurs upon decompression that finalizes the thread formation.

When looking at the theoretically predicted sp³ nanotubes: (3,0) tube, polymer I, and polytwistane, it is difficult to fathom how to create that complex structure from molecular benzene using traditional organic chemistry intuition. However an all sp³ hybridized nanothread can be imagined using traditional organic synthesis routes present within the benzene II crystal. Figure 5-17 shows a proposed reaction mechanism from a single column of benzene molecules extracted from the a-axis of the benzene II crystal to a diamond nanothread. The lowest energy covalent dimer of benzene has been determined to be the result of a [4π+2π] Diels-Alder cycloaddition⁵⁰. This product has been
synthesized via traditional wet chemical techniques, although it is very unstable, reverting back to molecular benzene when warmed above 0°C.  

Figure 5-17: Potential reaction pathways from the benzene II crystal structure to an sp³ nanothread. The leftmost column is a slipped stack a benzene molecules taken form the a-axis of the benzene crystal. It then undergoes a [4π+2π] cycloaddition followed by a zipper polymerization.

However it has been established by the same group that as the number of monomer units increase, the stability of the oligomer of benzene does as well. They even showed that under elevated temperatures and pressures that an all endo-product of hexaene can be formed. We propose that a similar reaction mechanism is occurring within the benzene II crystal along either the a- or b- axes. The geometric constraints of the surrounding crystal does not allow for the resulting all endo-product to bend as it would as a free molecule. The resulting all endo-product is what is proposed to form at high pressure. The resulting polymer has only 66% sp³ bonding and there exists an olefinic backbone. Through a tight binding geometry relaxation performed by Enshi Xu of the Crespi group, it was found that if the all endo-product is constrained to remain straight, the olefinic backbone undergoes a runaway zipper polymerization. This runaway reaction is highly exothermic and is where the slow decompression and kinetic control of the reaction becomes important. Due to the [4π+2π] cycloaddition being prone to cycloreversion it is important to dissipate the heat generated from the reaction. Luckily for us, diamond has
the highest thermal conductivity of any known material, therefore if the decompression rate is kept low the kinetics of the zipper reaction will be slowed and the heat can be more effectively dissipated. If the system is downloaded at a normal rate, the zipper cascade reaction occurs so rapidly that it rips apart the all endo- [4π+2π] cycloaddition backbone. The resulting dangling bonds react without a preferred orientation and result in a highly amorphous crosslinked polymer network, as has been seen in previous reports.

In an attempt to verify this reaction mechanism in situ Raman spectroscopy is underway. At the highest pressures achieved there is no evidence of polymerization. Future work will include monitoring this reaction to even higher pressures, up to 30 GPa, looking for three distinct changes to the spectrum. First, the benzene ring breathing mode at 1000 cm$^{-1}$ should disappear upon the onset of the [4π+2π] Diels-Alder cycloaddition. Additionally the carbon-carbon stretching mode should increase in peak position from 1680 cm$^{-1}$ to around 1750 cm$^{-1}$. This is because the bond distance of the sp$^2$ bonding will change from 1.41 Å of an aromatic bond to the 1.32 Å of a purely olefinic bond. The third change in the Raman spectrum should occur around 3000 cm$^{-1}$. This is the CH stretching region. For C-H stretch of an aromatic compound the peak should be between 3000 cm$^{-1}$ and 3100 cm$^{-1}$ while the C-H stretch to an aliphatic carbon will be below 3000 cm$^{-1}$. This measurement is still ongoing and will be reported along with the in situ diffraction data in a future publication.

5.4 Concluding Remarks

The diamond thread nanostructure promises Young’s moduli potentially in excess of those for sp$^2$ carbon nanotubes$^{30}$ and much in excess of those for traditional, two
stranded, ladder polymers, and unique opportunities for functionalization, doping, and novel microstructures. Most ordered carbon nanomaterials (i.e. sp$^2$ nanotubes, fullerenes) are formed in high-temperature gas-phase reactions. In contrast, our synthesis of ordered sp$^3$ carbon nanothreads occurs at room-temperature via topochemical reaction and thus provides a new means of kinetic control for carbon-based nanomaterials. Aromatic molecules incorporating heteroatoms or substituents can provide alternative nanothread precursors. Photochemistry, thermal treatment, or modification of the cycloaddition chemistry could reduce the reaction pressure. Nanothreads may be amenable to dehydrogenation (especially those of larger diameter), yielding well-ordered mixed sp$^2$/sp$^3$ carbon nanomaterials. The ability to attain ordered products will also open new routes towards understanding the interplay of pressure-induced and photo-induced reaction mechanisms. Substituted nanothreads offer the potential for improved load transfer through covalent bonding, efficiently transferring their mechanical strength to a surrounding matrix and thus allowing for technological exploitation in fibers or fabrics. The negative electron affinity of hydrogen terminated diamond surfaces has motivated the study of nanocrystalline diamonds as field emitters; these hydrogen capped diamond nanothreads may allow for very large electric fields at their ends in view of their small diameters, making them attractive for such applications (in addition to providing a novel geometry and reaction kinetics for overcoming the stringent doping limits encountered in sp$^3$ carbon). Our results may also shed light on the problem of how diamondoids formed in underground petroleum fluids, as the threads are formed under compression with no catalyst or plasma. There are prospects to obtain even better-ordered materials by further
tuning the decompression conditions: a small region of one sample shows hints of axial order with a periodicity close to that predicted by our structural models (Figure 5-18).

![HRTEM micrograph of diamond nanotreads](image)

Figure 5-18: HRTEM micrograph of diamond nanotreads (left) that have axial periodicity as well as transverse periodicity. The image auto correlation function image (right) verifies both axial and transverse periodicity.

Finally, the observation that the linear packing of the nanotreads is broken up by sonication (Figure 5-4) suggests that further work to improve their order or appropriate dispersants may allow for them to be processed in the liquid state, overcoming a key limitation of ladder polymers. These future directions will be expanded in the final chapter of this dissertation.
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6 Concluding Remarks and Moving Forward

Throughout this dissertation I have exhibited how carbon, a seemingly simple element can have a complex and interesting chemistry at high pressure. I have expanded the number of polycyclic aromatic hydrocarbons studied at high pressure in a search for a connection to the work down on cold compressed graphite. Additionally, I have related the starting molecular structure to the microstructure of the amorphous hydrogenated carbon products formed from the high pressure polymerizations. I have investigated a long standing controversy over what occurs to single walled carbon nanotubes at high pressure and determined that metallic tubes preferentially collapse under high non-hydrostatic pressures, leaving the semiconducting tubes for the most part intact. Finally, I have shown that we can gain kinetic control of the reaction of benzene at high pressure by performing a slow decompression of the system. This kinetic control afforded by the slow decompression results in the formation of an new 1-D carbon nanomaterial. After careful characterization we have deemed this new material a carbon nanothread and it is the closest known analogue to an sp\(^3\) hybridized single walled carbon nanotube made to date. These discoveries have impacted the fields of materials science, physics, solid state organic chemistry, and geochemistry and have the potential to be advanced further. In the following chapter I will outline some future work to be completed in our lab on these subjects started by me.

6.1 Advancements Toward a Molecular Analogue to Cold Compressed Graphite

As was stated in chapter 3, the goal of the work on cold compressing was to determine why graphite underwent a reversible sp\(^2\) to sp\(^3\) transition whereas small molecules like benzene\(^1,2\), furan\(^3\), and pentacene\(^4,5\) were historically shown to irreversibly polymerize.
From an analysis of Clar’s aromatic sextet theory\(^6\) a hypothesis was created that for a small molecule to reversibly undergo an sp\(^2\) to sp\(^3\) transition, the molecule had to be fully benzenoid in character, leaving no preferential reaction sites, and be peri-condensed, having carbon atoms that exist on the interior of the molecule.

Experiments were performed on both acene molecules and 2-D PAHa and all, besides triphenylene underwent their expected irreversible polymerizations. The high stability of triphenylene should be investigated in the future to determine at which pressure it will polymerize. As has been seen in melting point experiments and reactitons of PAH mixtures with strong acid, triphenylene is an amazingly stable molecule. However, as is observed in all systems with unsaturated bond, they will eventually become saturated. This would be a nice follow up to an old question posed by Malcolm Nicoll about the overall stability of a double bond\(^7\).

Moving on to molecules that are hypothesized to be reversible under pressure. The synthesized hexabenzocoronene molecule. This molecule and its more soluble and therefore easier to synthesize derivatives could be the best candidate structures for the reversible sp\(^2\) to sp\(^3\) phase transition. These molecules are fully benzenoid in character and they have many internal carbon atoms. We have shown in a previous report that breaking and forming bonds within the basal plane of graphite is more energetically favorable than doing so on the edges of graphene sheets. Hexabenzocoronene and even large fully benzenoid PAHs have been synthesized through an oxidative coupling reaction of hexaphenylbenzene like precursors. Having such a wide array of large graphite like starting structures offers a promising starting point for these experiments. Figure 6-1 shows a number of large fully benzenoid 2-D PAHs
which have been synthesized by the aforementioned method. As stated in chapter 3 peri-
hexabenzocoronene has been synthesized by me in our lab, which we are equipped to do.

A promising thought about this line of research includes that the initial proposal to study this system at the highly competitive HPCAT beamline at the Advanced Photon Source was met with very positive reviews. Researchers there have a long history of investigating cold compressed graphite and found the idea of approaching the problem from a molecular perspective particularly intriguing. This work should be pursued by future researchers within the group.

Not only is the cold compression of small molecules interesting, but another region of interest in solid state polymerization of small molecules will play a role is in the study of nitrogen vacancy centers within diamond. NV$^+$ centers have been intensely studied over the past few years for applications related to spintronics$^{8-10}$. A major technological problem associated with the study of NV$^+$ centers is the controlling the density of NV$^+$s within the system. High pressure, high temperature diamond synthesis has the potential to address this
issue relatively easily. It is well established that small PAHs can readily transform into diamond under pressures of only a few GPa and temperatures in excess of 1300 °C\textsuperscript{11}. By mixing small amounts of indole (figure 6-2) into the hydrocarbon precursor (naphthalene would work) the nitrogen content of the resulting diamond synthesis will be controlled.

Figure 6-2: Indole is a simple nitrogen containing molecule that can be mixed with another PAH such as naphthalene in controlled amounts to make a specific concentration of NV\textsuperscript{+} centers in HPHT synthesized diamond.

With the arrival of the Titan double aberration corrected TEM and new faculty members who have strong interest in NV\textsuperscript{+} centers, this is a project that could be explored quickly through already established collaborations.

6.2 Gaining Deeper Understanding of SWNT collapse at High Pressure

The major breakthrough of the work done concerning the SWNTs under pressure was discovering not a diameter dependent collapse of tubes, but a preferential collapse of the metallic tubes relative to the semiconducting tubes. The future work here seems straightforward. Purifying tubes based on electrical conduction and chirality has been an established technique for some time now. It would first be interesting to examine the collapse of tubes that are bundles of all metallic or all semiconducting in nature. The result of this work would determine what is the difference in mechanical strength of each type of tube. Additionally further purification by chirality would then be able to be done to determine the mechanical strength of each type of tube.
A major roadblock in comparing our result of nanopolyhedral graphite to the two aforementioned reports of an ultrahard phase being formed at high pressure is that no one has thorough in situ characterization\textsuperscript{12-14}. Further studies utilizing \textit{in situ} IXS need to be performed to determine if the high pressure phase is in fact \(\text{sp}^3\) in nature. Additionally, further development of our own in situ DUV Raman spectroscopy would be a good addition to the in situ characterization toolbox. During my graduate career I have modified our in situ DUV Raman spectrometer to perform in situ experiments within a type IIa DAC. This is a very powerful technique for the analysis of ice or wide band gap semiconductors, materials that do not have Raman modes in near that of diamond. However, work has been done to try and probe carbon based materials in situ. As of now the confocality of the instrument is not such that a standard loaded DAC can be used. Research was done to try and create a sapphire anvil cell and pressures upwards of 12 GPa were achieved. Xu et. al. demonstrated the operation of a sapphire anvil cell to 24 GPa\textsuperscript{15-17}. This work is still ongoing and should be pursued further. Sapphire anvils were cut, ground, and polished to have culet sizes on the order of 400 micrometers. These sapphires would break upon preindentation when a T301 stainless steel gasket was used, due to the high hardness of the steel. Therefore, titanium metal was used as the gasket material. Because of titanium’s low hardness, the maximum pressure was limited. To overcome this problem, a composite gasket material should be explored. The hypothesized gasket that would work includes a stainless steel gasket wrapped in a Cu-Be foil. The copper beryllium foil has the tensile strength to support the sapphire anvils upon preindentation into the steel. It also allows for the harder steel to be used allowing for higher maximum pressures. A second technique explored for in situ DUV Raman is to spatially separate the sample being probed from the diamond anvil, much like
that of a laser heating experiment. In this experiment a thin, 20 micrometer, plate of sapphire will be loaded in the DAC between the sample and the diamond anvil, resulting in a sandwich like sample chamber. It is hoped that the increased distance between the diamond anvil and sample will result in being able to probe the sample without interference from the resonantly enhanced diamond anvils.

6.3 Optimization of Benzene to Nanothread Transition

Chapter 5 showed the first kinetically controlled high pressure solid state reaction of benzene to form a crystalline nanothread. However, as was seen in the analysis of the new material there are still several challenges associated with the as synthesized product that need to be addressed. The three main points that will be addressed here are the axial periodicity, residual sp$^2$ content, and the high pressure needed for the reaction.

To address the axial periodicity issue the reaction mechanism needs to be fully figured out. To do this in situ Raman spectroscopy has begun to determine at what pressures the two step reaction pathway occurs. In addition to this more in situ XRD should be considered. The problem we have encountered in the past with in situ XRD is a high background signal from the Compton scattering associated with the diamond anvils. To overcome this challenge, perforated diamond anvils should be considered for XRD experiments. We have attempted to use a perforated diamond anvil in the past, figure 6-3, but it failed at low pressure. Others have successfully used perforated diamond anvils to pressures above the 20 GPa threshold needed in the synthesis of diamond nanothreads form benzene$^{18-20}$. By increasing our current ability to perforate diamonds via a DUV excimer laser we should be able to create highly reliable diamond anvils for in situ XRD of low Z
materials. In addition to gaining a deeper understanding of the reaction mechanism, greater control of the reaction is needed.

To gain control of the reaction we wish to try and perform the reaction of benzene at several different decompression rates (ranging from 10 GPa/hr to .1 GPa/hr) as well as several different temperatures. The current hypothesis is to generate a more ordered material in the axial direction we will need to use low temperature. This is a bit counterintuitive in the sense that the traditional way to increase crystalline order in a solid is to perform a high temperature thermal anneal. I currently believe the driving force towards amorphization in the axial direction results from the highly exothermic zipper polymerization results in retro-Diels-Alder reaction along the initial polymer backbone. By lowering the temperature we should be able to prevent the cycloreversion. Increased axial order is though to be possible in part because of figure 5-18 where beading is observed in the axial direction of the HRTEM micrograph.

As is shown in the ssNMR spectra along with the Raman of the diamond nanothreads, there exists a substantial sp² content in the final product. The GC-MS of a hexane extract
from the recovered nanothreads shows evidence of naphthalene, biphenyl, and two terphenyl isomers. The Raman spectroscopy indicates that the sp\(^2\) carbon is coming from an amorphous carbon component, Figure 6-4.

![Figure 6-4: Visible Raman spectrum of \(^{13}\)CH labeled diamond nanothreads. Notice the G peak indicative of amorphous sp\(^2\) bonding present in addition to the nanothread signature modes.](image)

ssNMR experiments are underway to determine if the sp\(^2\) content of the recovered threads decreases after washing with hexane solvent. To remove the amorphous carbon it may be useful to take a page from the PLV synthesis of SWNTs. In the PLV technique the resulting SWNT bundles are often covered in sp\(^2\) amorphous carbon. The amorphous carbon is typically removed via a peroxide etching method\(^{21}\). A similar method could be applied to the cleaning of the sp\(^3\) nanothreads. It is thought that the diamond nanothreads should be chemically inert.

Because the pressure required to synthesize the diamond nanothreads from benzene is so high at room temperature it will be important to try and determine a way to lower the pressure necessary for reaction. One approach to lowering the reaction threshold for the benzene polymerization is to replace the hydrogen atoms that terminate the benzene ring with
electron donating groups such as methyl groups. It is well established that a higher electron density within the ring of a benzene molecule will result in a lower reaction threshold\textsuperscript{22}. Current investigations of toluene and m- and p-xylene are underway. In addition to using chemical functionalization, temperature could play a major role in changing the reaction threshold pressure. Ciabini has shown that benzene undergoes its irreversible transition at pressures as low as 12-15 GPa at temperatures upwards of 700 K. Because the benzene synthesis seems to follow a two step reaction pathway, we could use high temperatures to initiate the 4+2 Diels-Alder reaction and then lower the temperature before decompression where the zipper cascade reaction is proposed to occur. By lowering the pressure to 15 GPa, larger sample volumes can be used and we can generate a higher yield of sample.

6.3 Moving Beyond C:H Nanothreads

In addition to just optimizing the synthesis of the current diamond nanothread with 1:1 C:H ratio, other more complex nanothread ideas have been explored since the initial discovery. First, the synthesis of a CN nanothread would be very exciting as CN systems have been studied for years as ultrahard materials. Two precursors that would be interesting to study as CN nanothread precursors are pyridine and triazine (Figure 6-5).

![Pyridine and s-Triazine](image)

Figure 6-5: Atomistic representation of nitrogen containing compounds to be used in an attempt to synthesize CN nanothreads from a kinetically controlled cold compression.
Both molecules have been studied under high pressure and have been shown to undergo irreversible room temperature polymerizations at elevated pressures to form amorphous products\textsuperscript{23-25}. Until our work, similar results were observed for benzene\textsuperscript{1,26,27}. We believe that the kinetic control we achieved with the benzene reaction can easily be applied to the CN systems and should be an immediate follow up project.

In addition to adding heteroatoms to the nanothread backbone adding functionality to the capping groups will be very important. A major drawback of these materials, as well as ladder polymers which were mentioned earlier is that they are highly insoluble. Being insoluble severely limits the processability of your polymeric network. By functionalizing the initial benzene molecule before reaction it may become possible to make these materials soluble. The first method of creating soluble nanothreads should be to add greasy sidechains to the initial benzene molecule. These could include either long aliphatic chains, similar to your standard ligands found in quantum dot synthesis\textsuperscript{28}, or t-butyl groups which are commonly used by the Mullen group during their synthesis of large PAHs\textsuperscript{29-32}. By making the nanothreads soluble we will increase their applications and processability potentially even above SWNTs. I will leave these ideas to future group members who will follow with this project.
REFERENCES


VITA

Thomas Fitzgibbons received his Bachelors of Science degree in Chemistry along with a Bachelors of Arts degree in Interdisciplinary Social Sciences with a minor in Political Science from the University at Buffalo, The State University of New York, in the Spring of 2009 with honors. Here he got his first experience with the world of laboratory research under the guidance of Dr. David Watson; while exploring dye sensitized solar cell fabrication. In the summer of 2009 he joined the Chemistry department at the Pennsylvania State University. Under the direction of Dr. John Badding, Thomas Fitzgibbons explored the realm of high pressure solid state chemistry as it pertains to the polymerization of small aromatic molecules into extended carbon networks. Throughout his research Thomas discovered novel reactions involving single walled carbon nanotubes, characterized the microstructure of amorphous hydrogenated carbon networks, and discovered a new form of carbon in an sp$^3$ carbon nanotread. In the summer of 2014, he will begin working full time as a Senior Chemist for the DOW Chemical Company in Freeport, TX.