STRUCTURAL AND CHEMICAL CHARACTERIZATION OF
MODIFIED GRAPHENES FOR HYDROGEN STORAGE

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Doctor of Philosophy

by

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STRUCTURAL AND CHEMICAL CHARACTERIZATION OF
MODIFIED GRAPHENES FOR HYDROGEN STORAGE

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ABSTRACT

The automotive industry is already showing signs of moving beyond a century long dependence on petroleum. The tens of billions of dollars in the electric vehicle (EV) consumer market are a powerful demonstration of this transition. Hydrogen fuel cell electric vehicles also offer a clean alternative to petroleum and have advantages to EVs in some transportation sectors. To grow the hydrogen economy, significant progress must be made in hydrogen storage systems. Adsorbent based storage systems have the potential to lower the pressure requirements while simultaneously improving the storage capacity of these systems.

The research presented in this dissertation focuses on the development and characterization of new adsorption storage systems based upon modified graphene. Early work involved substitutional doping of activated carbon with boron to alter the surface chemistry of the adsorbing surface with the goal of improving adsorption strength. Boron-doped samples were characterized with X-ray Photoelectron Spectroscopy to correlate specific boron chemistries to adsorption performance metrics. A maximum of 2% substitutional doping was observed. Later work focused on framework materials built up from graphene oxide and benzene diboronic acid (GOFs). GOFs are an ideal material to study the structural response of an adsorbent during adsorption due to their layered structure and relatively well-defined pore geometry. To study GOF's adsorption-induced structural response, we built a computer-controlled gas handling system for *in situ* neutron diffraction measurements at the University of Missouri Research Reactor. For the first time, supercritical adsorption-induced structural change was observed. Through correlation of adsorption and structural data, we are able to predict the rate of expansion in GOF based on the critical temperature and vdW diameter of the adsorbate molecule.

Chapter 1 – Introduction

The automotive industry is already showing signs of moving beyond a century-long dependence on petroleum oil. The tens of billions of dollars in the electric vehicle (EV) consumer market are a powerful demonstration of this transition.¹ Technical advances in battery performance have facilitated these market developments, but so have environmental and societal pressures. Concerns over fossil fuel depletion, fuel recovery methods and, notably, carbon emissions linked to climate change have all provided the impetus for the emerging EV market. Battery powered EVs have had market success despite significant concerns over refueling time.

Hydrogen fuel cell electric vehicles (FCEV) have not had the same commercial success as EVs. While hydrogen FCEVs promise shorter fill up times than EVs, progress is required in production, transportation, and storage of H₂. The current vehicular storage technology is compressed hydrogen, with pressures up to 700 bar being used in commercial vehicles. Current tank volumes are 35 gallons, much larger than for similarly sized gasoline vehicles. Compressed hydrogen remains the commercial option despite decades of research into alternative storage technologies.^{2,3}

Storage of hydrogen has, in part, been such a popular research area due to the vast numbers of new materials that have been produced: zeolites, chemical hydrides, activated carbons and MOFs are just a few of the various categories of materials that have been studied.⁴⁻⁸ Carbon based materials have been a particularly active area of study due to the emergence and popularity of graphene, carbon nanotubes, and their derivatives.^{9,10} Despite the variety of carbon materials created, each physisorbs molecular hydrogen roughly proportional to their specific surface area, a trend commonly referred to as

Chahine's rule.¹¹ The trend is approximately 2 wt% for every 1000 m²/g at 77 K.¹² Some modest improvements to these values have been suggested through pore size optimization and alteration of adsorption surface chemistry, but major improvements have not been successful.^{13,14} Furthermore, the surface areas obtained with traditional carbon synthesis methods have seemed to reach an upper bound of ~ 3000 m²/g. For progress to continue in hydrogen storage materials a new level of understanding and synthetic control must be obtained. This level of control must be realized at the nanometer and even atomic level. Graphene is a good starting point for this path of discovery, as it already exists as an atomically thin sheet, but graphene powder by itself has minimal available pore space.

One proposed method to generate pore space within a graphene-based material is to introduce spacer molecules (diboronic acids, diamines, 1-octanol, etc...) between individual sheets of graphene oxide.^{12,15-19} These Graphene Oxide Frameworks (GOFs) succeed in generating surface areas > 500 m²/g with a well-defined and stable network of sub-nanometer pores. GOFs have not, as of yet, improved upon the ultimate storage capacity of adsorbent systems, but their bottom up synthesis approach provides an avenue to develop new pore structures and geometries.

The nature of the bonding between the spacer molecules and the graphene oxide has been the matter of debate.^{12,15} A more rigid framework was proposed by Burrell *et al.* with spacer molecules covalently crosslinked to adjoining graphene sheets, whereas Mercier *et al.* preferred a model of GOF with adjoining sheets held together by non-bonding interactions between the spacer molecules and oxidized areas of the graphene sheet. The proposed bonding arrangements between linker and graphene could have

differing, and interesting, consequences for the dynamics of the system during adsorption. A true framework material would likely not allow for significant change in pore structure due to the relatively strong bond energies compared to energies of adsorption. A non-bonding model could present a more dynamic system, for which the strength of the interactions between graphene-linker and graphene-adsorbate are on the same order of magnitude. As the adsorbed gas approaches saturation, further compression of the adsorbate may be energetically more costly than separation of the sheets, leading to an adsorption-induced expansion.

The flexibility of certain types of metal organic frameworks (MOFs) has been an active area of research²⁰⁻²². The adsorption-induced breathing of MIL-53 has been well reported in the literature, but the structural change has only been observed with subcritical fluids, such as water²³ and CO₂²⁴. Upon adsorption of nitrogen, ZIF-8 has been reported to undergo a gate-opening transition in a completely closed-off pore architecture; but again, this transition occurred under sub-critical conditions²⁵. In GOFs, a supercritical adsorption-induced expansion is plausible due to the coupling of the graphene sheets through relatively weak non-bonding linkages. For the purpose of storing alternative fuels, having material properties that are activated by supercritical fluids is crucial, because both hydrogen and methane are supercritical at likely storage conditions.

Two fundamental quantities to consider when assessing a hydrogen storage material are porosity and adsorbed density. Here I wish to demonstrate that within a dynamic pore structure these quantities can be coupled to maximize storage performance,

but first I will put the two quantities in the context of DOE storage targets for hydrogen materials.

Figure 1-1. Important hydrogen storage quantities to keep in mind when considering potential storage materials. The current technology used by car manufactures is 700 bar tanks at room temperature.

In Figure 1-1, the DOE stored hydrogen density target is plotted with relation to the current technology and liquid hydrogen. The current technology used by industry involves storage at a pressure of 700 bar at room temperature. It falls about 20% lower than the target and requires high-pressure tanks. The density of liquid hydrogen at 20 K and 1 bar vapor pressure is about 40% higher than the target. We can use the liquid density as a touchstone for assessing what combination of porosity and stored density is required to achieve the DOE target in a porous material. Porosity is defined as

$$\phi \equiv \frac{V_{\text{pore}}}{V_{\text{pore}} + V_{\text{skeletal}}} \quad (1-1)$$

where V_{skeletal} is the non-accessible volume of the material. Then the stored density of the material can be expressed as

$$\rho_{\text{stored}} = \rho_{\text{pore}} * \phi \quad (1-2)$$

Figure 1-2. Schematic representation of a slit-shaped pore. $w \approx 3.35 \text{ \AA}$.

Equation 1-2 provides a basic physical relationship for achieving the DOE requirements, where ρ_{pore} is the density of the adsorbed film. ρ_{pore} is a difficult quantity to measure directly; but, by making reasonable estimates of it, we can determine whether a material with a given porosity may be used to reach the DOE goals. If we assume that a liquid-like density of 71 g/L (see Figure 1-1) is adsorbed in the pore, then the required porosity to achieve the DOE goal of 50 g/L would be 0.7. We can then ask what is the porosity of an idealized GOF structure, and is there sufficient pore space within the material to achieve the targeted density of 50 g/L? To get a rough answer to this question, we first make two simplifying assumptions: 1. the linkers take up no appreciable volume; and 2. the graphene sheets are sufficiently large that edge effects do not contribute significantly to the pore volume. Then the porosity is simply $\Gamma/(\Gamma + w)$, where Γ is the height of the pore and w is the thickness of an individual graphene sheet. Using this simplified expression of the porosity, we can then plot the stored density as a function of $(\Gamma + w)$, the interlayer spacing of GOF. In Figure 1-3, we plot the stored density as a function of

interlayer spacing assuming an adsorbed film density that saturates at the hydrogen liquid density of 71 g/L. In this simple model, an interlayer spacing of 11.5 Å and an adsorbed film density of 71 g/L achieve the DOE target. Such a pore geometry and density would entail multilayer adsorption of 3-4 layers of hydrogen.

Let us now refocus on the coupling of porosity and adsorbed density. As mentioned above, a slit-shaped pore must be large enough to accommodate multilayer adsorption, but the weak interaction strength between carbon and hydrogen and between hydrogen molecules implies that such multilayers would only be stable at reduced temperatures. One method of improving film stability and adsorbed density is by narrowing the pores such that the adsorbed molecules experience a multiwall interaction²⁶; but this, of course, decreases the porosity and reduces the space available for multilayer growth. An attractive means of balancing high porosity with strong adsorption is to have a material that expands upon adsorption. When the material is contracted, and gas is adsorbed in the first and second layers, the adsorbed film is stabilized by the multiwall interaction and a relatively high storage density is achieved at low pressure. At high pressure, pore expansion would increase porosity and allow

additional adsorbed layer formation. Whether or not an expanding pore diameter could be a mechanism for stable multilayer film growth formation is unknown.

Figure 1-3. Assuming an adsorbed film density equal to that of liquid hydrogen, an interlayer spacing of ~ 11.5 Å is required to achieve the DOE storage target in an idealized model of GOF.

Chapter 2 **Design and Characteristics of a Gas Handling System for *In Situ* Neutron Scattering**

2.1 *Introduction*

A gas handling system for *in situ* neutron scattering allows one to combine the thermodynamic measurements of an adsorption experiment with the structural and dynamic characterizations of a scattering experiment. This combination of measurements is particularly interesting when the interaction between adsorbent and adsorbate induces an unusual behavior at some point during the adsorption process. By doing the neutron scattering experiment *in situ*, one can zero in on the unusual behavior without having to correlate to a separate experiment. A measurement of the scattering process in the environment of a high-pressure gas requires a radiation source that can penetrate the containment vessel. The neutron's scattering length varies with atomic number randomly such that penetrable metals can be used for containment while still achieving high signal to noise. This chapter will focus on the technical design, characteristics, and measurement methods of the gas handling system used for our *in situ* experiments.

2.2 *Schematics and Specifications*

Our Gas Handling System (GHS) was specifically designed to achieve research utility while still falling within the safety guidelines for use at Beamports A, C, and D at the University of Missouri Research Reactor. The GHS is comprised of:

- the gas manifold (Figure 2-1)
- the sample station (Figure 2-2)

- the pneumatic lines
- the electronic components (Figure 2-3)

The components of the manifold are labeled: To Cryostat (port to the sample), Vacuum Pump, Vacuum Gauge [vacuum transducer (LPT1)], 245 bar transducer (HPT), Gas Inlet port, To Exhaust (gas exhaust port), and a 150 mL Lecture Bottle. The 245-bar pressure transducer is from OMEGA with accuracy determined by assuring the 5 points of a NIST traceable calibration curve fall within 0.08% full scale of best straight line fit. The LPT1 is from MKS model 974b QuadMag™ Cold cathode/MicroPirani™/Piezo Vacuum Transducer, which measures pressures in the range of 10^{-8} Torr to 1500 Torr. Room temperature measurement at the manifold is measured with a Dallas DS1820 one-wire temperature sensor.

Figure 2-1 Schematic of the MURR gas handling system manifold.

All pneumatic valves are Swagelok stainless steel bellow valves with ¼" VCR connections, SS-HBVCR4. Six normally-closed pneumatic valves (PV0-5) open/close the ports to each component excluding the high-pressure transducer which monitors the gas manifold at all times. A normally-open pneumatic valve (PV6) separates the gas-loading section of the manifold to the sample/vacuum pump section of the manifold. Thus, PV6 will allow for purging of the sample side without affecting the gas-loading side, a procedure which will be utilized for desorption measurements. To prevent damage in the event of an over-pressurization, a high-pressure relief valve (PRV) will allow gas to escape to the MURR gas exhaust line (Figure 2-2). The pressure relief valve will activate when pressures exceed 175 bar.

Figure 2-2. Schematic of the MURR gas handling system sample environment in the blue dewar.

All components are rated to pressures at 242 bar or higher; the only exceptions being the LPT1 and the cryo-capable manual valve (CMV) at the sample cell. The LPT1 is isolated from the high-pressure environment by two valves, PV3 and MV2. The CMV is rated to 172 bar with a built-in safety factor of 3:1, and thus will be protected by the 175 bar pressure-relief valve. The GHS will be connected to a pressure cell which is typically mounted either directly on the sample table or in the cryogenic environment (Figure 2-2).

Figure 2-3 Schematic of MURR gas handling system electronic components.

The data acquisition and control hardware (schematic in Figure 2-3) allows automated collection of data required for measurement of an adsorption isotherm. A separate excel spreadsheet transforms all the raw data into adsorption quantities; this analysis is the subject of the section on excess adsorption. The automated data collection

routines and user controls are carried out with custom-built LabView software.

Pneumatic valves are actuated by solenoid valves, which themselves are controlled by the solid-state relays of National Instrument's USB-6525 DAQ device. Custom-built Circuit Board 2 provides the appropriate power and wiring connections between the USB-6525 and the solenoid valves. The state of each valve is indicated on an LED board within the LabVIEW software, routed through Circuit Board 1 and the digital inputs of USB-6525. All electronic components are physically separated from the gas manifold; the gas manifold is located on a shelf above the electronics, so that in the case of a gas leak the gas will rise away from the electronics.

2.3 *Volume Calibration*

An adsorption measurement requires knowledge of the amount of gas contained in our system. We can map temperature and pressure values to a density through NIST density tables; but, to determine the actual number of molecules contained, we need to know the different volumes of our system. To determine these volumes, two separate measurements are taken where gas is allowed to freely expand after a valve, PV-5 in Figure 2-1, is opened. The first measurement consists of reading the pressure and temperature before and after a known gas freely expands from the dosing volume, V_d , into the reactor volume, V_r (see Figure 2-4 for a schematic of these volumes). After converting pressure and temperature into density, ρ , and assuming conservation of particle number during the free expansion, we have the following relationship between the two unknowns, V_d and V_r :

$$\rho_{1,d,i}V_d + \rho_{1,r,i}V_r = \rho_{f1}(V_d + V_r) \quad (2-1)$$

The second measurement, similar to the first, consists of reading the pressure and temperature before and after a known gas expands from the dosing volume to the reactor volume, but now the sample cell contains a known displacement volume (in our case, the displacement volume is a steel rod). Again, converting pressure and temperature to a density and assuming conservation of particle number, we have

$$\rho_{2,d,i}V_d + \rho_{2,r,i}V_r = \rho_{f2}(V_d + V_r - V_{dis}) \quad (2-2)$$

Solving equations (2-1) and (2-2) for the dosing and reactor volumes gives

$$V_d = -V_{dis} * \left[\frac{(\rho_{1,r,i} - \rho_{1,f})(\rho_{2,r,i} - \rho_{2,f})}{\rho_{1,d,i}(\rho_{2,r,i} - \rho_{2,f}) + \rho_{1,r,i}(\rho_{2,f} - \rho_{2,d,i}) + \rho_{1,f}(\rho_{2,d,i} - \rho_{2,r,i})} \right] \quad (2-3)$$

$$V_r = -V_{dis} * \left[\frac{(\rho_{1,d,i} - \rho_{1,f})(\rho_{2,r,i} - \rho_{2,f})}{\rho_{1,d,i}(\rho_{2,r,i} - \rho_{2,f}) + \rho_{1,r,i}(\rho_{2,f} - \rho_{2,d,i}) + \rho_{1,f}(\rho_{2,d,i} - \rho_{2,r,i})} \right] \quad (2-4)$$

2.4 Calculation of Excess Adsorption

2.4.1 Overview

Our desire is to calculate an adsorption isotherm defined as the amount adsorbed on our sample as a function of 3D gas pressure at constant temperature. Our experimental method for calculating the adsorption isotherm is commonly called the *volumetric method*. In the volumetric method, calculation of amount adsorbed is derived from measurements of volume, temperature and pressure. The volumetric method is distinguished from the gravimetric method, where direct mass measurements are made using a mass balance.

The fundamental principle behind the adsorption measurement is conservation of particle number. The measurements of temperature, pressure and volume during an experiment

determine the number of molecules in the gas phase. During the adsorption process, some gas molecules will leave the bulk gas phase and enter the adsorbed phase. The gas molecules removed from the gas phase will show up as a loss of mass because our measurement devices are only sensitive to the bulk gas phase. We take this lost mass to be that which is adsorbed.

The determination of mass in the bulk gas phase is made by mapping measurements of temperature and pressure to a density through NIST density tables. The state points in these tables are derived from most accurate thermodynamic and transport equations available²⁷. To complete our measurement of adsorption, we need to be able to determine the pressure and temperature in *each* part of our system. A rough schematic of our system is shown in Figure 2-4. A valve, PV-5 in Figure 2-1, separates the dosing volume, V_d , from the sample-containing reactor volume, V_r . When measuring adsorption at temperatures below room temperature, the reactor volume is divided into a warm volume, $V_{r,w}$, and cold volume, $V_{r,c}$. The system is equipped with one high pressure transducer in the dosing manifold where all pressure measurements are made. The system is also equipped with one temperature sensor at the dosing manifold and one Si diode temperature transducer at the sample cell.

Figure 2-4. Illustration of the volume breakdown of our gas handling system. A valve (PV-5) separates the dosing the volume from the reactor volume. For cryogenic measurements, the total system volume is divided into two temperature regimes: red (room temperature) and blue (sample temperature).

2.4.2 Room Temperature Measurements

For room temperature measurements, the cumulative excess adsorption is calculated with the analytic expression in Eq. (2-5) [See Table 2-1 for all quantities appearing in Eq. (2-5)]. During an adsorption measurement, the amount of gas contained in the reactor volume is first determined with the valve separating the dosing and reactor volumes, PV-5, open. PV-5 is then closed, the dosing volume is pressurized and bulk gas measurements are made to determine the amount of gas contained in the dosing volume. Then the valve is opened and the bulk gas measurements are made again after sufficient equilibration time. Mass that appears to be “lost” through these bulk gas measurements is assumed to be adsorbed. The excess adsorption at the n th data point is given by:

$$M_{\text{exc ads},n} = \sum_j^n [(\rho_{d,i} - \rho_{d,f})_j * V_d + (\rho_{r,i} - \rho_{r,f})_j * (V_r - V_s - V_{gw})] \quad (2-5)$$

Calculation of excess adsorption requires knowledge of the various volumes in the system. The dosing and reactor volumes are calculated according to the method in the

previous section. The skeletal sample volume and glass wool volume are calculated from helium pycnometry measurements.

Table 2-1. Definitions for symbols appearing in calculation of excess adsorption.

Symbol	Definition
$M_{\text{exc ads}}$	Mass of excess adsorption
$\rho_{\text{d,i}}$	Density of gas initially in dosing volume
$\rho_{\text{d,f}}$	Density of gas finally in dosing volume
$\rho_{\text{r,i}}$	Density of gas initially in reactor volume
$\rho_{\text{r,f}}$	Density of gas finally in reactor volume
V_{d}	Dosing Volume
V_{r}	Reactor Volume
V_{gw}	Volume of glass wool
V_{s}	Sample Skeletal Volume
V_{system}	$V_{\text{r}} + V_{\text{d}}$

The quantity calculated in Equation (2-5) is referred to as the Gibbs excess adsorption, or commonly just called the excess adsorption. The Gibbs excess is not a true measurement of the number of molecules in the adsorbed film. Excess adsorption is the mass of the adsorbed film minus the mass of an equal volume of gas, as shown in Figure 2-5. The reason for this discrepancy is that we claim to know the skeletal volume of the adsorbent through a helium pycnometry measurement, but we do not claim to know the volume of the film. So, when we subtract the bulk gas in Equation (2-5), we are subtracting some molecules in the adsorbed film. To know the absolute amount adsorbed, we must assume a film volume. An estimate of the film volume can be made from the by assuming it is equal to the total pore volume determined from a subcritical nitrogen isotherm. This approximation is still not ideal because the film volume will be a function of the amount adsorbed. Nevertheless, we can make a simple estimate of the absolute adsorption as

$$M_{\text{absolute}} = M_{\text{exc ads}} + \rho_{\text{bulk}} * V_{\text{pore}} \quad (2-6)$$

Figure 2-5. Schematic of the Gibbs excess adsorption.

2.4.3 Blank Isotherm

While in theory $M_{\text{exc ads},n}$ as defined in Eq. (2-5), should be sufficient for our calculation of an adsorption isotherm, in practice it is crucial to subtract a blank isotherm. A blank isotherm is defined as the measured adsorption by the empty sample cell. While the physical adsorption by the empty sample cell should be minimal, the measured adsorption may be non-zero due to small leaks, thermal instabilities, or non-linearity in the pressure transducer. Subtracting the blank isotherm from the sample isotherm allows us to account for some of our unknown sources of error. The blank isotherm is calculated with Eq. (2-7) where the adsorption at the n^{th} data point is given by:

$$M_{\text{blank},n} = \sum_j^n [(\rho_{\text{d},i} - \rho_{\text{d},f})_j * V_{\text{d}} + (\rho_{\text{r},i} - \rho_{\text{r},f})_j * V_{\text{r}}] \quad (2-7)$$

The blank and sample isotherms will not necessarily have a 1-1 correspondence in pressure values. Therefore, the blank isotherm is fit with a polynomial to interpolate between data points. The final result for calculating adsorption at the n^{th} data point is:

$$M_{\text{exc ads},n}^{(1)} = M_{\text{exc ads},n} - M_{\text{blank},n}^{\text{Fit}} \quad (2-8)$$

2.4.4 Cryogenic Measurements

For measurements made at $T < \text{room temperature}$, the reactor volume must be divided into separate temperature regions to calculate the bulk gas properties of each region. The simplest way to do this division is to take some effective fraction of the reactor volume as being at the sample cell temperature, and the complementary fraction being at room temperature as measured at the manifold. Subscripts with “w” and “c” refer to the warm and cold part of the reactor volume, respectively. To be clear, this is a simplification of our system. In reality, a thermal gradient will be established between the line leading into the cryogenic environment and the cold source; this gradient may not even be monotonic depending upon the specifics of the sample environment. Since we only have two temperature outputs, at either end of the temperature gradient, no additional accuracy is gained by a further subdivision of the temperature regimes. We then calculate adsorption based on bulk gas density measurements in three separate volumes:

$$M_{\text{exc ads},n} = \sum_j^n [(\rho_{d,i} - \rho_{d,f})_j * V_d + (\rho_{r,w,i} - \rho_{r,w,f})_j * V_{r,w} + (\rho_{r,c,i} - \rho_{r,c,f})_j * (V_{r,c} - V_s - V_{\text{gw}})] \quad (2-9)$$

When the reactor volume is at room temperature, Eq. (2-9) will simplify to Eq. (2-5).

2.5 Cold Volume Determination

Determination of the values for $V_{r,w}$ and $V_{r,c}$ is not always straightforward for each system due to the existence of thermal gradients and thermal disequilibrium during measurement. Furthermore, the effective cold volume of the system may be dependent upon the temperature of the measurement. To determine the effective cold volume of the reactor

two different methods were tried. Each method will be discussed along with their respective advantages and disadvantages.

2.5.1 Isosteric Cold Volume Determination

The first method developed here for determining a fractional cold volume is an isosteric cooling method. By conserving the total number of particles in the system while slowly cooling the sample, the drop in pressure can be correlated to an effective cold volume.

The cold volume of the reactor at some arbitrary thermodynamic state, f, is given by:

$$V_{r,c} = \frac{\rho_{w,f} - \rho_{w,i}}{\rho_{c,i} + \rho_{w,f} - \rho_{w,i} - \rho_{c,f}} * (V_{\text{system}}) \quad (2-10)$$

The initial state, i, is measured at room temperature. The advantage of the isosteric method is that in theory the fractional cold volume can be determined as a function of sample temperature over a wide range of temperatures in one experiment. In reality, the isosteric method only works if the sample cooling curve matches the equilibration curve of the cryostat, or if breaks are made in the cooling curve to allow for cryostat equilibration. For the blue dewar cryostat used for experiments at MURR, the existence of long equilibration times can lead to significant errors in cold volume determination.

The temperature is only measured at the sample cell in the cryostat; however, the gas supply line contains ~8.5 cm³ of volume inside the cryostat, and the temperature equilibration time of this line is hard to know. Analysis of isosteric data to determine the cold volume fraction of our blue dewar cryostat system at 81.5 K is shown in Figure 2-6. Approximately 30 hours pass between the sample cell reaching 81.5 K and the system reaching thermal equilibrium. As seen in Figure 2-6, not allowing sufficient equilibration time will lead to an *underestimation* of the cold volume fraction. Furthermore, long

equilibration times mean that small leaks in the system have time to compound. These leaks would lead to an *overestimation* of the cold volume. The isosteric method was not optimal for experiments using the sample environment available at MURR but could be useful sample environments with shorter or more well understand equilibration rates.

Figure 2-6. The effective cold volume as measured through the isosteric method reveals that the thermal equilibration time for our system is at least 30 hours.

2.5.2 Blank Isotherm Cold Volume Determination

The other method for determining fractional cold volume is to measure a blank isotherm at the desired adsorption isotherm temperature and adjust the cold volume fraction to minimize the excess adsorption. The reactor volume is divided into two separate volumes, $V_{r,w}$ and $V_{r,c}$, but there is only one free parameter to adjust since $V_{r,w} + V_{r,c} = V_r$ has been determined previously. Each point in the blank isotherm is calculated with Eq. (2-11) and then V_c is adjusted in order to minimize $\sum_n M_{\text{blank},n}$.

$$M_{\text{blank},n} = \sum_j^n [(\rho_{d,i} - \rho_{d,f})_j * V_d + (\rho_{r,w,i} - \rho_{r,w,f})_j * V_{r,w} + (\rho_{r,c,i} - \rho_{r,c,f})_j * V_{c,w}] \quad (2-11)$$

The blank isotherm method has the advantage of determining the cold volume under similar thermal gradient and thermal equilibration conditions as the actual sample isotherm. As with the room temperature blank isotherm, the blank isotherm at cryogenic temperatures is not identically zero after minimization with the cold volume fraction (see Figure 2-7). Subtraction of the blank isotherm from a sample isotherm is required to not falsely attribute this adsorbed quantity to the sample.

Figure 2-7 The blank isotherm of hydrogen at 81.5 K is plotted with varying cold volumes. A cold of 3.75 cm³ gives the smallest adsorption.

2.5.3 Comparison with Other Labs

Comparison of our results with other labs is important in validating our instrument and methodologies, but studies have shown significant variation between measurements at

separate labs. Zlotea *et al.* led a round robin test, where 14 independent laboratories measured adsorption on the same sample, with results commonly varying by 10% or more²⁸. To test the design and calibration of our instrument we have measured adsorption of hydrogen at ~80 K on a commercially available standard activated carbon, MSC-30, and compared to values obtained in the literature on the same sample²⁹. Our experimental results are compared with those from NREL, CalTech and the All-CRAFT group at the University of Missouri (Figure 2-8). The shape of our isotherm agrees well with the isotherm from NREL with a maximum around 50 bar. Our excess adsorption is slightly lower at pressures below 40 bar. This discrepancy could be due to our isotherm being at a slightly warmer temperature. We are also limited to 140 °C when outgassing the sample beforehand due to the indium seal used in our sample cell. All-CRAFT outgasses their sample to 200 °C and the other groups are thought to do something similar. Agreement with all three data sets seems good considering these differences. Our data is within 10% of the average isotherm values.

Figure 2-8. Experimental results are compared with those from NREL, CalTech and the All-CRAFT group at the University of Missouri.

Chapter 3 Graphene Oxide Frameworks: Synthesis and Characterization

3.1 *Introduction*

With graphene only recently discovered³⁰, the testing and understanding of its possible applications is still in its infancy. While many applications have focused on graphene's unique electrical properties, another possible application is as a building block for hydrogen storage devices.³¹ Any hydrogen storage device needs to be largely void space. By using graphene as the core component of an architecture, one could imagine stacking sheets with interspersed void spaces to achieve a highly porous material. Due to the strong interest in graphene and other two dimensional materials, assemblies of these materials has been an active area of research. Van der Waals heterostructures, where isolated atomic planes are reassembled into designer materials with layer by layer precision, have recently been fabricated and investigated.³² The focus of this chapter will be on the synthesis and characterization of Graphene Oxide Frameworks (GOFs). These GOFs are *not* fabricated with a layer-by-layer synthesis procedure, but, nonetheless, show a semi-ordered porous structure with graphene as the core building component. First I will discuss the material precursor, graphene oxide, then review work that has been done on graphene oxide frameworks, and finally look at our own synthesis procedures and the associated structural and pore space characterizations.

3.2 *Graphene Oxide*

Graphite oxide has been known about for many years, but has recently received renewed attention as a precursor for graphene.^{10,33,34} Graphite oxide is a layered material where graphene layers are separated by a spacing of about 7 Å. Each graphene sheet is oxidized on both top and bottom by a variety of oxygen functional groups. The oxygen groups fill the interlayer space between the graphene sheets, meaning graphite oxide is nonporous. Graphite Oxide is a non-stoichiometric compound; there is no unique structural model for graphite oxide because of the variety of oxygen functional groups that exist and the varying degree to which each material has been oxidized. Even the interlayer spacing will vary some amount based on the precise synthesis conditions.³⁵

Due to the lack of porosity, pure graphene oxide is not a good candidate for a hydrogen storage material. Graphene oxide, however, can be modified to introduce pores into the material. The most straightforward way of doing this is by removing oxygen in a partial reduction procedure either with heat or chemical treatment.^{10,36} In either procedure, oxygen is removed leaving behind gaps in voids in the interlayer space. Surface areas as high as 450 m²/g were achieved with these methods, but additional increases were not achievable as further oxygen reduction forces a collapse of the generated pore space.

One unusual property of graphite oxide is the structural response to various solvents. Unlike pure graphite, the oxide is hydrophilic. Water and alcohols will induce a swelling of the graphite oxide layers by as much as a factor of 2.^{37,38} Hydrated graphite oxide has even been shown to have a negative volumetric compressibility; when the hydrated graphite oxide is pressurized in a diamond anvil cell up to 1.3 GPa, the lattice

spacing is observed to increase continuously by 30%.³⁷ As much as 2-3 water layers may be intercalated between the graphene oxide sheets.³⁹ The enormous structural expansion of graphite oxide in water or alcohol suggests that it would be useful for solution-based intercalation of relatively large molecules.

3.3 Graphene Oxide Frameworks: A Literature Review

Pure graphite oxide is nonporous and thus not a good candidate for hydrogen storage applications, but methods for generating pore space within GO have been an active area of research. One method for generating pores makes use of the swelling properties of GO to introduce spacer molecules between the graphene sheets. A synthesis using an intercalation procedure was originally proposed by Burress *et al* in 2010.⁴⁰ The synthesis entailed dissolving benzene (1,4) diboronic acid in methanol and then intercalating the solution into graphite oxide. The intercalated material is next heated at 90 °C. The authors proposed a reaction of the boronic acid with the hydroxyl groups of

the graphite oxide resulting in a covalent cross-linking of the sheets as shown in Figure 3-1. They named their crosslinked material Graphene Oxide Framework (GOF).

Figure 3-1 Structural model of GOF with reaction between hydroxyl groups proposed by Burress *et al.*⁴⁰

The formation of the boronic ester crosslink was demonstrated with XPS by monitoring the intensity of the C 1s electron binding energy. They observed an increase in the intensity of a peak at 287 eV with increasing linker concentration. This peak at 287 eV is commonly attributed to a carbon atom which is bound to no more than one oxygen atom, as would be the case in the formation of the boronic ester crosslink. Carbon bound to a single oxygen, however, is already prevalent in graphene oxide in the form of hydroxyl groups. Therefore, claiming that the cross linking has occurred from interpretation of XPS data is inconclusive. Nevertheless, an increase in the spacing between graphene sheets was observed with X-ray diffraction after intercalation of the benzene diboronic acid, as shown in Figure 3-2. The *d*-spacing of the GOF materials was shown to be a function of the initial concentration of benzene diboronic acid that was used in the synthesis. The *d*-spacing increased from ~ 7 Å lattice spacing for pure GO to asymptotically approach 10.5 Å for linker concentrations above 1:1 linker: GO mass

ratio. The surface area also improved after insertion of the linker, increasing from 20 m²/g for the control GO up to 470 m²/g for the 1:1 linker: GO ratio. 470 m²/g is relatively low for hydrogen storage materials, but the authors claimed the material had anomalously high hydrogen uptake for its surface area. For this reason, GOF was an interesting material to study provided its surface area could be improved^{17,18,41}.

The basic model of covalently crosslinked graphene oxide sheets was later questioned by Mercier *et al*¹². The basis of their argument was that swelling should not be observed in a material that is crosslinked with covalent bonds. Instead, they observed a material with interlayer spacing that increased from 10.5 Å to 15.3 Å when subjected to an excess of water as shown in Figure 3-3. An alternative model of GOF was proposed, where the benzene diboronic acid molecules are physically adsorbed between oxidized areas of adjacent graphene sheets. The surface area is generated by a methanol reduction and removal of oxygen that is not stabilized by contact with the benzene diboronic acid. Thus, the methanol essentially etches out a porous network in the material by removing oxygen and leaving interconnected capillary space surrounding the parallel BDA linkers.

Figure 3-2 GOFs show an increase in d -spacing as compared to the graphene oxide precursor⁴⁰. The mass ratio of the precursor materials is plotted versus interlayer spacing in the inset.

Figure 3-3 GOF materials synthesized by Mercier *et al.* showed sample swelling when subject to an excess of methanol and water. They argued that this swelling precluded the crosslinking of graphene sheets¹².

Mercier *et al.* attempted to optimize the synthesis parameters of GOF to obtain a material with maximum surface area and maximum interlayer spacing. The parameters of linker concentration and reaction time were varied. The authors found that lattice spacing depended strongly on the length of the reaction time. The results of the different reaction times are shown in Figure 3-4. A reaction time of 24 hours generated materials with the largest d -spacing of 10.71 Å. The sample that was allowed to react for 96 hours had a d -spacing of just 7.39 Å and a surface area of 56 m²/g.; the authors concluded that after 96 hours the framework will collapse due to prolonged reduction of oxygen by methanol. The next parameter that was optimized was the mass ratio of graphene oxide to linker (GO:BDA). Three linker concentrations were tested: 1:1, 1:3, 1:6. The linker concentration of 1:3 was found to generate material with the largest surface area.

Figure 3-4 Mercier *et al.* optimized reaction time as a synthesis parameter. They found that a reaction of 24 hrs produced samples with the largest interlayer spacing.¹²

Mercier *et al.* also measured hydrogen uptake of their GOF material at pressures up to 100 bar. Despite promising initial reports of ~1 wt% at just 1 bar by Burrell *et al.*, hydrogen uptake at high pressure and 77 K was 1.5 wt%. The uptake saturated around a pressure of 35 bars of H₂ (see Figure 3-5). According to Chahine's rule, 1.5 wt% is slightly better than one would expect for a carbon material with a surface area of ~500 m²/g. Interestingly, the BET surface areas of GOF samples were measured before and after loading with hydrogen at high pressure. The surface area was observed to decrease by as much as 50% after pressurization, suggesting a partial collapse of the material.

Figure 3-5 Hydrogen adsorption measurements by Mercier *et al.* They observed a hydrogen uptake that is slightly improved over what one would expect given the surface area. Interestingly, a decrease in surface area was observed for some sample after pressurization with hydrogen. Surface areas before H₂ measurements are reported in parenthesis when available.

GOF materials were also studied by Hung *et al.* but using a different linker molecule.¹⁶ Three different diamine monomers were used: ethylenediamine, butylenediamine, and p-phenylenediamine. During the synthesis, GO and a diamine monomer were suspended in water. The suspension was run through a porous substrate that acted as a filter. The deposited material was then heated at 80 °C to promote cross-linking between GO and diamine. Hung *et al.* conducted the same sort of hydration studies as Mercier, in which the interlayer spacing of the sample was measured both in a

dry state and in excess of water. Interestingly, the diamine monitors did not undergo a significant lattice expansion in the hydrated state. The absence of a lattice expansion under hydration is consistent with a true covalent cross-linking of the graphene sheets when a diamine linker is used.

3.4 *Synthesis Procedure*

3.4.1 Graphene Oxide Synthesis

Graphene oxide was made using a modified Hummer's method.⁴² The steps of the synthesis are:

1. 65 mL of sulfuric acid is placed in a 500 mL Erlenmeyer flask with a stir bar. The flask is placed in a in an ice bath. The ice bath is placed on a stirrer plate with a heater. The stirrer is turned on.
2. Preheat Al beads to 40°C at this time.
3. The sulfuric acid temperature is measured with a thermometer. Once the sulfuric acid is at 0 °C, 3 grams of graphite flakes and 1.5 grams of sodium nitrate are added. This is then stirred for 10 minutes to allow for complete mixing.
4. 8.5 grams of potassium permanganate is then added to the sulfuric acid slurry. This is done in 1 gram aliquots to prevent the solution from exceeding 20 °C.
5. Once the final aliquot is added and the effervescence has reduced, the stir plate is slowed down.
6. The flask is removed from the water bath and the stir plate heater is set to 40 °C. This will be maintained for 30 minutes. The mixture should thicken into a paste. If the paste is too thick, the stir plate is shut off.
7. The flask is placed in a water bath to keep the solution below 90 °C in step 7.
8. Heat the beads to 90 °C at this time.

9. After 30 minutes, 130 mL of water is added to the paste. This is done extremely slowly. Once it is thin enough, the stir plate is turned back on. The temperature of the solution is kept below 90 °C by decreasing the rate of water addition.
10. The temperature of the solution is maintained at 90 °C for 15 minutes.
11. Warm water is added to bring the solution up to 400 mL. This is kept at 40 °C using the stir plate heater.
12. Up to 100 mL of 30% hydrogen peroxide solution is added until the solution turns bright yellow. This is kept at 40°C for 15 minutes.
13. The stir plate is then shut off and the solution is left overnight in order for the graphite to precipitate out.
14. The solution is carefully poured off the top, leaving the graphite oxide behind.
15. More water is added, and the solution is mixed and allowed to settle again.
16. Steps 13-15 are repeated until the pH is neutral.
17. The graphite oxide is removed from the flask and freeze dried.

After the graphite oxide has been freeze dried, XRD measurements are made to confirm that a layered structure is present with an interlayer spacing of ~ 7.5 Å. The synthesized GO had an interlayer spacing of 8.1 Å, which is slightly larger than typical. This increase could be explained by the GO being slightly hydrated after the freeze drying or if the sample was more oxidized than normal. The FTIR spectrum of the GO was also measured to confirm that the material has been extensively oxidized. For the FTIR measurement, the GO is pressed into a KBr pellet and the signal is read in transmission mode. Peaks at 1725 cm^{-1} , 1400 cm^{-1} , and 1100 cm^{-1} are attributed to the presence of carbonyl, hydroxyl and epoxide groups, respectively.

Figure 3-6. Confirmation of layered structure of graphite oxide. The interlayer spacing of 8.1 Å is relatively large for a graphite oxide.

Figure 3-7. FTIR spectrum of graphite oxide prepared as described above. The presence of multiple oxygen functional groups is noted.

3.4.2 GOF Synthesis

GOFs were made using the optimized synthesis parameters established by Mercier *et al.*¹²

A mass ratio of 1:3 GO: Benzene-1,4-diboronic acid (BDA) from Sigma-Aldrich was added to methanol. The solution was placed on a vortex shaker to dissolve the acid and disperse the GO and then decanted into a metal jacketed acid digestion vessel from Parr Instrument Company. The vessel was placed in an oven at 90 °C for 24 hours. After removal from the oven, the solution was decanted into a falcon tube and centrifuged to separate the GOF from solution with the extra methanol and BDA decanted off.

Centrifugation was repeated multiple times, adding methanol each time, to remove excess BDA. The sample was then dried in a vacuum oven at 60 °C.

3.5 *Structure and Micropore Characterization*

Three batches of GOF were made, each following the same procedure. Each batch was characterized with XRD and nitrogen adsorption to confirm that the GOFs shared characteristics with other materials reported in the literature. With insertion of benzene diboronic acid, GOFs in the literature had shown an increase in interlayer spacing of ~ 2 Å and a surface area of around 400 m²/g. All three GOFs demonstrated the appropriate increase in interlayer spacing (Figure 3-8), but only Batch3 showed an increase in surface area commensurate with the accepted properties (Table 3-1). With an interlayer spacing of 10.28 Å and a surface area of 390 m²/g, Batch2 was the best candidate for the *in-situ* neutron scattering that is the subject of Chapter 4.

Figure 3-8. XRD results from three different batches of GOF3. All three batches were made following the optimal recipe identified by Mercier *et al.* The interlayer spacing obtained from these batches of samples are consistent with other values reported in the literature.

The XRD measurements were taken with the sample exposed to air after outgassing at 80 °C for 24 hours. The radiation source was Cu $k\alpha$ with wavelength 1.54 Å. The interlayer spacing of Batch2, 10.28 Å, was slightly larger than what would be measured during the neutron scattering measurements. One possible reason for the difference could be the exposure to air. The Sherrer crystalline dimension, $\tau = \frac{\kappa\lambda}{\beta \cos \theta}$, was also extracted from the XRD data, where τ is the crystalline domain size, κ is a shape factor chosen to be 0.9, λ is the x-ray wavelength, β is the FWHM of the 001 reflection, and θ is the Bragg angle. The crystalline dimension of GO is ~13.7 nm and GOF2_Batch2 is 16.9 nm. Interestingly, both dimensions correspond to about 17 stacked sheets.

Figure 3-9. Sub-critical nitrogen isotherms of all three GOF3 batches. The larger adsorption at low pressure of Batch2 suggests higher number of small pores. The slightly increased d -spacing of Batch3 compared to Batch1 and Batch3 may allow the nitrogen to explore a larger network of pores.

Table 3-1. BET specific surfaces area obtained from the above nitrogen isotherms. Batch2 is consistent with surface areas measured by Mercier *et al.* and Burress *et al.*

Sample	Specific Surface Area (m ² /g)
GOF3_Batch1	60
GOF3_Batch2	390
GOF3_Batch3	120
GOF3_Mercier	420

Figure 3-10. Extended hysteresis loop observed in GOF3_batch2.

All subcritical nitrogen measurements were taken on a Quantachrome Autosorb 1-c. Samples were outgassed at 80 °C before measurement and then not exposed to air before nitrogen loading. The BET surface area was determined with a P/P_0 range of 0.01 to 0.03, suitable for nanoporous materials. The pore size distribution of each batch was extracted from the nitrogen data using the QSDFT⁴³ model for slit-shaped pores. Batch2 showed the highest percentage of slit shaped pores $< 10 \text{ \AA}$, which we assume to be pore space existing between the parallel graphene sheets in the ideal GOF model. Even batch2, though, had about 50% of pore volume $> 10 \text{ \AA}$. The source of these pores is assumed to be edge effects, angled sheets, and interparticle voids. While pores with

Figure 3-11 Pore size distribution generated from the nitrogen isotherms in Figure 3-9 using the QSDFT model assuming slit shaped pores. Batch2 has many narrow pores, suggesting that nitrogen can intercalate and adsorb in the interlayer space.

widths > 10 Å make a significant contribution to the total pore volume, their contribution to the total surface area is less significant (Figure 3-13). The narrower pores will have a larger surface area to volume ratio. The more commonly reported value for total specific surface area is the BET value. From the cumulative surface area plot, we can read the fraction of pores less than 10 Å and compare to the BET SSA. In the case of GOF3_batch2, about 77% of the 390 m²/g BET SSA (295 m²/g) comes from pores with width less than 10 Å. An extended hysteresis loop was observed between the adsorption and desorption legs of nitrogen in GOF3_batch2 (Figure 3-10). This hysteresis loop was one of the early indications that the pore structure may be changing as a function of amount adsorbed. Such a hysteresis loop is not one of the canonical sub-critical nitrogen adsorption plots enumerated by the IUPAC.

Figure 3-12. The cumulative and differential pore volumes of GOF3_Batch2. The differential pore volume is the same as plotted in Figure 3-11.

Figure 3-13. The cumulative surface area of GOF3_batch2 using the QSDFT model for slit shaped pores. ~75% of the surface area is derived from pores less than 10 Å in width.

3.5.1 Linker Concentration

In the course of a more rigorous modeling of our system, we may wish to know the ratio of linker molecules to carbon atoms. According to results from PGAA, the boron weight percent of the sample is 4%. To know the linker to carbon atom ratio we would need to know at least two of the three concentrations of boron, carbon and oxygen in our system. Since we only know boron at this point, we can make an assumption, based upon what others have found in the literature, for the mass ratio of carbon to oxygen to be 2:1^{12,40}. We then have two equations with which we can solve for the ratio of boron to carbon, and, thereby, the ratio of BDA to carbon.

$$\frac{M_O + M_C}{M_B + M_O + M_C} = 0.96 \quad (3-1)$$

$$\frac{M_C}{M_O + M_C} = \frac{2}{3} \quad (3-2)$$

Substituting Eq. 2 into Eq. 1, we find that the mass ratio of carbon to boron is 16:1 and thus the atomic ratio of C: BDA is 29:1.

Chapter 4 – Observation of Adsorption Induced Structural Changes by *In Situ* Neutron Scattering

4.1 *Motivation*

Motivation for studying adsorption induced structural changes can be found in both applied and fundamental modes of inquiry. Applications include hydrogen storage and gas separation. Investigation of nanoscale structure and basic interactions with various gases are of fundamental interest. In the following sections, I will discuss just a few examples of these interesting motivations.

4.1.1 Nanoscale Ordering in GOF

GOFs fall under the category of nanoscale materials made from graphene and graphene precursors. In modeling GOFs, the bonding and orientation of the linker molecule has been a matter of debate.^{12,15,17} For a more detailed summary of this debate, please see Sec. 3.2. Burrell *et al.* synthesized the material in 2010.¹⁵ They observed an order of magnitude increase in both surface area and total pore volume after insertion of benzene diboronic acid (BDA) between graphene sheets as well as a 3 Å increase in interlayer spacing, compared to the graphene oxide precursor. These observations were explained with a covalently cross-linked model where boronate ester bonds linked both sides of the molecule to opposite graphene sheets. The work by Burrell *et al.* was followed by the group of Dr. Talyazin in Umea, Sweden. After looking at the effects of many different synthesis conditions, their group proposed an alternative model¹² with graphene sheets separated by horizontal BDA molecules. The BDA molecules are not covalently linked

to the graphene, but, instead, are stabilized between the sheets by van der Waals attraction to oxidized parts of the graphene. Their group argued against covalent crosslinking after observing a 13.5 Å interlayer spacing of fully hydrated GOF, arguing that covalent bonds would neither stretch this much, nor break under these conditions. They also argued against the possibility of a pillared model with one end of the linker covalently bonded to a graphene sheet; they observed a collapse of the GOF structure after a 96-hour reaction time, something they argued would not occur if a covalent bond had formed. Observation of an adsorption induced expansion in GOF would provide a further challenge to the covalently cross-linked model, and support either a pillared or a pure van der Waals bonding model. The relatively weak interaction between adsorbate and graphene surface would not be strong enough to induce an adsorption-induced expansion of the layers in the covalently bonded cross-linked model. On the other hand, if the primary interaction determining the layer separation in GOF is the van der Waals interaction between BDA and oxidized areas of the graphene sheet, one might expect to see a layer expansion at high pressure.

4.1.2 A Corresponding States Principle for Adsorption Induced Expansion

Figure 4-1. Each of the 10 gases plotted deviates from ideality, as measured by the compressibility factor, to about the same degree when measured at the same reduced temperature and pressure. Plot taken from Thermal Physics (1999).⁵

According to the principle of corresponding states, all gases, when compared at the same reduced pressure and temperature, deviate from ideality to about the same degree. The reduced temperature and pressure are defined as the measured value divided by the critical value (for example, $T_r = T/T_c$). This principle is well summarized by Figure 4-1, where the compressibility factor is plotted as a function of the reduced pressure, P_r , and each line corresponds to measurements taken at a particular reduced temperature, T_r . An ideal gas has a compressibility factor of 1.0; and, as the state of the gas approaches the critical point, the more the compressibility factor will deviate from 1.

The remarkable feature of this plot is that all the different gas species, of which 10 are plotted below, have nearly the same compressibility factor when measured at the same value of T_r and P_r . The compressibility factor is a macroscopic measurement, but we can attempt to understand the corresponding state behavior from a microscopic analysis. Real gases deviate from ideality due to interparticle attraction that is not accounted for in the ideal gas model. The stronger this interparticle attraction, the more easily a gas will overcome its thermal energy and form a condensed phase. This relationship between interparticle interaction and phase change can be expressed more formally; for most classical gases, the well depth of the interparticle potential (the Leonard-Jones model for example) is directly proportional to the critical temperature, $\epsilon \cong kT_c$.⁴⁴ By observing the behavior of different gases at the same reduced temperature, one accounts for the differences in interparticle attraction.

Supercritical adsorption in a porous carbon is a decidedly more complicated system than the compressibility of a fluid. However, similar to the corresponding states of a pure fluid, a theorem of corresponding states of adsorption was observed for different gases adsorbed in porous carbons⁴⁵. Quinn *et al.* studied the adsorption of six different gases: Ar, CO, H₂, CH₄, N₂, and O₂. Despite the gases having different strengths of adsorption, when each isotherm was measured at the same reduced temperature, $T_r = 2.36$, five of the six gases were adsorbed in approximately the same amount when plotted versus reduced pressure (Figure 4-2.). The only anomalous gas was hydrogen, which was adsorbed in greater quantities than the other gases. Quinn attributed the relatively large uptake of hydrogen to its ability, with smaller molecular size, to explore small pore spaces that were unavailable to the larger gas molecules. Kim *et al.*

followed with computational work on the subject of the hydrogen's deviation from corresponding state behavior, arguing that size effects were important for materials with very small pore sizes, but that for purely mesoporous materials, the deviation of hydrogen could be explained solely by quantum effects.⁴⁶

With the theorem of corresponding states being successfully extended from a pure bulk fluid to a more complex system of supercritical adsorption in a porous material, one wonders whether the principle of corresponding states might be further extended to the physical response of a material during adsorption. The successful extension of

Figure 4-2. Adsorption on carbon follows a similar law of corresponding states as bulk gases as measured by Quinn⁶. When measured at the same reduced pressure and temperature, classical gases adsorb in the same amount. These particular measurements were performed at $T_r = 2.36$.

corresponding states of bulk fluids to adsorption relied upon the fact the parameters of the adsorption potential are related to the interparticle pair potential through combination rules. As long as the dominant interaction in our system of adsorption induced expansion can be related to the simple interparticle pair potential, then we may be able to devise a principle of corresponding states. As such, the structural response of GOF is an ideal system to study because the layered porous material is likely held together not by covalent bonds, but by non-bonding intermolecular interactions. If the energy scale of the adsorbate's intermolecular potential is comparable to the ordering energy of the GOF layers (i.e. the interaction between linker and graphene sheet), then changes in the interlayer distance of GOF after adsorption may be relatable to the intermolecular pair potential through combination rules.

4.2 *Experimental Setup*

Neutron diffraction data was collected on the two-axis diffractometer (2XC) at MURR (Figure 4-3), with a neutron wavelength of 4.33 Å. No collimator was placed between the graphite monochromator and the sample. The beryllium filter was maintained at liquid nitrogen temperatures during the experiments. A 1" slit-width was used at the beam aperture. Neutrons were counted for ~3 million monitor counts (~45 minutes) at each arm position. This counting time gave a (001) GOF peak height of ~2,000 counts above background. Background in the relevant Q -range was 15,000-30,000 counts depending upon the quantity and type of gas in the beam. The diffraction pattern at each pressure took ~24 hours to complete. The 2XC has 5 detectors separated nominally by 15°. Due to the long count times involved, the detector arm was scanned through only

$\sim 8^\circ$. At the beginning of each isotherm, though, a full window scan, rotating the arm through 20° , was completed on GOF and the graphene oxide. An example full window scan is plotted in Figure 4-4. Within the Q -range available, only the first reflection corresponding to interlayer separation is resolvable. The very small peak around $1.6 \text{ \AA}^{-1}$ is characteristic of the glass wool used to contain the powdered sample. A more extended Q -range was measured on the PSD (Position Sensitive Detector) diffractometer at MURR's beamport-D, as shown in Figure 4-5. The only additional information the larger Q -range provides is location of the (100) in-plane peak of graphene.

Figure 4-3. Schematic of 2XC neutron diffraction experimental set-up for monitoring the adsorption induced expansion of GOF3_batch2.

Figure 4-4. The diffraction pattern of graphene oxide (top) and GOF (bottom). The full Q -range available on 2XC is plotted. Both samples are contained in the aluminum pressure cell under vacuum.

Figure 4-5. The diffraction pattern of graphene oxide (top) and GOF (bottom) as measured on the PSD at MURR. No higher order (00 l) peaks are observed.

In the following section, the interlayer spacing will often be reported without plotting the diffraction pattern from which it was determined. Each interlayer spacing value was determined by fitting a Gaussian with a linear sloping background. The plots in Figure 4-6 are for hydrogen adsorption at room temperature, but all interlayer spacings for methane, xenon and measurements at reduced temperatures were analyzed in the same manner. The error bars of the interlayer distances are derived from the error of X_c in the Gaussian fitting parameters, specifically,

$$\Delta d(001) = \frac{\delta d}{\delta q} * \Delta q_c = -\frac{2\pi}{q^2} \Delta q_c \quad (4-1)$$

, where $q_c \equiv X_c$ (see Figure 4-6).

Figure 4-6. Plots of the typical GOF (001) peak. The peak is fit with a gaussian with a linear background. (LEFT) GOF3_batch2 under vacuum. (RIGHT) Fit Parameters.

4.3 Results

4.3.1 Adsorption Isotherms

Hydrogen excess adsorption, defined in Equation (2-5), was measured on GOF3_batch2 at two different temperatures: 293 K (room temperature) and 78 K. Hydrogen is the only supercritical gas to be adsorbed on GOF for which adsorption isotherms have been

published in the literature; high-pressure measurements were performed by Mercier *et al.* at both room temperature and 77 K.¹² The amount adsorbed by GOF3_batch2 was slightly less than the sample produced by Mercier *et al.* The difference in excess adsorption of about 15% corresponds to the difference in measured specific surface area of the two samples; the linear relationship between surface area and hydrogen excess adsorption has been well established in the literature¹¹. The hydrogen adsorption results give us further confidence that our GOF3_batch2 sample is representative of samples in the literature and that our methods for calculating excess adsorption are reasonable. In addition to hydrogen, adsorption of xenon and methane on GOF3_batch2 was also measured at 293 K. These measurements are characteristic of supercritical adsorption inside of a material with very narrow pores; the isotherms have a steep increase in adsorption followed by a plateau around 20 bar [Figure 4-9 and Figure 4-10]. The xenon measurement was limited by the relatively low bottle pressure of 48 bar. An attempt was made to measure the adsorption of methane on GOF3_batch2 at 233 K, but due to the inability to maintain a constant fractional cold volume, $V_{r,c}$ in Equation (2-9), the excess adsorption could not be determined. Maintaining a constant cold volume requires that the 4-foot-long capillary feed through in the cryostat maintains a constant temperature gradient throughout the measurement. For measurements at 77 K, the capillary line can be thermally anchored to the outer jacket of the blue dewar to maintain the temperature gradient. However, for methane at 233 K we did not anchor the capillary to the outer jacket as we did not want to form a methane ice plug in the line. Consequently, the thermal gradient appeared to vary as a function of time and how much gas was in the line. However, diffraction data versus pressure for methane adsorbed on GOF2_batch2 at 233

K can still be accurately measured. Figures 4-9 – 4-11 show the excess adsorption as a function of pressure. The excess adsorption, as detailed in section 2.2, is the most experimentally direct measurement of adsorption; but, it is not equivalent to the total amount adsorbed. When comparing the amount adsorbed to the interlayer spacing of GOF, we would like to make the comparison with absolute adsorption, the total amount stored within the pores of the material, defined in Equation (**Error! Reference source not found.**). We can plot the absolute adsorption of all gases in one figure by changing the adsorption units to mol/kg (Figure 4-12). The absolute adsorption is always greater than the excess adsorption, but the difference is more significant at high pressure (Figure 4-11).

Figure 4-7. The excess adsorption of hydrogen measured on GOF3_batch2. The results are consistent with hydrogen isotherms measured by Mercier *et al.* and are reproducible.

Figure 4-8. Hydrogen adsorbed on GOF3_batch2 at 78 K.

Figure 4-9. Methane adsorbed on GOF3_batch2 at 293 K.

Figure 4-10. Xenon adsorbed on GOF3_batch2 at 293 K.

Figure 4-11 Xenon adsorbed on GOF3_batch2 at 293 K. Comparison of excess and absolute adsorption. Excess adsorption is the same as in Figure 4-10 but with different units.

It is important to note that the absolute adsorption is not equivalent to the amount of gas stored between the layers of GOF, since some gas will be stored in non-interlayer pore space. From the cumulative surface area plotted in Figure 3-13, we see that in our sample GOF3_batch2 ~23% of the available surface area may come from larger pores. However, we assume that absolute adsorption will be proportional the gas stored in the interlayer pore space.

Figure 4-12. The absolute adsorption is a measurement of the total amount of gas adsorbed within the pores.

4.3.2 Neutron Diffraction

Each of the adsorption isotherms measurements plotted above were performed with the sample mounted in neutron beam at 2XC. At each point along the isotherm, a neutron diffraction pattern was collected after the gas was allowed to equilibrate. It should be noted that a neutron diffraction pattern was not collected for two low pressure hydrogen

data points at 78 K; it was not clear at the time of the measurement just how quickly the excess adsorption would saturate for this gas. Performing these measurements *in situ* allows us to make a direct correspondence between the interlayer spacing and the amount adsorbed. Before making this correlation, first we just look at the dependence of the interlayer spacing on pressure for each gas (Figure 4-13). Not only does the interlayer spacing systematically change as a function of pressure, but the change is as large as 4%. To our knowledge, this is the first time a structural change of this magnitude has been observed during supercritical adsorption. As a function of pressure, the effect is largest with xenon. Furthermore, the effect produced by xenon is still increasing when the maximum bottle pressure of 48 bar is reached. For each gas, the rate of expansion falls off quickly as a function of pressure. However, from the adsorption data, we also know that the rate at which molecules are adsorbed falls off quickly as a function of pressure. To see how the effect varies as a function of molecules adsorbed between the layers of GOF, we convert the x -axis to absolute adsorption. The rate of expansion has gone from sharply decreasing as a function of pressure, to being linear but with an inflection point at ~ 2 mol/kg.

Figure 4-13. The expansion of the GOF(001) interlayer distance as a function of pressure varies for each gas. The largest observed expansion (~4%) is for xenon and is continuing to expand at the maximum observed pressure. The expansion is always fastest at low pressure and then slows down.

Figure 4-14. The GOF (001) interlayer spacing increases as a function of the absolute amount of gas adsorbed in the pores. Unlike the plot of $d(001)$ versus pressure, the expansion does not slow down at higher absolute adsorption, but the expansion does vary for each gas.

4.4 Discussion

The first feature of the neutron data to understand is simply the presence of the adsorption induced expansion. This expansion is not obvious given the original model of GOF with covalently crosslinked sheets. After observing an expansion of 4% with xenon and the presumed further increase that would occur at higher pressure, the covalent cross-linked model can be ruled out; we can be confident that xenon would not interact chemically with the ether bonds forming the linkages, and this degree of chemical bond elongation is energetically unfavorable. To further support this claim, preliminary molecular dynamics simulations have been performed with methane adsorbed in a crosslinked model of GOF with no evidence of expansion (see appendix A).

Differentiating between the pillared model and the horizontal BDA non-bonding model is more difficult. Both models showed an expansion in preliminary MD simulations; but, to make a quantitative comparison the simulation size will need to be increased. From the simple considerations of bond lengths and complementary steric effects, the expected interlayer spacing of a pillared model is around 12.5 Å, compared to the observed 9.5 Å *d*-spacing. Simulation results of the parallel model also result in an initial interlayer spacing that is 1.5 Å smaller than experimentally observed. However, the simulation is performed with graphene layers rather than graphene oxide layers. The Mercier model of parallel linkers stabilized by oxygen surface groups on the graphene would result in a larger initial interlayer spacing; simulations with oxygen surface groups are planned. Nonetheless, the simulation results give further credence to the horizontal linker model. Our data is most consistent with the non-bonding horizontal linker model proposed by Mercier *et al.*

With the data in Figure 4-14 we can return to the discussion of applying a corresponding states analysis to adsorption-induced expansion. Plotting the interlayer spacing as a function of absolute adsorption, we see that all three gases produce a different magnitude of expansion at high pressure. The differences are expected due to the different adsorption potentials for each gas. Although the functional form of the interlayer spacing $d(001)$ is unknown, it will presumably be a function of the bulk gas pressure and temperature, the number of molecules adsorbed, and the strength of molecular adsorption, as well as inherent properties of the GOF material. We make the ansatz that, whatever the functional form, the dominant term will be a product of the number of molecules adsorbed between surfaces y , N_{ads} , and the depth of the interaction potential of molecule x on carbon surface y , ϵ_{xy} .

$$d(001) = F(N_{\text{ads}} \cdot \epsilon_{xy}) \quad (4-2)$$

We can recast Equation (4-2) in terms of the single-phase pair potential through use of combination rule

$$d(001) = F(N_{\text{ads}} \cdot \sqrt{\epsilon_{xx}\epsilon_{yy}}) \quad (4-3)$$

ϵ_{yy} is an inherent property of the adsorbent material and will not be a variable in our comparison of states. We would like Equation (4-3) to be in terms of thermodynamic state variables. Employing the proportionality between the pair potential and critical temperature, $\epsilon_{xx} = k_b T_{c,x}$, we have

$$d(001) = F(N_{\text{ads}} \cdot \sqrt{T_{c,x}}) \quad (4-4)$$

Equation (4-4) is the general form of our corresponding states function for $d(001)$. It states that, no matter what van der Waals gas is adsorbed between graphene-oxide sheets, the interlayer expansion will be a function of $N_{\text{ads}} \cdot \sqrt{T_{c,x}}$. We can test the validity of

our ansatz by scaling the x -axis in Figure 4-14 by a factor of $\sqrt{T_{c,x}}$. To maintain the x -axis units of moles, we have normalized all the critical temperatures to that of xenon. Our corresponding states function, Equation 4-4, has been written in terms of N_{ads} , the amount of gas in the interlayer pore space. There is no way to determine N_{ads} experimentally. We assume, though, that N_{ads} is proportional to the experimentally determined absolute adsorption, N_{absolute} , and that the proportionality is the same for each gas. The exact value of this proportionality is irrelevant to our corresponding states function because it is the relative magnitude of expansion between the gases that is important. After scaling, the methane and xenon data points now *nearly* lie on the same curve. Their overlap indicates that our ansatz was a good starting point; the interlayer expansion does appear to be a function of $N_{\text{ads}} \cdot \epsilon_{xy}$.

Table 4-1. Parameters used in scaling of the adsorption data

Gas	T_c (K)	b (L/mol)
Xenon	289.7	0.051
CH ₄	190.6	0.043
H ₂	33.2	0.027

Figure 4-15. CH₄ and H₂ are scaled to have same the interaction strength with the graphene sheets as for Xe.

Hydrogen, however, has not fallen onto the same curve as the other two gases.

Hydrogen is a smaller molecule than either methane or xenon. Thus, it is reasonable to assume that the same pore space could accommodate more hydrogen molecules than for either methane or xenon. To account for this molecular size effect, we perform a further scaling of the data along the x -axis in seeking a “universal” curve for all three gases. We assume the three molecules to be spherical in shape and that they fill the space between GO sheets with the same packing fraction. Because the pore opening in GOF (Γ in Figure 1-2) is ~ 6.2 Å (the interlayer spacing minus the thickness of an individual graphene sheet) and the molecular diameter of hydrogen is ~ 3 Å, we take hydrogen to

have 3 degrees of freedom and normalize by the volume occupied by an H_2 molecule relative to xenon.

The molecular diameters of methane and xenon are close to the dimension of the pore, so we assume that only one layer of these gases will fit in the interlayer pore space. Therefore, to account for size differences between methane and xenon, we normalize only by the vdW footprint area and not the volume of the molecule. For the volumes we take the van der Waals size parameter tabulated in the handbook of chemistry and physics⁴⁷. The footprint area scale factor is taken to be the vdW ratio to the 2/3 power. After scaling hydrogen and methane by the size factor relative to xenon, we see that all three gases fall close to a common curve. After this size scaling, the

Figure 4-16. A “universal” curve of expansion is obtained by scaling CH_4 and H_2 to have the same size and interaction strength with the graphene sheets as for Xe. Dashed lines are guide to the eye.

hydrogen data points have shifted to low coverage, which is a result of the relatively weak interaction of H₂ with the GO sheets and its small size.

Next, we note that for both Xe and CH₄ the expansion of the interlayer spacing increases more rapidly above an inflection point, $N_{\text{ads,c}}$, at ~ 1.5 mol/kg. We think that the change in expansion rate may be related to the completion of a fully compressed monolayer within the pore. Further addition of adsorbate molecules will lead to a buckling of the monolayer plane which might explain the increase in rate of expansion. In an ideal GOF material, with only uniform slit shaped pores, the specific surface area could then be related to $N_{\text{ads,c}}$ by assuming that adsorbed molecules form a triangular lattice in the monolayer. Then the specific surface area is

$$\text{SSA} = N_{\text{ads,c}} * (2r)^2 * \sin 60^\circ \quad (4-5)$$

where r is the vdW radius of the adsorbate. For several reasons, however, making a quantitative connection between the observed inflection point and the SSA is problematic. Perhaps the biggest problem in making the connection is the inhomogeneity of the sample. Our model assumes that we have uniform slit shaped pores, but the pore size distribution in Figure 3-2 provides evidence that a non-negligible (~ 23 %) amount of the sample's SSA arises from pores with width > 10 Å. Pores of this size would likely be due to void spaces between small grains, grain defects, or non-parallel graphene sheets. The relative rates of adsorption for these different types of pores is not clear and will affect when monolayer completion occurs in the interlayer pores. Another problem with our simplistic model has to do with the idea of a "monolayer" in pores of near molecular dimensions, especially when the adsorbing surface has inhomogeneities due to chemically bound oxygen groups remaining from the precursor graphene oxide material.

It is perhaps more appropriate to think of the gas molecules either adsorbing at particular sites within the confines of the pore or arranged in a distinct distribution associated with the particular pore geometry and chemical structure. For the sake of completeness, we will follow through with the monolayer analysis and compare to the standard BET surface area. Assuming a Xe footprint area derived from a molecular radius of 2.16 Å and taking $N_{ads,c} = 1.5 \text{ mol/kg}$, the SSA of the GOF from Eq. 4-5, in this idealized model, would be $146 \text{ m}^2/\text{g}$. The measured BET surface area is $390 \text{ m}^2/\text{g}$.

We can also make the argument that at the inflection point of 1.5 mol/kg it becomes easier to separate the sheets of the GOF than it is to further compress the gas between the sheets. At near liquid densities the repulsive part of the gas interaction potential makes compression of the fluid more difficult. By estimating the density of the adsorbed gas and comparing to the liquid density at the critical point, we can make a qualitative estimate of the relative compressibility of the adsorbed gas to the elasticity of the GOF. With absolute adsorption, we have already calculated the total amount of gas stored within the pore space of the material. To estimate the adsorbed density, we normalize the absolute adsorption by the total pore volume of the material,

$$\rho_{ads} = \frac{M_{abs}}{V_{pore}} \quad (4-6)$$

The total pore volume has been determined from the measurement of a subcritical nitrogen isotherm. It is important to note that the liquid density changes significantly as a function of temperature near the critical point. The value plotted in Figure 4-17 (determined from NIST density tables) will differ from reported liquid densities further from the critical point. The inflection point in terms of adsorbed density falls

remarkably close to the liquid density for both xenon (Figure 4-17 left) and methane (Figure 4-17 right).

Figure 4-17. The density of the adsorbed fluid inside the pore space of GOF is compared to the liquid density at the critical point. For both xenon (left) and methane (right) the rate of adsorption induced expansion increases as liquid density is approached.

4.5 Conclusions and Future Work

In conclusion, we have measured the expansion of GOF induced by adsorption of xenon, methane and hydrogen. The observed adsorption-induced expansion, together with preliminary MD simulations, provides further evidence of a non-bonding parallel linker model of GOF. We can now explain the hysteresis loop the sub-critical nitrogen isotherm by inferring that adsorption-induced expansion of the interlayer spacing generated additional pore space in the material and that the expansion was, at least partially, inelastic. We have also developed an empirical method for predicting the adsorption-induced expansion in GOF for any classical gas based solely upon knowledge of the molecular size and critical temperature of the adsorbate. Finally, we have analyzed the different rates of expansion that appear at low and higher coverage for each

adsorbate. We have determined that the rate of expansion increases as the adsorbed film density approaches liquid density.

In the future, we would like to test our ability to predict the adsorption-induced expansion of GOF by measuring the expansion with nitrogen. Based upon the critical temperature of nitrogen, 126 K, and the vdW size parameter, 0.0387 L/mol, we can predict the expansion by scaling relative to the xenon adsorption points. In Figure 4-18, the predicted nitrogen data points are obtained by scaling the xenon absolute adsorption values by:

$$N_{\text{absolute}, \text{N}_2} = N_{\text{absolute}, \text{Xe}} * \left(\frac{b_{\text{Xe}}}{b_{\text{N}_2}} \right)^{\frac{2}{3}} * \sqrt{\frac{T_{\text{c}, \text{Xe}}}{T_{\text{c}, \text{N}_2}}} \quad (4-7)$$

Figure 4-18. Prediction of nitrogen-induced expansion based upon scaling of experimental xenon data.

We also may wish to measure the adsorption induced effects of hydrogen at 78 K at low coverage, as our current measurements leave a gap in this regime.

Further improvements can be made to the theoretical modeling of our system. Our modeling of the expansion has been based on a simple ansatz (Equation 4.2) and further adjustments based on empirical results. A more sophisticated modeling of the system is desirable. One proposed modeling for the system was that, at higher coverage, it becomes easier to expand the GOF layers than it is to further compress the adsorbed molecules, but this does not explain the expansion at low pressure. At low pressure, one could imagine looking at the total energy of simple model systems with gas adsorbed between GOF at different interlayer spacing values. As mentioned previously, more realistic models of GOF are being worked on for MD simulations.

Chapter 5 XPS analysis of boron doped activated carbon

5.1 *Introduction*

X-ray photoelectron spectroscopy was used to determine both the elemental composition of boron doped carbons as well as gain insight into the arrangement of atoms in the material. The hypothesized arrangement of atoms is a direct substitution of boron for carbon into a graphene like sheet, maintaining the hexagonal honeycomb lattice of sp^2 sigma bonds. Such a boron atom would have an electronic configuration of $1s^2(sp^2)^3$. With a graphitic carbon atom, the p_z orbitals are maintained and participate in mobile pi bonds with neighboring carbon atoms, as understood in the aromatic model. Boron, however, would require a charge donation to fill its p_z orbital. Thus, three possible models are proposed for the out of plane electron density: (1) the orbital remains unoccupied and the boron is a free radical, (2) charge is donated from a neighboring atom and the boron atom is ionic, (3) the delocalization of charge in the aromatic system results in a partial charge transfer to the boron atom and thus the effective charge is somewhere between neutral and anionic. Our results suggest that boron is not in an anionic state, and, by doing a quantitative and simultaneous analysis from multiple elemental spectra, we conclude that no more than 2 wt% of boron is being substitutionally doped into the system.

5.2 *Literature Review*

Cermignani et al. have done some of the original work in chemical characterization of boron doped carbons⁴⁸. 1-2 μm thick boron-carbon films were synthesized by high temperature chemical vapor deposition using benzene and boron

trichloride for the purpose of creating oxidation resistant materials. Samples with boron concentrations of 9 and 10% were synthesized and characterized with XPS. B_4C and B_2O_3 were used as calibration compounds. $B1s$ spectra were fit with 5 components. The lowest energy component, 187.5 eV, was attributed to formation of B_4C . The peak at 188.5 eV was attributed to boron incorporated in plane with carbon. This assignment was made with reference to Kaner et al. with no other proof or justification. The highest energy peak was attributed to B_2O_3 with energy 193 eV. Two intermediate peaks were attributed to mixed B-C and B-O bonding types. Interestingly, they observed that after oxidation at 600 °C, the peak at 193 eV decreased while lower binding energy peaks increased.

Jaques et al. followed with work synthesizing $\sim 10 \mu m$ thin boron-containing pyrocarbons by LPCVD method.⁴⁹ They used boron trichloride and propane in the temperature ranges of 850-1150 °C, synthesizing materials with boron atomic percent ranging from 8-23, an improvement over what Cermignani had been able to do a year earlier. Four samples with varying boron contents along with a standard amorphous boron powder were characterized using XPS. The $B1s$ spectra was fit with 6 components; the five that had been assigned by Cermignani plus an additional amorphous boron component. They found that the boron standard had a binding energy of 187 eV, whereas in their deposits amorphous boron had a peak at 186.5 eV. They explained this difference by claiming that a dispersion of small clusters of boron within a carbon material will alter the Fermi level within those clusters and thus the core binding energy. They attributed the peak at 188.8 eV to boron substituted in graphite providing reference to the paper by Cermignani. They also attributed the three highest binding

energy peaks to a mix of B-C-O and boron oxide. They concluded that as total boron content increases the fraction of amorphous boron in the sample increases.

In 1998 Koh and Nakajama synthesized long filamentous deposits of BC_x materials on a nickel powder substrate using benzene and boron trichloride.⁵⁰ Samples were prepared at temperatures between 800 and 1100 °C, with boron concentrations varying from 2 to 25 at%. They characterized the samples with XPS before and after sputtering with argon. The B1s spectra were fit with four different components with energies 186.5 (B_4C or boron cluster), 188.6 (B_2-BC), 190.6(BC_3), 192.7(B_2O_3) eV. They observed that after sputtering with argon the peak at 165.5 eV disappeared and the peaks at 192.7 and 190.6 eV decreased significantly in size. They justify their assignment of BC_3 instead of an oxide at 190.6 eV by claiming the oxygen content of the sample is not high enough to attribute this peak to an oxygen environment. However, the samples with the highest oxygen content also have the most dominant peak around 190.6 eV.

Shirasaki et al. prepared boron carbon films in 2000 with a thermal chemical vapor deposition method using acetylene, boron trichloride and hydrogen gas.⁵¹ Films with boron concentrations of 6, 13 and 23% were prepared and characterized with XPS. Before measurement the samples were cleaned by precision scratching of the surface under vacuum. B_4C was used as a calibration compound. They observed two peaks in the C1s spectrum. One peak is at 283.8 eV, which they assign to in-plane carbon atoms without boron as a nearest neighbor. This is lower than that of graphite (284.5) and they attribute this to the lowering of the material's Fermi energy as a result of boron incorporation. The second peak in the carbon spectrum is at 282.6 eV which they claim

is carbon with boron as a nearest neighbor. The B1s spectra are fit with just two components. Notably, there is no evidence of any peaks above 190 eV. All B1s spectra have a main peak at 188.1 eV. They attribute this peak to boron atoms substituting carbon atoms, with any number of neighboring boron atoms. They justify this claim by asserting that with boron clusters and boron nitride being at 186.5 eV and 190.5 eV respectively, boron substituted in carbon would be between those two. A shoulder at a lower binding energy of ~186.5 eV is attributed to boron clusters not removed by scratching. There is no mention of a boron oxide component. This paper has SSNMR data accompanying the XPS work.

Maquin et al. also synthesized boron carbon materials by CVD, but they obtained powders with small particles (diameter ~10nm) and specific surface area of 270 m²/g. Boron wt% ranged from 3 to 19%.⁵² They assigned 7 peaks to their B1s spectra, 4 of which were boron with various degrees of oxidation (BE>189.5 eV). They then assigned peaks at 186.5, 187.6, and 188.7 eV to boron incorporated in the carbon plane with a decreasing number of neighboring boron atoms. They dismissed the possibility of having boron carbide because of the lack of signature in the carbon spectrum. They also dismissed the possibility of boron clusters because of the high concentration of carbon in the vapor. They made no references and no comparison to standards.

In 2012 Hashim et al. synthesized boron-doped carbon nanotubes by cvd using triethylborane.⁵³ They assigned 5 peaks, including B₄C (187.7 eV), BC₃ (188.8 eV), and three states of progressively increasing oxidation. They cited Cermignani to justify their peak assignments.

Bult et. al. synthesized BC_x coated activated carbons by depositing vapors from benzene and boron trichloride onto an activated carbon substrate.⁵⁴ They saw significant decreases in SA by doing so. They assigned 4 peaks to their spectrum: 186.6 eV (B_4C), 188.6 eV and 190.4 eV (sp^2 boron in carbon lattice), and 192 eV (boron-oxygen). They cited Ci et al as proof for the sp^2 assignments, but the paper by Ci is of a BCN material where they attribute the peak at 190.4 eV to boron nitride and the peak at 188.6 eV to boron in carbon.

5.3 XPS and relation to a simple electron density model

Unlike infrared or ultraviolet spectroscopy, XPS is not directly probing valence electron bond energies. Instead, it probes the binding energy of core electrons, which are, of course, a function of the nearby electron environment. The binding energy of the electron is determined by taking the following measurement:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \quad (5-1)$$

where E_{binding} is the binding energy of the electron, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer (not the material). In a simple electrostatic model, the potential energy of the core electron can be represented as a function of the interaction with the nucleus and the surrounding charge,

$$V = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + \frac{e^2}{4\pi\epsilon_0} \sum_i \frac{1}{r_i} . \quad (5-2)$$

The relationship between E_{binding} and V is

$$V + KE = -E_{\text{binding}} . \quad (5-3)$$

Thus, we have

$$E_{\text{binding}} = \left[\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} - KE \right] - \frac{e^2}{4\pi\epsilon_0} \sum_i \frac{1}{r_i} . \quad (5-4)$$

To make a quick estimate of the relative size of these terms, let's assume we have a 1s boron electron that satisfies the Schrodinger equation for the hydrogen like atom case.

Then the term in parenthesis is equal to $13.6\text{eV} * \frac{Z^2}{n^2}$. Thus, with $Z=5$ and $n=1$, we find the first term gives 340 eV. Experimentally, we know the binding energy for boron is on the order of 200 eV, and thus the second term must also be quite large. In other words, small changes in the outer shell electron density can have a measurable effect on the inner shell electron binding energy. This is the idea behind bond and chemical analysis with XPS. We can, experimentally, illustrate this point by again looking at boron.

Figure (5-1) shows XPS spectra for both sodium tetraphenylborate and boron oxide. In the case of sodium tetraphenylborate the boron atom is modeled to be in an anionic state with a counter charge provided by the sodium cation⁵⁵. Conversely, the highly electronegative oxygen atoms in boron oxide will draw charge away from boron leaving the atom with a smaller effective electron charge density. Thus, the second term in equation (2) will be larger for sodium tetraphenylborate than for boron oxide resulting in a smaller binding energy for the former. This is what we observe in Figure 5-1. In summary, we say that with an increasing effective charge on the boron, we would see a decrease in binding energy of the 1s electron.

Figure 5-1. B1s spectra for sodium tetraphenylborate (top), boron oxide (middle) and boron carbide (bottom). Boron's higher effective charge in triphenylborate than boron oxide results in a 7 eV lower binding energy of the 1s electron. The boron oxide and carbide spectra are taken from Carminiani et al.⁴⁸

5.4 A search for boron in the trigonal sp^2 bonding structure

5.4.1 Calibration Compounds

Several groups have tried synthesizing boron doped carbons and characterizing their product with XPS. A summary of the literature on the subject can be found in appendix 1. Many of the original investigations were an application towards oxidation resistant materials. More recently there has been interest in boron doped carbons for hydrogen storage applications. Despite numerous efforts, no definitive proof for the B1s binding energy of boron incorporated into graphene has been made. One problem for previous

groups is that finding suitable calibration compounds is difficult because XPS is not only sensitive to what elements are bonding, but also the structure in which they are bonding. For example, boron carbide possesses boron atoms bound to carbon, but the boron atoms in this material are in icosahedral structures with a more exotic 3d sub-shell binding structure.⁴⁸ Boron carbide also possesses linker boron atoms, modeled to be in a linear, divalent bonding structure. Evidence of the two different boron arrangements is seen in the XPS graph of Figure 5-1. The sodium tetraphenylborate is modeled to have four sigma bonds between boron and neighboring carbons, as compared to the three in our aromatic model. Additionally, the boron is understood to be anionic, counterbalanced by the sodium cation. This compound, with four sigma bonds and an excess charge, has a high electron density, which is evidenced by the low binding energy in Figure 5-1. Perhaps the best model compound for our system is triphenyl borate $B(C_6H_5)_3$; in $B(C_6H_5)_3$ the boron atom is connected to three carbon atoms with sigma bonds, as seen below in Figure 5-2. The phenyl groups are measured to be rotated at angles of 30° with the plane. The ordering of the crystal is not thought to be a result of traditional covalent or ionic bonds, but may be a result of van der Waals interactions.⁵⁶ $B(C_6H_5)_3$ is experimentally difficult to measure with XPS, though, as the material sublimates and/or decomposes at room temperature when under ultra-high vacuum. Due to excessive outgassing of the sample we have not been able to gather XPS data on this sample to date. The next step is to try diluting the sample with an inert powder in order to reduce the rate of gas production during the measurement.

Figure 5-2. Left: One common structure of boron carbide. Middle: Structure of tetraphenyl borate, with the boron atom modeled as being in an anionic state. Right: Structure of triphenyl borate. The phenyl groups are rotated at angles of 30° out of the plane.

5.4.2 Computational Work

In addition to calibrating our experimental B1s spectra with calibration compounds, we have also made an effort to computationally model the situation. An orthorhombic graphite cell was created and relaxed from the experimental lattice parameters with the VASP program. The unit cell was expanded to a 144-atom supercell to serve as a model for substituting boron into graphite. Graphite has two crystallographically inequivalent sites so there are two sites for B substitution. A boron atom was substituted at each site separately and relaxed the cell to allow for adjustment due to the substituted atom. The all-electron OLCAO method was then used to compute the B 1s core energy level for

both cases. Figure (3) shows the results of the calculation.

Figure 5-3. (Left) Charge transfer from the atoms in our computational model. Boron is in the bottom left corner. The electron density has moved closer to the three neighboring carbon atoms leaving boron with an effective charge <5 . (Right) Computationally predicted spectrum for boron in the arrangement on the left. The FWHM and intensity has been made to fit our experimental spectrum.

The graph on the left shows the partial charge transfer from each atom, calculated using a Mulliken population analysis. The boron atom (bottom left corner) has an effective charge of 4.62 electrons, meaning it would be in a partially cationic state. This is not saying that the cationic state is more stable than an anionic state. But in the absence of a free charge, the boron atom would lose some charge density to the more electronegative carbon atoms. The graph on the right shows the computed B1s spectrum overlaid on an experimental spectrum of a boron doped carbon. The computational model predicts a B1s binding energy of around 189 eV. This value is around 1 eV less than what we have taken for our B1s value in our experimental fits. One thing that the computational model does not account for is the effect that oxygen surface groups would have on the B1s binding energy. It is reported by a few groups in literature that oxygen will have an effect of raising the Fermi energy of the material.^{49,50} This will translate into a rising of the binding energy of the individual B1s electrons. The extent of this effect is unknown.

Future computational work hopes to model a system where oxygen surface groups are present on the carbon.

5.5 Experimental

5.5.1 Measurement

All measurements were taken on a Kratos Axis 165 Photoelectron Spectroscopy System at Missouri University of Science and Technology-Material Research Center. Great care was taken to keep the sample as free as possible from atmosphere exposure and surface contaminants. The spot size analyzed is $300\mu\text{m} \times 700\mu\text{m}$. Each sample is entered into the analysis chamber one at a time, and not repositioned until all the analysis data is collected for that particular sample. Within the analysis chamber, the analysis is performed under ultra-high vacuum levels of 10^{-8} torr or higher. For best elemental resolution, the monochromatic Al source (1486.6 eV) was used for excitation. A broad survey scan is taken first to identify if any unexpected elements may be in the sample. High resolution scans are then taken on the boron, carbon and oxygen regimes.

5.5.2 Multi-Spectrum Analysis

XPS spectra can be notoriously hard to fit because of the number of deconvolutions that one can make. Fitting numerous components to an individual spectrum is done with good reason, especially in organic materials; for example, the surface chemistry of an activated carbon can be quite complicated due to its amorphous nature and variety of functional groups. For this reason, well known textbooks on the subject have stated that fitting XPS spectra is part science, part experience, and part art. As already stated we

have started by analyzing an XPS spectrum through literature review, calibration compounds, and computational models. In addition, we have developed a method where XPS spectra are analyzed by quantitatively requiring consistency in multiple elemental spectra for a particular sample. Six equations have been developed to aid in the quantitative analysis of XPS spectra. These equations seek to improve consistency in the identification of chemical environments. Consistency is improved by requiring that if a compound of elements is observed in one high resolution elemental spectra, then that same compound must be observed in the complementary elemental spectra. For example, if we believe we observe the compound BC_3 in the high-resolution boron spectrum, then we require an equal amount of BC_3 to show up in the high-resolution carbon spectrum. Because saying with complete certainty what the exact oxygen surface groups are is difficult, we have modeled all surface oxides to be of the form B-O or C-O. The first three equations have been named the consistency equations. They require that the total concentration of each element be accounted for. For the concentration of a single element, the accounting takes place over all the different elemental spectra. The equations are:

$$x_B^{BO} X_B + x_C^{CO} X_C + x_O^O X_O = X_O \quad (5-5)$$

$$3x_B^{BC_3} X_B + x_O^{CO} X_O + x_C^C X_C + x_C^{CH} X_C = X_C \quad (5-6)$$

$$\frac{1}{3} x_C^{C_3B} X_C + x_O^{BO} X_O + x_B^{BB} X_B = X_B \quad (5-7)$$

For the materials we investigate, we will only concern ourselves with the presence of boron, carbon and oxygen. We will only consider interactions between two elements at a

time. In principle, any number of elemental spectra could be used, and any number of different elements compounded together could be accounted for, assuming the structural information is well known.

The second three equations have been named the reciprocal equations. They require that, for a compound composed of two elements, that compound must be observed in equal parts in the compound's two separate elemental spectra. The equations are:

$$\sigma_C x_B^{BC_3} A_B = \sigma_B x_C^{BC_3} A_C \quad (5-8)$$

$$\sigma_O x_B^{BO} A_B = \sigma_B x_O^{BO} A_O \quad (5-9)$$

$$\sigma_C x_O^{CO} A_O = \sigma_O x_C^{CO} A_C \quad (5-10)$$

Every value in these equations is either a constant or is a value determined from the spectral fit; there is nothing that is explicitly solved for in these equations. In fact, there are 9 unknown values from the fit and only six equations; the system cannot be solved for explicitly. Instead, an individual sample's three spectra are initially fit using what is known from literature, computational models and intuition. Then the parameters from that fit are plugged into the above equations. How well the two sides of the equations agree guides what subsequent changes will be made to the fitting of the three spectra. The process is iterated until the two sides of the equations are indeed close to equality. The meaning of each of the symbols is found in table (1).

Table 5-1 Parameter list for equations 5-10 and what they correspond to in the XPS spectrum.

Parameter	Description	Peak Position (eV) (initial setting)	FWHM (eV) (initial setting)
χ_B^{BB}	Fraction of B1s spectrum with atoms in a BB bonding environment	188.5	2.0
$\chi_B^{BC_3}$	Fraction of B1s spectrum with atoms in a BC ₃ bonding environment	191.0	2.5
χ_B^{BO}	Fraction of B1s spectrum with atoms in a BO environment	193.0 eV	1.9
$\chi_C^{C_3B}$	Fraction of C1s spectrum with atoms in a BC ₃ bonding environment	283.5	1.0
χ_C^{CC}	Fraction of C1s spectrum with atoms in a CC bonding environment	284.5	0.8
χ_C^{CH}	Fraction of C1s spectrum with atoms in a CH environment	285.0	1.5
χ_C^{CO}	Fraction of C1s spectrum with atoms in a CO bonding environment	286.5	1.5
χ_O^{CO}	Fraction of O1s spectrum with atoms in a CO bonding environment	532.8	1.8
χ_O^{BO}	Fraction of O1s spectrum with atoms in a BO environment	531.8	1.8
σ_x	Relative sensitivity factor of element x.		
A_x	Atomic percent of element x. Determined by integrating over all counts in the element's region and comparing to counts in other elemental regions. All appropriate sensitivity factors are used.		

In practice, all the spectrum fitting is done within the CasaXPS program and the equation matching is done within Excel. A screen shot of the program is shown in Figure 5-4. An initial fit is made with the values listed in columns 3 and 4 from table 1. These values are then relaxed to a value within +/- .3 eV of the initial settings, allowing the program to find the best fit. The line-shape used is a product of a Gaussian and Lorentzian, equally weighted. After the program finds the best fit given these initial constraints, the values in the %Area column are read and plugged in for the parameters in equations 5-10. These parameters are plugged into an Excel spreadsheet, also shown in Figure (5-4), containing

the equations 5-10. These equations then provide additional constraints to the fits. Given the information provided from how well equations 5-10 agree, the percent area of different components in a spectrum will be constrained to move the equations closer to equality. The spectrum is then refit given the new constraints to peak areas. The %Area values are then plugged back into the Excel document and this process is iterated until both a visually good fit to the spectrum is achieved and the equations are in reasonable good agreement.

Figure 5-4. Screen shots of the fitting process. Spectrum fitting occurs in CasaXPS.

5.6 Results

The resultant fits from our best performing sample, 5K-0215, are shown in Figure (5-5), along with accompanying information in table 2. For a complete set of spectra for each sample, along with relationships between various parameters, please see the accompanying information. One interesting result from the 3-spectrum analysis is that 20% or less of the boron is making its way into the carbon. The majority of boron is staying as boron complexes; some is forming oxides or incorporated in carbon. Once the boron gets above ~2 wt% the oxygen sites become saturated the surface of the material. We can track the surface chemistry with increasing amount of boron to estimate how the

surface chemistry is formed. This is shown in Figure 5-6. We see that boron oxides are the first environment to form, which may be precluding the formation of boron incorporated in carbon. Once the boron gets above ~2 wt% the oxygen sites become saturated

Table 5-2. Various boron percentages as determined by XPS. We give PGAA values to show consistency amongst measurements. We also include oxygen wt% and E_B for further comparison.

Sample	B_{tot} (wt%, PGAA)	B_{tot} (wt%, XPS)	B_{B-C} (wt%)	$B_{B-C/B}$ (%)	O (wt%)	E_B (kJ/mol)
4K-0240	1.5 (1.5)	1.2	0.0	0.0	6.2	6.9
4K-0244	1.3 (2.0)	1.7	0.0	0.0	7.8	7.2
4K-0245	3.9	4.1	0.7	17.6	10.0	7.3
4K-0748	5.6	5.2	1.0	18.6	7.9	7.2
3K-0205	9.7	7.5	0.9	12.5	9.0	7.4
3K-0211	6.2	7.6	0.6	8.5	10.9	
5K-0215	8.1	8.4	1.7	20.7	8.7	9.3
3K-0208	13.7	14.6	1.7	11.7	9.7

Figure 5-5. A three spectra fit of sample 5K-0215. All three spectra are required to be consistent through equations 5-10. Sample 5K-0215 has been measured to have the highest heat adsorption of any MU boron doped carbon.

and the boron surface chemistry starts to become more varied. Above 2 wt% we start seeing the emergence of both boron complexes and boron in carbon. Specific units are not included on the y-axis because of variations in x-ray intensity that occurred with different measurements. We note here that we have assigned the BC_3 peak to be at a binding energy of ~ 190.5 eV. In terms of XPS, this is a long way from the 185.8 eV of the anionic boron of $NaB(C_6H_5)_4$. This is also an even higher binding energy than what was calculated in the ab-initio computations, and those calculations had already predicted cationic boron. All this information is consistent with boron not being in an anionic state.

Figure 5-6. B1s spectra as a function of increasing boron weight percent. (Top left) All boron is in the form of boron oxide. (Top right) By the time we get to 4.1 wt% the oxygen traps have been saturated. We start to see the emergence of BC₃ type structures as well as boron clusters. (Bottom) Boron clusters and BC₃ components continue to increase until in sample 3K-0208 the BC₃ component is as large as the boron oxide.

Appendix A

Preliminary molecular dynamics simulations model the expansion of GOF in the presence of adsorbed methane. The first set of simulations compares the three different linker orientations (cross-linked, pillared, and horizontal non-bonding) in a model of GOF with no oxygen groups present on the graphene sheets. The crosslinked model did not expand upon methane adsorption, suggesting it is not an accurate model of our system. The pillared model and the horizontal model did show an expansion, but the original interlayer spacing of the pillared model is too large (~ 12 Å) and the amount of expansion ($\Delta d = 4$ Å) is too large for the horizontal model.

Figure A - 1. Crosslinked model of GOF with methane adsorbed.

Figure A - 2. Pillared model of GOF with methane adsorbed

Figure A - 3. Distribution of carbon atoms in the GOF as a function of height. The initial states plotted in blue and final state with methane adsorbed is plotted in red. (Top) Crosslinked model shows no expansion after adsorption. (Bottom) Pillared model shows 5% expansion, but the initial interlayer spacing is larger than observed in experiment.

Figure A - 4. Parallel non-bonding linker orientation of GOF with methane adsorbed.

Figure A - 5. Plot of Interlayer spacing of parallel non-bonding GOF versus number of methane molecules adsorbed.

Appendix B

UNIVERSITY OF MISSOURI-COLUMBIA MISSOURI UNIVERSITY RESEARCH REACTOR

PROJECT APPLICATION and HEALTH PHYSICS EVALUATION for UTILIZATION OF RADIOACTIVE MATERIAL/RADIATION UNDER MURR REACTOR LICENSE

1. **Project Leader:** Helmut Kaiser

2. **MURR Affiliation:** Neutron Scattering and Neutron Materials Science Program

3. **Project Name:** Gas Handling System for *in situ* Adsorption Measurements for 2XC (RL-33), PSD (RL-61) and TRIAX (RL-46)

Expiration Date: XX/XX/XX

4. **Radiation Source:** Beamport C (upstream 60°, 81°, and 102° beam holes on west side), Beamport D (RUR 248) and Beamport A (RUR 258).

5. **Location Requested:** **Room/Area Restricted:** YES (X) NO ()
 Level I ()
 Level II (X)
 Level III ()
 Level IV ()
 Other ()
 Beamport floor area is a restricted Level II area and only accessible by authorized personnel. The location and monthly survey of the area is adequate for this project.

6. **Purpose and Description of Project:**

 The purpose of this Gas Handling System (GHS) is to pressurize accurately and controllably a 2.5 cm³ sample cell, containing adsorbent materials, up to a pressure of 170 bar. This procedure is implemented by carefully measuring the pressure of a gas as it expands from a 150 cm³ lecture bottle, initially at 200 bar, into the 2.5 cm³ sample cell. Gases used for pressurization will be:
 N₂, CO₂, H₂, CH₄, D₂, CD₄, He and Ar. The total volume of gas brought into

containment is approximately 30 liters at standard temperature and pressure (STP). Exact quantities of all these gases can be found in Table 1 of Attachment 1A.

Adsorbent materials investigated will be graphene oxide frameworks (GOFs), metal organic frameworks (MOFs), complex metal hydrides, hydrogen bonded supramolecular frameworks and activated carbons. Neutron scattering measurements will be taken on these novel adsorbent materials *in situ* of the pressurized gas environment to reveal their structure and dynamics. The experiments will use the MURR 2XC (BP ‘C’), the PSD (BP ‘D’), and the TRIAX (BP ‘A’).

The sample cell that will be pressurized by the GHS is a pressure cell previously approved for off-site loading with flammable and non-flammable gases **up to 200 bar in RL-77 and in**

RL-84, respectively. The temperature of the sample cell will also be an experimental variable; we will be able to take measurements from room temperature down to 77 K.

In summary, the GHS will allow trained individuals to perform *in situ* elastic and inelastic neutron scattering measurements to obtain structural and dynamical information on a variety of gases as a function of sample temperature and loading pressure.

The GHS schematics can be found in Attachment 2. The GHS is comprised of:

- the gas manifold (Figure 1)
- the sample station (Figure 2)
- the pneumatic lines (Figure 3)
- the electronic components (Figure 4)

A detailed description of operation protocol for the GHS is the subject of Attachment 3. This operation protocol includes:

- Filling of the 150 cm³ lecture bottle with the desired gas. This operation occurs outside of containment in a location to be determined by the Health Physics and Safety Manager.
- Connection of the GHS manifold to the sample station on the 2XC.
- Dosing procedure during an adsorption experiment.
- Dosing procedure during a desorption experiment.

Custom LabView software has been designed to control the electronic relay unit [National Instruments (NI) Model USB-6525], and thereby the rest of the GHS. The software is also designed to monitor pressure and detect leaks in the GHS. One flammable gas detector is installed on the gas manifold and another on the cryostat near the capillary feed-through. An extensive leak check will be performed prior to installation of the GHS on the beam port floor, and leak checks using non-flammable gases will be performed periodically thereafter. All electronic components are physically separated from the gas manifold; the gas manifold is located on a shelf above the electronics, so that in the case of a gas leak the gas will rise away from the electronics (see **Figure 5 in Attachment 2**).

The components of the GHS are labeled (see Figures 1 & 2 in Attachment 2) as: To Cryostat (port to the sample), Vacuum Pump, Vacuum Gauge [vacuum transducer (LPT1)], 245 bar transducer (HPT), Gas Inlet port, To Exhaust (gas exhaust port), and a 150 mL Lecture Bottle. The 245-bar pressure transducer is from OMEGA, and the LPT1 is from MKS model 974 QuadMag™ Cold cathode/MicroPirani™/Piezo Vacuum Transducer, which measures pressures in the range of 10^{-8} Torr to 1500 Torr. Six normally-closed pneumatic valves (PV0-5) will be used to open/close the ports to each component excluding the high-pressure transducer which will monitor the gas manifold at all times. A normally-open pneumatic valve (PV6) will separate the gas-loading section of the manifold to the sample/vacuum pump section of the manifold. Thus, PV6 will allow for purging of the sample side without affecting the gas-loading side, a procedure which will be utilized for desorption measurements. To prevent damage in the event of an over-pressurization, a high-pressure relief valve (PRV) will allow gas to escape to the MURR gas exhaust line (see Figure 8 in Attachment 2). The pressure relief valve will activate when pressures exceed 175 bar.

All components are rated to pressures at 242 bar or higher; the only exceptions being the LPT1 and the cryo-capable manual valve (CMV) at the sample cell. The LPT1 is isolated from the high-pressure environment by two valves, PV3 and MV2. The CMV is rated to 172 bar with a built-in safety factor of 3:1, and thus will be protected by the 175 bar pressure-relief valve. The GHS will be connected to a pressure cell which is typically mounted either directly on the sample table or in the cryogenic environment (blue dewar cryostat for 2XC, PSD and TRIAX). For more details, see Figure 8 in Attachment 2.

The GHS has been designed such that the failure of a single component will not lead to quick release of gas into containment.

These experiments call for the use of hydrogen and methane, which are regarded as flammable gases. However, an explosion cannot occur in any volume that contains only hydrogen or methane; an oxidizer, such as oxygen, must be present in a concentration of at least 10% pure oxygen or 41% air (see Attachment 5). No oxidizers are used in these experiments. Under the operational conditions of these experiments methane and hydrogen will not become explosive. To ensure that explosive conditions are not met is the subject of section 8. A response to the safety analysis by EHS (Attachment 4) regarding potentially explosive conditions is specifically addressed in section 8.b. At no point will explosive materials be irradiated or allowed to generate in the neutron beam, as prohibited in Technical Specification 3.6.d.

7. Special Facilities/Utilities/Equipment Required:

Before operating the GHS, its exhaust must be connected to the gas exhaust line near the PSD via the designated 1/4-inch Cu tube. Equipment necessary for operation of the PSD and 2XC have been listed in RL-61 and RL-33, respectively. The additional equipment necessary for the cooled experiments includes liquid nitrogen for the cryostat.

The facilities and utilities are adequate. Equipment is specifically designed for this purpose and is adequate for the work to be performed. The radiation monitors used for dose rate measurements are maintained under the MURR Health Physics Instrument Program.

8. Safety Analysis:

The hazards and accident analysis below outline the possible scenarios that may arise during the normal operation of the GHS and their mitigation.

a) Gas Leak into Containment Air Space

Scenario 1: A gas leak is detected by one of the two flammable gas detectors.

The gas manifold portion of the GHS is equipped with a flammable gas detector. A second flammable gas detector is located on the cryostat near the capillary feed-through. If a leak is detected, the valve to the exhaust line, PV0, will automatically be opened, allowing gas to leave through exhaust rather than into the reactor air space. To minimize the exposure of leaked gas to a possible ignition source, the control valves are all either manually or pneumatically operated and mounted atop the cart's middle shelf; the electronic components are mounted below this shelf (See photos, Figures 6 and 7, in Attachment 2). The gas portion and the electrical portion of the gas manifold are well-separated. Thus, in the event of a gas leak (all the flammable gases in this project will rise), the risk of exposure of sparks to the gas has been mitigated.

Scenario 2: The flammable gas detectors are not responding (due to low leak rate or device malfunction) and/or PV0 is not opening (due to low pneumatic pressure or valve malfunction).

In this scenario the gas will be quickly diluted into the 6371 m³ volume of containment. The maximum volume of any gas at STP to be on the beam port floor is 0.0379 m³ (1.4 ft³) (see Table 1, Attachment 1A). The lower flammability limits for H₂, CH₄, D₂, and CD₄ are 4.0, 4.9, 5.0 and 5.0%, respectively. Once expanded into the large volume of the beam port floor, the gases will be at concentrations around 6×10^{-4} %, 4 orders of magnitude below each gas's lower flammability limit. A passive release of gas into fresh air is expected to rise quickly, with turbulent mixing of gas with the air, pulling the plume apart. The air within containment is cycled at a rate of 20,000 ft³/minute. The air is refreshed at a rate of 2,000 ft³/minute. Thus, the air in containment will be turned over in under 2 hours ensuring removal of any flammable gases.

b) Gas Leak into Cryostat Vacuum Space

The sample cell is contained within a 15 L vacuum space of the cryostat (vacuum jacket). A potentially hazardous situation could emerge if 1) a leak of flammable gas occurs from the sample cell into the vacuum space and 2) a leak of air occurs from the environment into the vacuum space. A combination of these two situations is improbable, but to mitigate exposure to these conditions a vacuum gauge, LPT3, is installed on the vacuum jacket as shown in Figure 9. The pressure inside the vacuum space will be constantly monitored and logged into the data collection system. If the pressure begins to rise and exceeds 100 torr, the experiment will automatically be stopped, and the following actions have been programmed to automatically occur: PV1 will be closed, PV5 will be opened,

and PV0 will be opened, allowing all gas in the system to safely pass through the exhaust line.

c) Over-Pressurization

The GHS is equipped with a Pressure Relief Valve (PRV) assembly on the cryostat near the sample cell (see Figure 8 in Attachment 2). This PRV has been designed to open when the pressure exceeds 175 bar. This pressure was chosen to protect the cryogenic valve (CV) rated to 172 bar. The cryogenic valve has a built-in safety factor of 3:1, as reported by Swagelok, the valve manufacturer. Under normal operating procedures, the CV will never see a pressure over 150 bar (See Attachment 1B). The only event which could lead to over-pressurization of this valve would be failure of the cryostat; the details of such a failure are discussed further in Sections 8.d and 8.e. The outlet of the pressure relief valve is connected to the gas exhaust line, and in the event of an over-pressurization, the PRV will open and gas will safely exit through the containment exhaust line.

d) Failure of Cryostat

The cryostat allows cooling of the sample cell down to 77 K. During measurements taken at cryogenic temperatures, a higher density of gas will collect in the cold sample cell than elsewhere in the GHS. If the cryostat fails (runs out of or stops circulating liquid nitrogen), the gas in the sample cell will start to warm up. During normal operation, the warming gas will safely expand back into the GHS manifold. If the pressure exceeds 175 bar the PRV will open and gas will safely exit through the containment exhaust line (See Attachment 1D).

e) Power Outage

In the event of a power outage to the GHS computer and electronic components, the pneumatic valves will close to contain any gas within the GHS. The only normally-open valve is PV6. PV6 does not connect to a gas port, and the opening of PV6 will not lead to a release of gas. The cooling system relies on liquid nitrogen; a power outage will not directly result in the failure of the cryostat. However, in the event of an over-pressurization during a power outage the PRV will open and gas will safely exit through the containment exhaust line (See Attachment 1E).

f) Reactor Shutdown

During a Reactor Shutdown - either scheduled or unscheduled - the operation of the GHS will be affected in the following way:

- 1) If facility electrical power is maintained during the shutdown period, the GHS operation will be unaffected.
- 2) If a facility power failure occurs during a reactor shutdown, the considerations listed in Section 8.e will apply.

g) Reactor Isolation or Facility Evacuation

A Reactor Isolation or Facility Evacuation will shut down the reactor and the reactor containment exhaust system isolation valves will close. All personnel in the containment building are required to exit. If this situation occurs, the operation of the GHS will be affected in the following ways:

- 1) Exhaust System Isolation Valves Closure: With the containment exhaust system valves closed there will no longer be a path for exhaust gases to exit the containment building. Any gases exhausted by the GHS system will migrate into the 6371 m³ (6.371 E+9 mL) containment building free volume. If this occurs the resulting concentration of GHS exhausted gas in the containment volume would be ~6 E-4 % which is four orders of magnitude lower than the lower flammability limit of any gases used.
- 2) GHS Unattended for Prolonged Period: Throughout the duration of a Reactor Isolation or Facility Evacuation, the GHS will be unattended and inaccessible. Neither the gases used, nor the materials studied are time-sensitive; if left unattended, they will not become hazardous. The only time-sensitive aspect of the system is the cryostat cooling. The cryostat relies on liquid nitrogen, which will slowly evaporate if left unattended for an extended period of time. Once evaporated, the sample cell will start to warm up and the cooled gas will expand. If pressures then exceed 175 bar, the PRV will open to maintain safe pressure in the system and the gases would be exhausted to the containment building free volume.

9. Handling Procedures for Radiation Safety Purposes:

The handling procedures for radiation safety purposes of 2XC (RL-33), PSD (RL-61) and TRIAX (RL-46) apply. The GHS will not be exposed to the neutron beam during normal operation. Only the sample cell (RL-78, RL-84) will be exposed to the beam.

- a) The parts of the pressure cell which are exposed to the beam are made of aluminum alloy T6-6061. No long-term activation of the pressure cell, powder sample or the gases is expected.
- b) When the pressure cell that has been exposed to the neutron beam is removed from the instrument it will be surveyed for activation. Parts may be surveyed by instruments provided by Health Physics. If there are any concerns Health Physics or Reactor Operations will be contacted.

If a sample is to be removed from the beam port floor area, it must be checked and cleared by Health Physics. In general, when a new sample and its associated shielding are placed in the neutron beam, the immediate area around the instrument will be surveyed by the approved worker to ensure that a high radiation field has not been created.

- c) Activated samples are stored depending on the level of radioactivity in one of the storage ports or locked away in the Neutron Scattering Group designated storage cabinet.
- d) It is the responsibility of the approved worker to ensure they are wearing a whole body dosimeter, EPD, and extremity dosimetry (finger rings) each time they perform experimental manipulations such as sample changes.
- e) No special emergency procedure is required. The general facility emergency procedures apply.
- f) Approval for the Project Leader is requested from the Reactor Health Physics Manager, since these individuals' training and experience meet the requirements listed in Section 10. Authorizations for approved workers will be documented on the RL-88 Project Personnel Approval form.
- g) The method for handling irradiated radioactive materials removed from the neutron beam is specified in the project application. No additional emergency planning should be required beyond that described for general emergency response to a containment isolation. In the event that the local area radiation monitor alarms, personnel will evacuate the local area and go to the containment entry foyer and contact Health Physics and/or Reactor Operations.

10. Administrative Controls and Training Requirements:

Persons involved in this project are either Authorized Supervisors (scientists and postdocs who work with that project extensively and are typically involved longer than one year), Approved Workers (collaborators, visiting experimenters, graduate students and others who work on the project), or visitors (collaborators, students and others who work with that project for a short time and are typically involved for less than one week).

Due to the potential high radiation levels in the beams and higher radiation levels around the beams, all workers on this project will be trained and their training documented in the following manner.

- a) All workers will complete the MURR Training Program, Parts I and II. All individuals who desire unescorted access to the beamport area will need to complete "Beamport Area Radiation Safety" training and form after they have been granted containment and beamport floor access.
- b) All workers will complete a MURR Form 150 "Statement of Individual Training," to document their radiological experience and obtain a Class II level of training. A Class II level of training can be completed at MURR. The Project Leader and the Reactor Health Physics Manager may approve equivalent training/experience at other facilities.
- c) All workers will complete specialized training on the 2XC, PSD and TRIAX prior to being allowed to work unsupervised on any of these instruments. "2XC diffractometer at Beamport C", "PSD diffractometer at Beamport D" and

“TRIAX at Beamport A” training will be conducted by an Authorized Supervisor on site and documented on the training form. Training documentation for all Approved Workers and Authorized Supervisors will be maintained by the Project Leader.

- d) Authorized Supervisors, at a minimum, will need to complete Class I level of training.
- e) Approved Workers performing any work on this project are required to complete all training listed under Section 10.b.
- f) Visitors performing any work on this project are required to complete Part II training and complete training listed under Section 10.c.

11. Anticipated Radiation Doses and Contamination Levels:

Radioactive materials will be stored in a way to minimize and contain contamination and maintain exposure rates in compliance with ALARA (as low as is reasonably achievable). In order to obtain exposure rates ALARA, it is recommended that the time spent close to the concrete reactor biological shielding and the sample stage area be kept at a minimum during the operation of the instrument.

Whole body and extremity doses are expected to be reasonable during operation and set up and consistent with other beamport floor experiments. The use of gloves and prudent handling should be adequate to control the spread of contamination.

12. Transfer, Waste Production, and Disposal Requirements:

Transfer of radioactive samples to other MURR areas shall be handled in accordance with RP-HP-105, “Transfer of Radioactive Materials-In Facility” or approved equivalent.

Any transfer of radioactive material from the facility to another campus location must have prior approval from MU Environmental Health & Safety and be transferred by the Shipping Group.

Samples/components removed from the beamport floor area will be surveyed by Health Physics prior to leaving the building or carried to offices or other non-radiation areas.

Radioactive waste will be minimal in volume and will be processed through routine radioactive waste disposal.

13. Other Approvals/Authorizations/Interfaces Required:

None required.

14. Revision Analysis:

This is a new project.

- 15.** I have read the MURR Radiation Worker Procedures and recognize its application to my requested project in the utilization of radioactive material/radiation under the MURR Reactor License. I recognize my responsibility as a project leader to inform and provide a safe work environment for individuals at MURR in accordance with University and NRC requirements.
I recognize my responsibility to maintain proper and current documentation in regard to utilization of radioactive material/radiation under this project authorization.

Evaluation Conducted and Submitted By:

Health Physics: _____ Date: _____

Project Leader: _____ Date: _____

16. Approvals:

Reactor Manager: _____ Date: _____

Health Physics Manager: _____ Date: _____

A. Estimation of Amount of Gas in Containment

The quantity of gas transported to the beam port floor is calculated by simply considering the volume and pressure of the lecture bottle plus extra volume up to PV1; this method is valid because all other tubing and components are under vacuum when transported to the beam port floor. Thus, the total volume of gas at standard temperature and pressure (STP) (20 °C and 1 bar), used on the beam port floor, is determined with the following equation:

$$V_{\text{STP}} = V_T * \left(\frac{\rho_2}{\rho_1} \right)$$

Where $V_T = 153.9 \text{ cm}^3 \rightarrow (150 \text{ cm}^3 \text{ lecture bottle} + \text{extra volume up to PV1})$,

$\rho_1 \equiv$ number density of gas at 20 °C and 1 bar,

$\rho_2 \equiv$ number density of gas at 20 °C and 200 bar.

We can then calculate this volume of gas as percentage of the total volume of air in containment, $V_{\text{BPF}} \equiv 6,371 \text{ m}^3$. These values are provided in Table 1, along with the Lower Flammability Limit (LFL) of the flammable gases. This shows that the quantities of gases are small, and in the event of a leak, will be quickly diluted into the volume of containment.

Table 1

The maximum volume of each gas at STP, V_{STP} , is tabulated along with the corresponding concentration assuming dilution into the volume of containment.

Each concentration is well below the LFL.

Gas Species	ρ_1 (mol/L)	ρ_2 (mol/L)	Total Mass (g)	V_{STP} (L)	$V_{\text{STP}} / V_{\text{BPF}}^*$ 100 (%)	LFL (%)
Hydrogen	0.0410	7.29	2.3	27.3	4.30E-04	4.0
Nitrogen	0.0410	7.80	33.6	29.2	4.59E-04	NA
Helium	0.0410	7.49	4.6	28.1	4.42E-04	NA
Argon	0.0410	8.68	53.4	32.6	5.11E-04	NA
Methane	0.0411	10.1	25.0	37.9	5.94E-04	5.0
Deuterium	0.0410	7.31	4.5	27.5	4.31E-04	4.9
CO ₂ *	0.0412	4.34	27.9	16.2	2.54E-04	NA
CD ₄ **	0.0411	10.1	34.9	37.9	5.94E-04	5.0

* CO₂ is a liquid above 56 bar, and thus ρ_2 is determined at 56 bar.

** Number density values for CD₄ are not available from the NIST WebBook, but can be reasonably approximated as equal to that of methane.

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1. E.W. Lemmon, M.O. McLinden and D.G. Friend, "**Thermophysical Properties of Fluid Systems**" in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, (retrieved December 19, 2013).

B. Maximum Sample Pressure at Room Temperature

The maximum pressure inside the sample cell is calculated for an adsorption measurement performed at room temperature. This pressure is determined by considering the volume and initial pressure in the lecture bottle, as well as the combined volume in the lecture bottle, V_T , the sample cell, V_S , and the manifold, V_M , as well as the volume of tubing connecting the two, V_{CON} . The ideal gas law can be used to calculate what the final maximum pressure, $P_{f,RT\ max}$, will be:

$$P_{f,RT\ max} = P_i \left[\frac{V_i}{V_f} \right]$$

$V_i = V_T = 153.9\text{ cm}^3 \rightarrow (150\text{ mL lecture bottle} + \text{extra volume up to PV1})$

$V_S = 2.5$

$V_M = 23.5$

$V_{CON} = 25.8$

$V_f = V_T + V_S + V_M + V_{CON} = 205.7\text{ cm}^3$

$P_i \equiv \text{initial pressure in lecture bottle} = 200\text{ bar}$

Plugging in these values, the maximum pressure in the sample cell during an adsorption measurement at room temperature is 150 bar.

C. Maximum Sample Pressure at Liquid Nitrogen Temperature

When the sample cell is held at 77 K, a temperature gradient will form, extending from the sample cell up to the feedthrough on the vacuum jacket. Rather than dealing with this gradient directly, the volume is divided into three temperature zones. This approximation will simplify the calculation of the maximum pressure when the sample cell is at 77 K. The temperatures of the three different zones are 77 K (liquid nitrogen temperature), 293 K (room temperature), and 185 K (halfway between 77 K and room temperature). The specific volumes within each temperature regime are:

$V_{77\text{ K}} \equiv \text{Sample cell and all tubing extending from the sample cell to the radiation shield} = 6.5\text{ cm}^3$

$V_{185\text{ K}} \equiv \text{All tubing extending from radiation shield to the vacuum jacket feed through} = 3.4\text{ cm}^3$

$V_{293\text{ K}} \equiv \text{All tubing from the vacuum jacket feedthrough to, and including, the lecture bottle} = 195.85\text{ cm}^3$

With these temperature regimes defined, the ideal gas law can be used, conserving the total number of gas molecules, to calculate what the maximum pressure in the sample cell will be when held at 77 K:

$$\frac{V_T P_i}{T_{293}} = P_{f,77\text{ K}\ max} \left[\frac{V_{293}}{T_{293}} + \frac{V_{185}}{T_{185}} + \frac{V_{77}}{T_{77}} \right]$$

$$\rightarrow P_{f,77\text{ K}\ max} = \frac{V_T P_i}{T_{293}} \left[\frac{V_{293}}{T_{293}} + \frac{V_{185}}{T_{185}} + \frac{V_{77}}{T_{77}} \right]^{-1}$$

The maximum pressure in the 77 K sample cell is 136 bar.

D. Maximum Sample Pressure during Cryostat Warming (PV5 open)

During normal operation of the GHS, the cryostat will not be allowed to warm up from 77 K to room temperature while the sample is at the maximum pressure of 136 bar. However, in the event that the cryostat begins to warm up, gas will expand from the sample cell back into the capillary and manifold portion of the GHS (during normal operation, PV5 is kept open and PV1 is closed). The following calculation is what the maximum pressure increase at the sample will be when the cryostat warms from 77 K to room temperature and PV5 is open. Again, the volume is divided into three different temperature regimes.

$$P'_{f,max\ 77 \rightarrow 293} = P_i \left[\frac{V_{77}}{T_{77}} + \frac{V_{185}}{T_{185}} + \frac{V'_{293}}{T_{293}} \right] * \left[\frac{T_{293}}{V_{77} + V_{185} + V'_{293}} \right]$$

Where,

$$V_{77} = 6.5 \text{ cm}^3$$

$$V_{185} = 3.4 \text{ cm}^3$$

$$V'_{293} = 41.9 \text{ cm}^3 \rightarrow \text{The volume from cryostat feedthrough up to PV1.}$$

The maximum pressure in the sample when the cryostat warms from 77 K to room temperature with PV5 open is 189 bar. Thus, the pressure relief valve (PRV) would open and maintain the pressure below 175 bar.

E. Maximum Sample Pressure During Cryostat Warming and Power Loss (PV5 closed)

A loss of power will cause PV0 – PV5 to automatically close. Closure of PV5 means that gas from the sample cell cannot flow back into the gas manifold. Thus, during a power loss combined with a warming of the cryostat, the pressure will increase on the sample side of the system. The following calculation is what the maximum pressure rise will be during a forced closure of PV5. As in the previous section, the system is divided into three temperature regimes: 77 K, 185 K, and 293 K. With the sample cell at 77K, the maximum pressure on the sample side of the instrument, as determined in Section C, is 136 bar. We can calculate how much the pressure will rise as the sample cell warms from 77 K to 293 K.

$$P_{f,max\ 77 \rightarrow 293} = P_i \left[\frac{V_{77}}{T_{77}} + \frac{V_{185}}{T_{185}} + \frac{V''_{293}}{T_{293}} \right] * \left[\frac{T_{293}}{V_{77} + V_{185} + V''_{293}} \right]$$

Where,

$$P_i = 136 \text{ bar}$$

$$V_{77} = 6.5 \text{ cm}^3$$

$$V_{185} = 3.4 \text{ cm}^3$$

$$V''_{293} = 18.4 \text{ cm}^3 \rightarrow \text{The volume from cryostat feedthrough up to PV5.}$$

Therefore, $P_{f,max\ 77 \rightarrow 293} = 233 \text{ bar}$. However, at 175 bar the pressure relief valve will open ensuring the pressure never exceeds this value.

The maximum allowable pressure at 77 K can also be calculated so that upon warm-up, an over-pressurization does not occur. The equation to solve for an initial pressure, assuming that the final pressure is 170 bar, is as follows:

$$P_{i,\max} = P_f \left[\frac{V_{77} + V_{185} + V''_{293}}{T_{293}} \right] * \left[\frac{V_{77}}{T_{77}} + \frac{V_{185}}{T_{185}} + \frac{V''_{293}}{T_{293}} \right]^{-1}$$

The maximum sample pressure that will not trigger a pressure relief valve opening upon cryostat warming is 122 bar.

GHS Schematics

Figure 1

GHS manifold schematic. This portion of the GHS is housed on the cart.

Table 2

Component abbreviations and their meanings.

Component Abbreviated Name	Component Description
LFC#	Low-flow constrictor
PV#	Pneumatic Valve
MV#	Manual Valve
HPT	Pressure Transducer
LPT#	Vacuum Transducer
PRV	Pressure Relief Valve
CMV	Cryo-capable Manual Valve

Figure 2**Sample Station Schematic**

This portion of the GHS is housed on the blue cryostat. The sample station is connected to the GHS manifold by a 1/8-inch diameter stainless steel tube.

Figure 3

Pneumatic supply system schematic

The Swagelok bellows valves in the manifold are actuated pneumatically. The 125 psi supply of nitrogen to the bellows valves is controlled by the Humphrey solenoid valves.

The solenoid valves are controlled by the electronic circuitry shown in Figure 4.

Figure 4
Electronic Components Schematic

Figure 5**GHS on 4-Wheel Cart**

Includes (from the bottom going up): nitrogen supply tank for pneumatics, LED panel, gas manifold, laptop computer designated for instrument control. All the electronics are housed behind the LED panel.

Figure 6
Top-Down View of Manifold

Figure 7

GHS Electronics (housed behind the LED panel)

Figure 8**Sample Station of GHS**

During a measurement the sample would be enclosed by the vacuum jacket and radiation shield.

Figure 9**Cryostat Vacuum Monitoring System**

The low-pressure transducer (LPT3) constantly measures the pressure inside the cryostat vacuum jacket. The pressure is logged by the GHS computer and in the event that the pressure begins to rise and exceeds 100 mtorr, the experiment will automatically be stopped and the gas in the system will be vented through the exhaust line.

Operational Protocol

1. Filling of 150 mL lecture bottle in a location to be determined by the Health Physics and Safety Manager:
 - 1.1. Confirm that Vacuum Pump is turned off, all valves are closed, Regulator on H₂ gas cylinder is closed, and H₂ cylinder valve is closed.
 - 1.2. Connect H₂ gas cylinder to Gas Inlet. Keep regulator and cylinder valve closed.
 - 1.3. Open valves PV1, PV2, PV3, PV4, PV6, MV2, and LFC1.
 - 1.4. Turn on Vacuum Pump.
 - 1.4.1. Wait until vacuum level < 1 mTorr on LPT1.
 - 1.5. Close PV4.
 - 1.6. Open PV2.
 - 1.7. Open H₂ cylinder valve.
 - 1.8. Slowly open H₂ regulator to read 1 bar.
 - 1.8.1. Confirm on LPT1 that pressure is ~ 1 bar.
 - 1.9. Close valve PV2.
 - 1.10. Open PV4.
 - 1.10.1. Wait until vacuum level < 1mTorr.
 - 1.11. Close PV4.
 - 1.12. Open PV2.
 - 1.12.1. Confirm on LPT that pressure is ~ 1 bar.
 - 1.13. Close PV2.
 - 1.14. Open PV4.
 - 1.14.1. Wait until vacuum level is < 1mTorr.
 - 1.15. Close PV4.
 - 1.16. Close MV2 and PV3.
 - 1.17. Open PV2.
 - 1.18. Slowly increase pressure on regulator to 200 bar.
 - 1.18.1. Confirm on HPT that pressure is 200 bar.
 - 1.19. Close PV2, Regulator, and cylinder valve.

- 1.20. Close PV1.
- 1.21. Open PV0 to vent manifold to ~ 1 bar.
- 1.22. Close PV0.
- 1.23. Open PV4, PV3, and MV2.
 - 1.23.1. Wait until vacuum level < 1mTorr.
- 1.24. Turn on Turbo Pump.
 - 1.24.1. Wait until vacuum level < 10^{-5} mTorr.
- 1.25. Close PV4.
- 1.26. Turn off Turbo Pump.
 - 1.26.1. Wait until RPM is 0.
- 1.27. Turn off Vacuum Pump.
- 1.28. Disconnect H₂ cylinder from Gas Inlet.

Status: 200 bar in lecture bottle up to PV1; the remainder of GHS manifold is under vacuum
< 1 mTorr.

2. Connection of GHS Manifold to Sample Station:
 - 2.1. Confirm sample cell has been properly dried and outgassed and CMV is closed. Sample cell is under vacuum < 10^{-2} mTorr.
 - 2.2. Mount Sample Cell on Cryostat and connect to Sample Station piping.
 - 2.3. Connect Sample Station to PV5 on Manifold.
 - 2.4. Connect PRV and Manifold Exhaust to containment exhaust line.
 - 2.5. Open MV3, MV4 and PV5.
 - 2.6. Turn on Vacuum Pump Station.
 - 2.6.1. Wait Until Pressure at LPT1 ~ 1 mTorr.
 - 2.7. Turn on Turbo Pump.
 - 2.7.1. Wait until pressure at LPT2 is no longer decreasing.
 - 2.8. Close MV4, PV4 and PV5.
 - 2.9. **Open CMV.**

- 2.10. Turn off Vacuum Pump Station.
- 2.11. Mount Radiation Shield and Vacuum Jacket.
3. Dosing Procedure During a Typical Adsorption Experiment:
 - 3.1. Confirm PV0 – 5 are closed, MV2 is closed, and PV6 is open.
 - 3.2. Set cryostat to desired temperature (between RT and 77K).
 - 3.3. Set LFC1 to desired flow setting.
 - 3.4. Open PV1.
 - 3.4.1. Wait until HPT reads 30 bar.
 - 3.5. Close PV1.
 - 3.6. Open PV5.
 - 3.6.1. Wait until pressure equilibrates.
 - 3.6.2. Measure Pressure on HPT.
 - 3.6.3. Take neutron scattering measurement.
 - 3.7. Close PV5.
 - 3.8. Open PV1.
 - 3.8.1. Wait until HPT reads 50 bar.
 - 3.8.2. Close PV1.
 - 3.9. Open PV5.
 - 3.9.1. Wait until pressure equilibrates.
 - 3.9.2. Measure Pressure on HPT.
 - 3.9.3. Take neutron scattering measurement.
 - 3.10. Close PV5.
 - 3.11. Open PV1.
 - 3.11.1. Wait until HPT reads 70 bar.
 - 3.11.2. Close PV1.
 - 3.12. Open PV5.
 - 3.12.1. Wait until pressure equilibrates.

- 3.12.2. Measure Pressure on HPT.
- 3.12.3. Take neutron scattering measurement.
- 3.13. Close PV5.
- 3.14. Open PV1.
 - 3.14.1. Wait until HPT reads 90 bar.
 - 3.14.2. Close PV1.
- 3.15. Open PV5.
 - 3.15.1. Wait until pressure equilibrates.
 - 3.15.2. Measure Pressure on HPT.
 - 3.15.3. Take neutron scattering measurement.
- 3.16. Close PV5.
- 3.17. Open PV1.
 - 3.17.1. Wait until HPT reads 110 bar.
 - 3.17.2. Close PV1.
- 3.18. Open PV5.
 - 3.18.1. Wait until pressure equilibrates.
 - 3.18.2. Measure Pressure on HPT.
 - 3.18.3. Take neutron scattering measurement.
- 3.19. Close PV5.
- 3.20. Open PV1.
 - 3.20.1. Wait until HPT reads 120 bar.
 - 3.20.2. Close PV1.
- 3.21. Open PV5.
 - 3.21.1. Wait until pressure equilibrates.
 - 3.21.2. Measure Pressure on HPT.
 - 3.21.3. Take neutron scattering measurement.
- 3.22. Close PV5.
- 3.23. Open PV1.

- 3.23.1. Wait until HPT reads 130 bar.
 - 3.23.2. Close PV1.
 - 3.24. Open PV5.
 - 3.24.1. Wait until pressure equilibrates.
 - 3.24.2. Measure Pressure on HPT.
 - 3.24.3. Take neutron scattering measurement.
 - 3.25. Close PV5.
4. Dosing Procedure During a Typical Desorption Experiment (immediately follows Step 3):
- 4.1. Adjust LFC2 to desired flow rate.
 - 4.2. Open PV0.
 - 4.2.1. Wait until HPT reads 100 bar.
 - 4.3. Close PV0.
 - 4.4. Open PV5.
 - 4.4.1. Wait until pressure equilibrates.
 - 4.4.2. Measure Pressure on HPT.
 - 4.4.3. Take neutron scattering measurement.
 - 4.5. Close PV5.
 - 4.6. Open PV0.
 - 4.6.1. Wait until HPT reads 80 bar.
 - 4.7. Close PV0.
 - 4.8. Open PV5.
 - 4.8.1. Wait until pressure equilibrates.
 - 4.8.2. Measure Pressure on HPT.
 - 4.8.3. Take neutron scattering measurement.
 - 4.9. Close PV5.
 - 4.10. Open PV0.
 - 4.10.1. Wait until HPT reads 60 bar.

- 4.11. Close PV0.
- 4.12. Open PV5.
 - 4.12.1. Wait until pressure equilibrates.
 - 4.12.2. Measure Pressure on HPT.
 - 4.12.3. Take neutron scattering measurement.
- 4.13. Close PV5.
- 4.14. Open PV0.
 - 4.14.1. Wait until HPT reads 40 bar.
- 4.15. Close PV0.
- 4.16. Open PV5.
 - 4.16.1. Wait until pressure equilibrates.
 - 4.16.2. Measure Pressure on HPT.
 - 4.16.3. Take neutron scattering measurement.
- 4.17. Close PV5.
- 4.18. Open PV0.
 - 4.18.1. Wait until HPT reads 30 bar.
- 4.19. Close PV0.
- 4.20. Open PV5.
 - 4.20.1. Wait until pressure equilibrates.
 - 4.20.2. Measure Pressure on HPT.
 - 4.20.3. Take neutron scattering measurement.
- 4.21. Close PV5.
- 4.22. Open PV0.
 - 4.22.1. Wait until HPT reads 20 bar.
- 4.23. Close PV0.
- 4.24. Open PV5.
 - 4.24.1. Wait until pressure equilibrates.
 - 4.24.2. Measure Pressure on HPT.

4.24.3. Take neutron scattering measurement.

4.25. Close PV5.

4.26. Open PV0.

4.26.1. Wait until HPT reads 10 bar.

4.27. Close PV0.

4.28. Open PV5.

4.28.1. Wait until pressure equilibrates.

4.28.2. Measure Pressure on HPT.

4.28.3. Take neutron scattering measurement

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