NMR CHARACTERIZATION OF THE HYDROGEN STORAGE PROPERTIES OF MICROPOROUS MATERIALS

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A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics and Astronomy.

Chapel Hill 2011

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ABSTRACT

ROBERT JAMES ANDERSON: NMR Characterization of the Hydrogen Storage Properties of Microporous Materials

(Under the direction of Yue Wu and Alfred Kleinhammes)

Nuclear magnetic resonance techniques were employed to study properties and characteristics related to hydrogen storage within a variety of carbon nanomaterials. NMR methods were established for studying adsorption at temperatures of 100 and 290 K, and hydrogen pressures up to 10 MPa. A standard interpretation of the NMR spectra of molecular hydrogen in microporous materials was developed. The characterization of three samples are included here: boron-doped graphite, activated PEEK (a polymer), and zeolite-templated carbon. In all of the studies discussed here, each sample necessitated a custom approach to interpreting the data. The chemical shift, a relaxation filter, and low temperature dynamics were needed to uncover a significantly enhanced binding energy in the boron-doped graphite. The key result of the activated PEEK work was that at 100 K, the pressure-dependent behavior of the chemical shift of the micropore spectral component could be directly linked to the dimensions of the pore. The zeolite-templated carbon displayed local paramagnetic behavior within its pores but was diamagnetic in the bulk form. Pressure-dependent chemical shift analysis revealed that the paramagnetic behavior could be related to the numerous edge sites present.

To Natosha "Matosha" Correro Anderson,

my wonderful wife and the woman who saved my scientific career.

TABLE OF CONTENTS

LIST OF TABLES ix		
LIST OF FIG	URESx	
LIST OF AB	BREVIATIONS xvii	
CHAPTER		
I.	INTRODUCTION AND PREVIOUS WORK	
	1.1 Basic Principles of Experimental Spin-1/2 NMR2	
	1.2 Characterization of Porous Media by NMR12	
	1.3 Hydrogen Storage16	
	References	
II.	EXPERIMENTAL SETUP	
	References	
III.	NMR OF HYDROGEN IN MICROPOROUS CARBONS	
	3.1 Review of the Chemical Shift	
	3.2 Susceptibility Shift of Molecules Near a Graphitic Surfaces	
	3.3 Effects of Molecular Averaging on the NMR Timescale	

	3.4 General Interpretation of the NMR Spectra	40
	3.5 Brief Discussion of "Invisible Micropores"	45
	References	47
IV.	HYDROGEN STORAGE IN BORON-DOPED GRAPHITE	48
	4.1 Sample Preparation	50
	4.2 Measurement of the Binding Energy at Room Temperature	52
	4.3 Further Separation of Components via T_1 Measurements	57
	4.4 Low Temperature Kinetics	64
	4.5 Boron-doped Graphite Conclusions	67
	References	70
V.	HYDROGEN STORAGE IN ACTIVATED PEEK	71
	5.1 Sample Preparation	73
	5.2 Spectral Fitting and Calibration	75
	5.3 General Results	78
	5.4 Determining a Critical Pore Size	82
	5.5 Relative Pore Diameter	84
	5.6 Upper Limit of Pore Size Associated with Peak B	86

	5.7 Uptake and Binding Energy at 100 K	88
	5.8 Structure of Pores at High Burn-Off	.94
	5.9 Activated PEEK Conclusions	.97
	References	.99
VI.	HYDROGEN STORAGE IN ZEOLITE-TEMPLATED CARBONS 1	01
	6.1Sample Preparation1	06
	6.2 Features of the Spectra at 290 K1	09
	6.3 The T_2 Measurement at 290 K1	11
	6.4 The Expected NMR Line-shape of H ₂ in Ordered Materials1	14
	6.5 The T_1 Measurement at 290 K1	15
	6.6 The Creation and Characterization of a Multi-phase Sample1	18
	6.7 Behavior of the Chemical Shifts Relative to H_2 in a Large Void1	20
	6.8 Temperature Dependence of the Overall Spectral Chemical Shift1	22
	6.9 Spectral Evolution at 100 K and Paramagnetism in ZTC-231	24
	6.10 Pore Blocking via Exposure to Atmosphere at 290 K	27
	6.11 Correlating Multiple Peaks with Multiple Phases	.30
	6.12 H ₂ Displacement of O ₂ at 290 K	.33

	6.13 Calibration of the NMR Intensity138
	6.14 The Calibrated 100 K Isotherm and Its Implications for P7(2)-H141
	6.15 ZTC Conclusions147
	References150
VII.	CONCLUSIONS AND FUTURE WORK

LIST OF TABLES

TABLE

5.1 Activated PEEK samples characterized by NMR in this study76

LIST OF FIGURES

FIGURE

1.1 a) Pulse sequence and vector model representation of Free-Induction Decay. b) Visualization of the Fourier transformation. c) Two peaks, one with $\delta = 7$ ppm and area $A = 3$, the other with $\delta = -5$ ppm and area $A = 1$. The area is directly proportional to number of nuclei	1
1.2 Pulse sequence, vector model, and sample data for a) Saturation- Recovery and b) Inversion Recovery T_1 measurements	5
1.3 a) Vector model representation of the spin-echo phenomenon for both a solitary nucleus and multiple nuclei in different chemical environments. The pulse sequence, vector model, and sample data for b) the Hahn Echo and c) the CPMG sequences.	7
2.1 Langmuir adsorption isotherm simulations of hydrogen storage for E_b = 5 kJ mol ⁻¹ at (a) 80 K, (b) 100 K, (c) 120 K, (d) 160 K, (e) 290 K. Parameter fitting of the characteristic curve for data below 10 MPa is difficult in (d) and nearly impossible in (e)	3
2.2 Diagram of the experimental setup (not to scale))
3.1 a) An external field is aligned along the principle axes of a molecular grouping with a susceptibility tensor that is axially symmetric around the <i>z</i> -axis. The chemical shift in each case is graphically depicted and is dependent on the probe molecule's position in the <i>x</i> - <i>z</i> plane, delineated by <i>r</i> , the radial distance of the probe molecule from the center of the grouping; θ , which is the angle between the <i>z</i> -axis and the location of the probe molecule in the <i>x</i> - <i>z</i> plane; and χ_{\perp} and χ_{\parallel} which are the molar magnetic susceptibilities of the grouping perpendicular and parallel to the <i>z</i> -axis, respectively. b) When the probe molecule is located above the graphene plane, $\theta \sim 0^{\circ}$ and $r \sim z$.	7
3.2 a) Due to a random orientation of the slit pores with respect to the external magnetic field, an NMR experiment based on stationary H ₂ molecules would produce a characteristic powder pattern. However, since the NMR timescale is on the order of 3 ms, each H ₂ molecule will explore many different slit pores (b) essentially sampling all orientations and producing a Gaussian (or nearly Gaussian) spectral shape centered at the average of the contributing susceptibility tensors.)

3.3 Surface plots of the expected chemical shift due to the ring current effect of the graphitic surfaces, as a function of distance z from the left wall, for slit-pores with widths of a) 0.8 nm, b) 1.2 nm, c) 3 nm, and d) 5 nm. The spheres represent hydrogen molecules located on the pore wall (white) and in the middle of the slit pore (black). The minimum shift (black molecule) is appreciable for $d = 0.8$, 1.2 nm and has dropped to less than -1 ppm for $d = 3$ nm; by 5 nm it is roughly equal to that of a free hydrogen molecule. In the 0.8 nm slit pore there is little distinction between the two cases. In (e) the 1.2 nm pore is divided into discrete regions determined by the thickness of an adsorbed monolayer of H ₂ . Despite being a continuous function, the chemical shift in the pores can be well-approximated by a free region and an adsorbed region. For all plots, $\lambda = 0.25$ ppm nm ³ , or $(\chi_{\parallel} - \chi_{\perp}) \sim -9.5 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$.	43
4.1 A scanning electron microscopy (SEM) image of the B/C studied was used to estimate an exposed surface area of less than 2 m ² g ⁻¹ .	51
4.2 The ¹ H spectrum of B-doped graphitic carbon exposed to H_2 gas at 290 K and 10 MPa. The black line is the experimentally obtained spectrum while the colored lines are the three components that fit the spectrum very well: the two expected peaks representing H_2 in large voids (A) and H_2 in micropores (B), in addition to H_2 in the calibration capillary (C).	53
4.3 Three different perspectives of the spectra of the H_2 in the B/C at 290 K (room temperature) as it evolves with pressure. Peak B is dominant at low pressures while Peaks A and C are dominant at higher pressures. It is also shown that the chemical shifts of the peaks do not evolve with pressure.	54
4.4 The room temperature isotherms derived from the integrated intensities of Peaks A, B, and C of Figures 10 and 11. Peak B exhibits a non-linear relationship with pressure, which can be fit as a Langmuir adsorption curve, in contrast to Peaks A and C, which obey the linear ideal gas law.	56
4.5 The saturation recovery curve of the magnetization of Peak C at $P = 7.5$ MPa showing the characteristics of double-exponential decay	60
4.6 The values of T_I plotted as a function of pressure for Peaks A and C, and the two components of Peak B, B1 and B2.	60

4.7	Isotherms of the two components of Peak B, as identified by T_1 measurements. B1 is associated with the long- T_1 component and B2 is associated with the short- T_1 component. Here both lines are fit with only one Langmuir adsorption term, although using the binding energy determined for B2 plus an ideal gas term will give a nearly identical fit for B1.	63
4.8	Low temperature spectra of boron substituted graphitic carbon exposed to H_2 gas. The sample is first exposed to 10.0 MPa H_2 at room temperature and then cooled under pressure to 100 K (the pressure is reduced to 7.5 MPa due to the cooling). The pressure is then further reduced at 100 K and ¹ H spectra are taken at each new pressure. Inset: Spectrum when the sample is cooled under dynamic vacuum to 100 K and is subsequently exposed to 10 MPa H_2 gas. Here, Peak B is absent (C is also absent because no capillary was used in this case).	65
5.1	PEEK in an alumina combustion boat (a) before and (b) after thermal treatment under CO_2 (steam produced a very similar product). (c) The chemical structure of one subunit of PEEK. (d) A post-treatment PEEK-CO ₂ -9-80 is used to display a typical TEM image in which small diameter pores are evident.	72
5.2	Steam-9-35 spectrum at 10 MPa and 100 K demonstrating the method of using a 0.1 MPa spectrum to decompose Peaks A and B. The 0.1 MPa spectrum (a) is scaled (b) and shifted (c) to give a good approximation of Peak B. Subtracting this from the full 10 MPa spectrum (d) gives Peak A.	76
5.3	Steam-9-35 NMR spectra with and without capillary, and spectrum of empty sample holder containing only hydrogen, all acquired at room temperature under 10 MPa of H ₂ . The arrows indicate the regions corresponding to known volumes.	78
5.4	Evolution of the NMR spectra as a function of pressure for CO2-9-59 at 100 K. Peak A on the left evolves linearly with pressure and does not have a significant contribution at low pressures while Peak B is present even at the lowest pressure and approaches saturation at higher pressures.	
5.5	Spectra of H_2 in CO2-9-59 at 100 K demonstrating a pressure dependence in the chemical shift of Peak B. The maximum of Peak B is indicated by each spectrum's respective marker, ranging from about -10 ppm at the lowest pressures to approximately -6 ppm at 10 MPa. The chemical shift is plotted against pressure with a logarithmic axis (inset) to emphasize this dynamic behavior	80
	iogarianne axis (mset) to emphasize uns dynamic benavior.	

5.6	Chemical shift of the micropore peak versus pressure at 100 K. A noticeable change in shift with varied pressure is expected only in samples whose average pore size is larger than ~1.2 nm. All nine samples appear to have the same low pressure limit of about -10 ppm, indicating little variation in the degree of graphitization of the adsorbent surface. The error of the shift is approximately ± 0.2 ppm and is represented by the size of the data points.	81
5.7	Chemical shift of the micropore peak at 0.1 MPa and 100 K versus burn-off. The pore diameter is approximately inversely proportional to the absolute value of the shift.	85
5.8	Non-normalized NMR spectra for all nine samples at 10 MPa and 100 K. All but Steam-9-95 clearly exhibit a Peak A and a Peak B	87
5.9	High pressure (0.1-10 MPa) isotherms at 100 K for seven of the nine samples, with Langmuir adsorption fits.	89
5.10	H_2 uptake of the micropores versus burn-off at 100 K for 10 and 0.2 MPa. CO2-9-59 shows the highest uptake at both pressures, despite not having the largest SSA. This is thought to be a result of the limitations of the NMR method and an increase in the mobility between regions in the material.	90
5.11	Binding energies extracted from high pressure isotherms (estimated 5% error) and full pressure-range isotherms (estimated 2.5% error), versus burn-off for seven of the nine samples. The trend of decreasing binding energy with increasing burn-off can be correlated to the increasing widths of the pores in both cases; this is more noticeable in the higher binding energies associated with the narrower pores.	92
5.12	2 Fitting of Steam-9-20 (a) and CO2-9-59 (b) isotherms for extracting binding energy using the entire pressure range and just the high pressure data (insets). This illustrates that the higher binding energy Langmuir term can be approximated to be saturated at 0.1 MPa and therefore replaced with a constant, allowing for the lower binding energy to be determined from partial data sets.	93
5.13	B Pressure-dependent evolution at high pressures (a) and low pressures (b) for Steam-9-95 at 100 K. Peak B is clearly distinct in (b) but cannot be resolved at all in (a) indicating that the average micropore size is ~2.4 nm (or larger), the experimental upper limit of Peak B. Above 1.0 MPa (a), a component due to exchange between the two regions appears between Peaks A and B. This was not observed in any of the other samples.	95

5.14	When plotted relative to the same reference shift (200.0835 MHz), a comparison of the 10 MPa, 100 K spectra of CO2-9-80 and Steam-9-95 shows that the position of the dominant peak in the Steam-9-95 is very near the midpoint between Peaks A and B of CO2-9-80, an indication of significant exchange present only in samples with very high BO.	96
6.1	Diagram illustrating how a ZTC acquires the inverse pore structure of its zeolite Y parent (reprinted with permission from Ref.17)	102
6.2	Structural model of ZTCs, which features an unsaturated cubic lattice (a) comprised of buckybowls (b) and containing various functional groups (d). A nano-cage pore structure is seen in the large-sized molecular model (c), which is constructed with the buckybowl units (b) in the structure of the cubic lattice (a). The inset of (b) shows the structure of the buckybowl sub-unit.	103
6.3	Evolution of the NMR spectra as a function of pressure for ZTC-23 at 290 K. Above 1.5 MPa, at least four features become apparent, in contrast to only two peaks observed in the B-doped Graphite and Activated PEEK samples.	109
6.4	The 9.7 MPa at 100 K spectrum as it decays with 2τ , scaled relative to Peak D for comparison of decay rates. Peak D has a longer T_2 than the other Peaks and appears to have a powder pattern line-shape	112
6.5	The 9.7 MPa, 100 K spectra decomposed into two components, with the T_2 values of the identifiable peaks, including a "hidden" Peak E. The significant contribution to the intensities of most of the other peaks by Peak D is shown.	114
6.6	The 9.7 MPa at 100 K spectrum as it recovers with τ , scaled relative to Peak A for comparison of recovery rates. All peaks except D are present at short values of τ , including the previously obscured Peak E	116
6.7	Comparison of the spectral features of Peaks A, B, C, and E at 9.7 MPa and 290 K as arrived at via T_1 (red) and T_2 (green) filtering methods. All peaks are present in both and have corroborating chemical shifts.	117
6.8	The vertically zoomed $\tau = 25 \ \mu s$ spectrum reveals at least three additional features with relatively low intensities.	117
6.9	Thermal profile of the horizontal tube furnace and the corresponding positions. A variation as high as 80 °C was observed at 900 °C	119

6.10 Due to its long decay constant, the peak arising from the hydrogen in the gap is easily identified in the scaled decaying spectra from the T_2 experiment at 290 K and 9.6 MPa. Its appearance in the middle of the spectra indicates that ZTC-23 has bimodal magnetic susceptibility: paramagnetic internally and diamagnetic externally.	121
6.11 The experimentally determined T_2 values of select shifts, as found at 9.6 MPa and 290 K in the gapped sample. The far right is identified as Peak D by its T_2 value of ~6 ms, while the dominant middle peak has a decay constant 2 ms longer and must be the H ₂ in the gap	122
6.12 Comparison of the 9.7 MPa spectra for 100 K and 290 K. There is a difference in their positions of 1.952 ppm, which is consistent with graphene particles the size of the buckybowls. Chemical shift aside, there are only minor differences in their respective line-shapes (spectra are normalized to unity).	123
6.13 Normalized spectra of ZTC-23 at 100 K illustrate the equal effect of pressure on the position of all the spectral features (top). The peak of the maximum intensity in each spectrum is plotted versus the logarithmic pressure scale to depict this relationship (bottom).	125
6.14 Comparison of the isothermal spectra at 290 K of the baked sample and of the sample exposed to the atmosphere (to scale). The molecules adsorbed from the atmosphere clearly block access to a large number of pores. Peak D is unaffected as expected. Peaks A and E also are unaffected, which is not expected.	128
6.15 Evolution of the peaks excluded from the spectra by pore blockage	129
6.16 Predicted spectrum of Phase 6 at 290 K and 9.7 MPa. The peak associated with H ₂ within Phase 6 is expected to be narrower and have greater relative intensity than shown here.	133
6.17 Time evolution of the spectra of the exposed ZTC-23 at 9.6 MPa and 290 K. Note the initial loss in intensity of Peak D between the first two data points in addition to the upfield trend.	134
6.18 Time evolution of the total integrated intensity of the exposed sample. There is a ~15% increase of the period of 1000 minutes. In the inset, the increase is modeled as an exponential recovery process with a characteristic time of 125 minutes.	136
6.19 Time evolution of the chemical shift of the spectra of the exposed sample, fit with an exponential recovery curve with a characteristic time of 126 minutes, identical within error to the value for the recovery of the intensity.	137

6.20 The 100 K spectral evolution of H_2 in ZTC-23 at 1.0 MPa and above, showing that none of the features show signs of saturation.	142
6.21 The calibrated 100 K isotherm gives a saturation uptake value of 6.5 wt%.	143
6.22 Predicted isotherm at 290 K and its components based on the fit of the 100 K isotherm, compared to the corresponding calibrated experimental values.	144
6.23 Comparison of the high pressure isotherm of P7(2)-H to the predicted uptake of ZTC-23 at 290 K reveals an excellent fit of the data (adapted from Figure 8 in Ref. 1, reprinted with permission). Despite not exactly replicating the structure of P7(2)-H, ZTC-23 appears to be nearly identical in terms of H ₂ storage capacity and binding energy	145

LIST OF ABBREVIATIONS

AC	Activated Carbon
atm	atmosphere
B/C	Boron-doped graphitic carbon
BET	Brunauer-Emmett-Teller
BG	Background
BO	Burn-Off
CPMG	Carr-Purcell-Meiboom-Gill
CVD	Chemical vapor deposition
DOE	[U.S.] Department of Energy
FID	Free-Induction Decay
FM	Ferromagnetic/ferromagnetism
FT	Fourier Transform
HSCoE	Hydrogen Sorption Center of Excellence
ID	Inner Diameter
IUPAC	International Union of Pure and Applied Chemistry
kPa	kilopascal

LJ	Lennard-Jones (interaction theory)
LT	Low Temperature
MPa	megaPascal
MRI	Magnetic Resonance Imaging
NHSP	National Hydrogen Storage Project
NMR	Nuclear Magnetic Resonance
OD	Outer Diameter
Pa	Pascal
PEEK	Poly(etheretherketone)
PFG	Pulsed-Field Gradient
PSD	Pore size distribution
psi	Pounds per Square Inch
pw	pulse width
RCE	Ring Current Effect
RT	Room Temperature
SSA	Specific Surface Area
soom	

sccm

SNR	Signal-to-noise ratio
SWCNT	Single-Walled Carbon Nanotube
T _C	Curie Temperature of a ferromagnet
TMS	Tetramethylsilane
UHP	Ultra-high Purity

CHAPTER ONE

INTRODUCTION AND PREVIOUS WORK

Applying NMR to study the potential of various materials to effectively store hydrogen has necessitated synthesizing several sub-disciplines in the fields of physics and chemistry into one coherent approach upon which future work in the area can have a solid foundation. It is natural to begin with an understanding of the base ingredients of which our approach is composed. In this introductory chapter, a few fundamentals of the NMR experiment will be discussed, in addition to a review of the previous work done using NMR to characterize porous media and an outlining of the issues and the challenges that arise when attempting to store hydrogen in vehicles. In the two following chapters, the surface science (adsorption properties, susceptibility, etc.) of the studied materials will be touched upon, included in the discussions of the factors determining our chosen experimental setup and of the basic expected observations. This will provide a framework for the interpretation of the results obtained from several specific samples, each one with increasing complexity in comparison to its predecessor. Lastly, after a brief conclusion, future work and the potential expansion of these methods into the realm of quantitative pore size distributions will be expounded on.

1.1 Basic Principles of Experimental Spin-1/2 NMR

NMR is a powerful experimental technique, which allows for local, non-intrusive probing of matter on the atomic scale. When a nucleus with nonzero magnetic spin I is placed in an external magnetic field B_0 , the degeneracy of its magnetic energy levels is broken. Its spin must be discretely oriented such that the values of its component along the arbitrarily defined *z*-axis (parallel to the external field) are m = I, I-1,... -I. This creates 2I + 1 non-degenerate energy levels with the energy of each sub-level expressed as

$$E_m = -m\hbar\gamma B_0 \tag{1-1},$$

where γ is the gyromagnetic ratio and \hbar is the Planck constant. For the simplest and most common nucleus used in NMR, the proton, or ¹H, the value of γ is 42.58 MHz/T.¹ Also, I = 1/2 for the proton, so there are only two values that m can assume (+1/2, -1/2). This results in only one possible transition, with an energy of, using eq. 1-1, $E_{\Delta m} = -\hbar\gamma B_0$. Under equilibrium conditions, the populations of m = +1/2 and m = -1/2 are described by Boltzmann statistics. For small values of the quantity $[\hbar\gamma B_0/k_BT]$, the first-order approximation of $(exp(x) = 1 + x - \frac{1}{2}x^2 + ...)$ can be used to calculate a net difference of $\left(\frac{1}{2}\frac{\hbar\gamma B_0}{k_BT}\right)$, and thus a net equilibrium magnetization M_0 proportional to this is created along the z-axis. Here, k_B is the Boltzmann constant. Therefore, in equilibrium $M_z = M_0$. This magnetization can be pictured as a vector aligned along the z-axis of a Cartesian coordinate system (this is known as the vector model). Magnetic moments and ensembles comprised thereof that are not directly aligned with an external magnetic field are known to precess around the field with an angular frequency:

$$\omega_0 = \gamma B_0 \tag{1-2}.$$

This is analogous to the precession of a spinning top that has been tipped off-balance. The value defined as $f_0 = \omega_0/(2\pi) = \gamma B_0/(2\pi)$ is known as the Larmour frequency. The physical picture can be simplified significantly by a coordinate transformation which still is Cartesian in nature but is rotating at the Larmour frequency.² Equation 1-2 is not limited exclusively to the external field of the NMR magnet, however. An antenna broadcasting a radio frequency pulse close to or equal to f_0 can create a field B_1 , which is perpendicular to M_z in the *rotating* frame. According to eq. 1-2, M_0 will be rotated about the applied field's axis by a so-called tipping angle:

$$\theta(t) = t\omega_1 = t\gamma B_1 \tag{1-3},$$

which depends upon the duration of the pulsed field *t*. This is known as the pulse width (pw). After this pulse, *M* (the general term for the net magnetization) will precess about the *z*-axis at the Larmour frequency with a component along the *z*-axis and a component rotating in the transverse (*x*-*y*) plane. The irradiating antennae used in the NMR experiment are usually in the form of either a solenoid coil or a saddle coil. While these are unable to detect any magnetization along the *z*-axis since it is static, the rotating transverse magnetization will induce a current in the coil and can thus be measured. Experimentally it would be ideal if all of *M* were to be tipped into the transverse plane. A rotation of $\pm 90^{\circ}$ would do just this. The crucial 90° pulse-width (*pw90*) is usually found by varying *pw* (which is in units of time) for a fixed *B*₁ until the intensity of *M*_{x-y} = 0 is called the 180° pulse-width (*pw180*), and *pw90 = V*₂ *pw180*. At the core of the

modern NMR measurement is 1) tipping M into the transverse plane (coil transmitting), and 2) recording the induced current as M rotates in the transverse plane (coil receiving). The actual pulse sequences are used are rather diverse and can be quite sophisticated.³



Figure 1.1 a) Pulse sequence and vector model representation of Free-Induction Decay. b) Visualization of the Fourier transformation. c) Two peaks, one with $\delta = 7$ ppm and area A = 3, the other with $\delta = -5$ ppm and area A = 1. The area is directly proportional to number of nuclei.

The simplest of these pulse sequences is the Free-Induction Decay (FID) in which a *pw90* pulse tips M_0 directly into the transverse plane and data acquisition of the oscillating induced current in the time-domain begins immediately thereafter, save for a minimal amount of dead-time required by the hardware (see Figure 1.1a). In this case it is much easier to process and evaluate the data in the frequency domain, so it is very common for the FID data to be Fourier-transformed (FT) (Figure 1.1b). If a nuclei is locally shielded from B_0 , it will precess in that local field B_{loc} at an offset frequency $f_{loc} = [\gamma/(2\pi)](B_{loc} - B_0)$. In many cases B_{loc} is proportional to B_0 ; therefore the Fourier-transformed spectra have this shift δ along their *x*-axes expressed relatively in parts-per-million (ppm, or 10^{-6}):

$$\delta = \frac{(f_{loc} - f_0)}{f_0} \ x \ 10^6 ppm \tag{1-4}.$$

The variable δ is known as the chemical shift and will be discussed further in Chapter 3. In practice, f_0 in eq. 1-4 is often replaced with an externally calibrated reference frequency f_{ref} to determine the zero-shift of the *x*-axis of the spectra. It should also be noted that, for purely historical reasons, this axis is usually displayed as running from positive-to-negative when going left-to-right, whereas the opposite is typical in almost all other fields. The NMR spectrum provides detailed information about the local magnetic environment of nuclei acting as *in-situ* probes. Figure 1.1c shows an example in which one-quarter of the nuclei in the sample are in an environment with a characteristic $\delta = -5$ ppm, while the other three-quarters have $\delta = +7$ ppm. This example shows that information can be obtained not only about the chemical shifts, but also the relative fraction of the nuclei in each environment.



Figure 1.2 Pulse sequence, vector model, and sample data for a) Saturation-Recovery and b) Inversion Recovery T_1 measurements.

Spin-Echo (Refocusing)



Figure 1.3 a) Vector model representation of the spin-echo phenomenon for both a solitary nucleus and multiple nuclei in different chemical environments. The pulse sequence, vector model, and sample data for b) the Hahn Echo and c) the CPMG sequences.

Apart from the chemical shift, two principle concepts in NMR are 1) the recovery of M_z as the system returns to equilibrium after being perturbed from it, and 2) the decay of the coherence of M_{x-y} . These are commonly referred to as the *spin-lattice* (or longitudinal) and the *spin-spin* (or *transverse*) relaxations, respectively.² They are empirically taken to be of exponential form and have respective characteristic relaxation times of T_1 and T_2 . If the nuclei in an NMR experiment were to be completely isolated (i.e., not interacting with the lattice in which they reside) after a 90° pulse (or any arbitrary pulse) created a non-equilibrium state, M_z would remain constant for an infinite amount of time. However, interactions such as collisions in the gaseous and liquid states and thermal vibrations of the lattice in the solid state will eventually restore the system to equilibrium. This exponential recovery is characterized by T_1 , and has the general form

$$M'_{z}(\tau) = (M_{z}^{0} - 1)e^{-\frac{\tau}{T_{1}}} + 1 \qquad (1-5),$$

where M_z^0 is the value of M_z after the system is initially brought into disequilibrium and τ is the experimental time since $M'_z(0) = M_z^0$. It should be noted that M_0 is commonly normalized to unity. In the most common measurements, eq. 1-5 takes on the forms

$$M'_{z}(\tau) = M_{0}(1 - e^{-\frac{\tau}{T_{1}}})$$
 (1-6a), and
 $M'_{z}(\tau) = M_{0}(1 - 2e^{-\frac{\tau}{T_{1}}})$ (1-6b).

Equation 1-6a corresponds to the pulse sequence and vector evolution in Figure 1.2a. In the first part of the sequence, M_z is saturated by repeated 90° pulses around the four axes of the transverse plane, resulting in $M_z^0 = 0$ at $\tau = 0$. This is called the Saturation-Recovery measurement. In eq. 1-6b (Figure 1.2b), a 180° pulse is used to invert M_0 completely such that $M_z^0 = -M_0$ at $\tau = 0$. This is known as the Inversion-Recovery (IR) measurement. Equations 1-6a and 1-6b were derived by substituting the appropriate vales of M_z^0 into eq. 1-5. In both cases, after a delay time τ another 90° pulse rotates M_z into the transverse for measurement.

If B_0 were uniformly homogenous and all the nuclei in the NMR experiment were static (and ignoring T_i effects), a magnetization vector in the transverse plane $M_{x\cdot y}$ would have the form $M'_{x-y}(\tau) = \sum M^{0,i}_{x-y} e^{-i\tau\omega_i}$, where $\sum M^{0,i}_{x-y}$ is constant with time (i.e., it remains coherent even if individual nuclei are precessing with different ω^i_{loc}). Local variations in the chemical shift, dipole-dipole interactions, collisions, diffusion and other effects can cause ω^i_{loc} to vary on the timescale of the NMR experiment (usually ~ 3 ms), leading to an exponential decay in the overall coherence. A useful picture for understanding this is the illustration of a room full of analog clocks that are all set to read precisely the same time at $\tau = 0$. If they are not all running at exactly the same rate, then after $\tau = \tau'$ one would observe them reading a distribution of times. After long enough τ , this distribution will become completely random (zero coherence). Such is the case with the nuclei precessing ("keeping time") in the transverse plane, giving an additional exponentially decaying factor:

$$M'_{x-y}(\tau) = e^{-\tau/T^2} \Sigma M^{0,i}_{x-y} e^{-i\tau\omega_i}$$
(1-7).

In order to measure T_2 , the phenomenon of spin-echo, first discovered by Hahn,⁴ is employed. This involves allowing M_{x-y} to precess for a time τ , after which a refocusing 180° pulse is applied along the axis with which M_{x-y}^0 was initially aligned. The effect this has on M'_{x-y} is that its component along the original transverse axis remains unchanged while the component along the perpendicular axis experiences a change in sign. After another delay equal to the original τ ($t = 2\tau$), the nuclei will have precessed the same amount as they did during the original τ if ω_i of the individual nuclei remained constant. However, the flipping of the perpendicular component will have resulted in precession *towards* the original axis instead of *away* from it causing the magnetization of each nuclei to realign along the original axis (see Figure 1.3a). Thus, $\Sigma M_{x-y}^{0,i}e^{-i\tau\omega_i} = M_{x-y}^0$, and eq. 1-7 assumes a much simpler form:

$$M'_{x-\nu}(2\tau) = M^0_{x-\nu} e^{-2\tau/T^2}$$
(1-8a).

Returning to the example of the clock room, due to an analogous 180° pulse time will begin to run *backwards*. Despite each clock running at a rate not correlated to that of the other clocks, at time 2τ they will all display precisely the same time. A quantum mechanical treatment shows that "reversing time" is indeed a rather accurate view of the situation.²

A common pulse sequence used to measure T_2 is the Hahn Echo, which is the application of a 90° tipping pulse of the magnetization into the transverse plane followed by a 180° refocusing pulse at $t = \tau$, and finally data acquisition at $t = 2\tau$ (Figure 1.3b). The experiment is repeate using different values of τ . This creates an array of data that can be fit with eq. 1-8a. Since this requires multiple additive scans (executions of the pulse sequence) for each value of τ in order to increase the signal-to-noise ratio (SNR), this can be a time-consuming experiment (using multiple scans to reduce the SNR is general to the NMR experiment, not just the Hahn Echo). In order to significantly reduce the experiment time without sacrificing high SNR, Carr and Purcell⁵ and Meiboom and

Gill⁶ devised a pulse sequence that used a series of *n* 180° pulses equally-spaced by delay $2\tau_E$ after the initial 90° pulse to create a train of echoes in-between each pair (Figure 1.3c). This sequence, called CPMG after its inventors, allows *n* data points to be acquired in *each* scan. For an idea of the magnitude of this advantage, consider an experiment with $\tau_E = 1ms$ and a 1s acquisition time, both typical of many situations. Over 1000 data points can be acquired during each scan, compared to the single data point of the Hahn Echo. However, it should be noted that one distinct advantage of the Hahn Echo over CPMG is that it provides sufficient time-domain data to produce a frequency-domain spectrum, while the CPMG sequence only records the magnitude of the first few points of the FID due to the limited amount of time $2\tau_E$ between pulses for data acquisition. This is important when the shifts of different components in the spectra provide valuable information. As in eq. 1-8a, when diffusion effects are ignored the magnetization of the CPMG experiment follows this form:

$$M'_{x-y}(2n\tau_E) = M^0_{x-y}e^{-2n\tau_E/T^2}$$
(1-8b).

If it is expected that the spin populations can take on only a few distinct values of T_2 , then this can be fit with two to eight parameters (for one to four components). On the other hand, if a distribution of T_2 values are expected, which is not uncommon particularly in the case of gas in a porous medium with a range of pores sizes, the data is often fit using an [unstable] inverse Laplace-transformation. However, CPMG is better suited for characterizing the range of pore sizes in meso- and macroporous systems than the narrow ranges typical in microporous materials, and is thus not employed in the current studies.

1.2 Characterization of Porous Media by NMR

Primarily, these sequences are used in the NMR characterization of porous media. Which particular sequences are implemented depends on several factors such as experimental time constraints, probe molecule used, and physical and chemical characteristics of the particular porous medium. However, of these, the length-scale of the pores is the most relevant. The International Union of Pure and Applied Chemistry defines micropores as those having characteristic diameters of 2 nm of less, mesopore diameters as ranging from 2 nm to 50 nm, and macropores as having diameters above 50 nm,⁷ while in other disciplines such as soil sciences these terms have very different meanings. For example, the upper limit of a micropore can be as high as $10 \ \mu m$,^{8.9} four orders of magnitude larger than the IUPAC definition. Such a broad definition of micropores is ill-suited for the length scales in this work, so for the purpose of this study the IUPAC standards will be used exclusively.

In microporous materials (and some mesoporous ones) the surface interaction between the probe molecule and the pore wall is apt to be the most significant contribution to any observable NMR characteristics. This is especially true of carbonaceous materials where the ring current effect (RCE) produced by the aromatic structures in the external magnetic field can give rise to significant chemical shifts for nearby molecules.¹⁰ Because of this, the structure of the NMR spectra in these types of studies provides the majority of novel information. Simple FID experiments are often more than adequate for robust characterization of the system. While the sequence itself is rather straight-forward, there is an array of other experimental parameters that can be varied for in-depth study of a number of features of the system. Probe molecules, which have been used to investigate media with a significant proportion of pores on this length scale, include (but are not limited to) water,¹¹⁻¹⁴ benzene, ^{11-13,15,16} nitrobenzene,¹⁷ acetone,¹³ acetonitrile,^{11,16,18} methane,^{13,19} dimethylsulfoxide,¹³ 1-2 dichloroethane,¹⁸ dichloromethane,¹⁶ xenon,^{20,21} cyclohexane,^{12,22} carbon tetrachloride,¹⁶ and, most recently, hydrogen.²³ In the case of graphite intercalated with alkali metals, the intercalated atoms themselves are sometimes used as the "probe" molecule, if they have a non-zero magnetic moment.²⁴⁻²⁶ A wide variety of materials have been investigated with these molecules, from activated carbons^{13,15,18,27} to zeolites,^{20,21} and many others in between: exfoliated graphite,¹¹ graphite oxide,²⁸ amorphous and carbonized silica,¹⁴ porous silica,²⁹ zeolite-templated carbons (ZTCs),³⁰⁻³³ single-walled carbon nanotubes (SWCNT),^{19,23, 26,34-37} and even porous biological tissues.³⁸

The two most common experimentally varied system parameters are the concentration/pressure of the probe molecule and the overall temperature of the system. The pressure here refers to the external pressure of the gaseous probe^{19-21,23} or the partial pressure^{26,29,35,37} (filling fraction) when the experimental temperature is in the neighborhood of the probe's boiling point, while the concentration is applicable in the case of probe molecules suspended in a solvent liquid.¹⁶ This experimental latitude is crucial for studying adsorption and pore-filling processes. Also, regularly of scientific interest is the general temperature dependence of the NMR spectra (chemical shift, linewidth, intensity, etc.) and the relaxation times (T_1 and T_2),¹⁵ but variation of the temperature also can be used to obtain pore size distributions (PSDs) via calculation of the distribution of Gibb's free energies³⁸ or melting temperatures,^{12,22,39,40} with the latter commonly referred to as NMR cryoporometry.²⁴ In the case of adsorption studies where

the probe molecule is used as the adsorbate, the relationship between the binding energy E_b and the experimentally observable adsorption coefficient *b* is an exponential function with (E_b/k_BT) as its argument.⁴¹ It is very useful to have the ability to "tune" the temperature of the experiment to a regime where E_b can be accurately characterized. If the temperature is too low, the surface will have already saturated at low pressure and the adsorption isotherm will have a slope of zero. If the temperature is too high, the adsorbate may not saturate the surface until the pressure has reached an experimentally unattainable value, resulting in an approximately linear isotherm from which *b* and, therefore, E_b cannot be extracted.

As already noted, the basic FID sequence is the convenient option in experiments where the chemical shift reveals useful information about the porous medium due to, for example, the spatial nature of susceptibility effects^{13,16,19,28} or the probe-probe interactions seen in confined xenon.^{20,21,25} In addition, it is also excellent for tracking the total intensity of the NMR time-domain signal as it changes with temperature in Gibb's free cryoporometry experiments. Although they are most useful when energy and characterizing meso- and macroporous materials, $T_1^{16,42}$ and T_2 measurements^{15,16,29} can provide a substantial amount of helpful data to aid in the overall characterization of microporous materials. On occasion, a CPMG measurement will appear in the literature,¹⁷ although it is rarely used to directly characterize the micropores themselves. In addition to the aforementioned NMR sequences/methods, Pulsed-Field-Gradient NMR (PFG-NMR) is very useful for measuring self-diffusion and related phenomena. However, its applicability is limited to length scales of $10^{-7} - 10^{-4}$ m⁴³ and therefore is only truly useful for studying macroporous systems. Similarly, Magnetic Resonance Imagining (MRI) techniques, which also depend on an external field gradient, have difficulty accurately characterizing smaller pores.⁴⁴ The validity of the other methods in the micropore regime is not as definite. For the most part, the theory behind xenon gas experiments has been limited primarily to materials with a significant amount of order in their structure, such as zeolites. It was recently shown²⁵ that due to the disordered nature of the materials, it is generally ineffective for studying carbons. However, the same paper also showed that the xenon experiment could possibly be adapted so that the chemical shift term arising from binary Xe collisions could be correlated to a mean micropore size within the material. NMR cryoporometry is applicable down to at least pore diameters of at least 5 nm;²² experimentally this lower limit is below 1 nm.¹² Similarly, PSDs derived from T_1 measurements extend partially into the micropore region,⁴² and T_2 studies are thought to be accurate starting at approximately 1 nm.²⁹ In all of the three preceding instances the methods are best suited for mesoporous materials and their accuracy decreases when nearing the microporous regime. This is not surprising, however, since this is where most systems transition from being macroscopic, statistically averaged and classical to microscopic, discrete and more sensitive to quantum effects. This makes theoretical considerations much more nuanced and complicated. It should be noted, though, that a comparison of these methods to more traditional methods, specifically mercury-intrusion porometry and Brunauer-Emmett-Teller (BET) derived PSDs,⁴⁵ represents an advancement in the accurate characterization of micropores.

A review of the literature shows that the most recent work in characterizing microporous media with NMR is predominately solid-state NMR and xenon gas studies. One major exception to this would be A.A. Turov and his colleagues who have

extensively used NMR to investigate many adsorbate-surface and adsorbate-pore interactions, many of which have been microporous in nature (the extent of their influence is evident in the Bibliography section of this chapter). Water,^{26,34-37} methane,¹⁹ and molecular hydrogen²³ in SWCNTs have been a topic of interest within a small niche of the NMR community in the past several years as well. While this is not an exhaustive list of all the work done in this field, it does give a good sampling of what is relevant to the studies discussed herein. For the interested reader, a more thorough review of NMR methods used for characterizing porous media is suggested.⁴⁶

1.3 Hydrogen Storage

In January 2003, then-President Bush launched the Hydrogen Fuel Initiative, effectively allocating \$1.2 billion over the next five years for accelerated research towards science and technology, which would allow for large-scale commercialization of hydrogen fuel cell vehicles.⁴⁷ He did so with good reason: according to a 2006 U.S. Department of Energy (DOE) report,⁴⁸ the U.S. will have to increase the percent of its imported oil supplies from 55% (current at time of report) to 68% by 2025 under the "business as usual model"—if current consumption trends continue and if no revolutionary alternative energy technologies appear in the meantime. With the transportation sector accounting for about two-thirds of the nation's oil usage, it is the largest contributor to our energy dependence on foreign entities—along with the national security issues that often arise when those entities' interests and ideologies are in direct or indirect conflict with our own. It would be of real benefit, then, if a significant portion of

the current transportation fleet could be replaced with a hydrogen fuel cell powered equivalent. The energy needed for producing hydrogen fuel potentially could be derived from a plethora of domestic resources both nonrenewable (e.g., natural gas, coal, nuclear) and renewable (geothermal, hydro, solar, wind, etc.). Using nonrenewable options has the additional advantage of producing zero over-the-road emissions while allowing any necessary emissions to be centrally produced, which are then more easily preventable or captured. Given the increase in scientific support for global warming being at least partially correlated with human activity, any development that would result in a decreased environmental impact should be welcomed.

Making these aspirations a reality, however, turns out to be a rather non-trivial task. In order for hydrogen vehicles to be commercially viable, it is assumed that they must meet the same demands that consumers currently place on fossil-fuel vehicles. This tension has been nicely laid out by Satyapal, et al.⁴⁹ in their 2006 report on the progress of the DOE's National Hydrogen Storage Project:

"There are three primary barriers that must be overcome to enable industry commercialization of hydrogen fuel cell vehicles: (1) on-board hydrogen storage systems are needed that allow a vehicle driving range of greater than 300 miles [500 km] while meeting vehicle packaging, cost and performance requirements; (2) fuel cell system cost must be lowered to \$30 per kilowatt by 2015 while meeting performance and durability requirements; (3) the cost of safe and efficient hydrogen production and delivery must be lowered to be competitive with gasoline (a target of \$2.00 to \$3.00 per gallon gasoline equivalent, delivered, untaxed, by 2015) independent of production pathway and without adverse environmental impact."

They continue on to point out that all of these issues are at their heart cost-driven, with one major exception: on-board fuel storage. No technology or approach currently exists that can simultaneously meet packaging requirements such as volumetric and gravimetric
constraints, performance requirements such as fuel loading/unloading and on-demand availability (needed for accelerating to beat a train across a train crossing, for example), and the range requirement of 300 miles. Of the Hydrogen Fuel Initiative's \$1.2 billion, \$150 million has been earmarked for the aforementioned National Hydrogen Storage Project (NHSP) with its primary purpose being to develop a hydrogen storage system that will be able to meet performance targets set by the DOE by 2010, with additional benchmarks set for 2015.⁵⁰ Integral to this concerted effort is basic science research.

There are three primary approaches to solving the storage problem within the NHSP, each with their own set of advantages, drawbacks, and challenges:⁴⁹ metal hydrides, chemical storage, and storage via physisorption in carbon-based materials with high surface areas. The work here has been performed under the Hydrogen Sorption Center of Excellence (HSCoE), a NHSP collaboration of academic, industrial, and national laboratory partners pursuing the latter of the three research paths. Therefore, issues related to the other two approaches will be omitted from further discussion. The attractiveness of physisorption of molecular hydrogen (H₂) in lightweight sorbent materials is its reversibility and fast kinetics. Of course, this approach is not without its own major challenges, which range from weak binding energy (due to the intrinsic strength of van der Waals interactions), to demanding material engineering of extremely large specific surface area (SSA).

Thermodynamic considerations indicate that the H₂ binding energy E_b ideally should be around 15 kJ mol⁻¹ for room temperature operation under moderate pressure (P< 10 MPa).⁵¹ For energies much lower than this, the adsorbing surface is unable to saturate, resulting in inefficient storage of the H₂. Higher binding energies easily

overcome the saturation issue but at the expense of reversibility only being possible with vacuum pressures or a significant rise in the operating temperature. Unfortunately, binding energies on the order of 15 kJ mol⁻¹ for molecular hydrogen are rarely seen in natural sorbent materials. For instance, lightweight sorbent materials of metal organic framework (MOF)^{52,53} and activated carbon aerogels⁵⁴ have BET surface areas of up to 5640 m^2/g and 3200 m^2/g , respectively. However, the measured enthalpy of H₂ adsorption is typically less than 7 kJ/mol for both cases.⁵²⁻⁵⁴ As a consequence, the room temperature storage capacities at 10 MPa in these materials are below 1 wt%,⁵⁵ despite having achieved saturated H₂ capacities of 7.5 wt% and 5.3 wt% at 77 K in MOF-177 and carbon aerogel, respectively. In general, binding energies based on the van der Waals interaction alone are typically 4-7 kJ mol^{-1.56} Materials with large surface area and with binding energies in this range support high H₂ capacities at 77 K. Although cryogenic storage systems are already being designed, room temperature applications are ultimately desired and require interaction mechanisms that lead to H₂ binding energies in the range of 10-20 kJ/mol.

In addition to the issues with binding energy, the majority of these materials commonly encounter the problems of low surface areas and unstable or inaccessible pores, all of which limit the amount of H₂ that they are able to store. This is unfortunate because it has been shown that, in the systems of interest here, the surface area should be the main determinant of the total uptake.⁵⁷ Besides requiring a large surface area for maximum hydrogen uptake, a material also needs an almost exclusively microporous (d < 2 nm) structure.⁵¹ It is no surprise, then, that among this group of storage candidates, it is thought that nano/microporous carbon materials have the pore diameters best suited for

 H_2 uptake.⁵⁸ However, it has proven non-trivial to achieve both the large surface area and the micropore diameters necessary for optimized H_2 storage.⁵⁹ Among the array of approaches to synthesizing such porous materials are inorganic⁶⁰ or organic⁶¹ templating and activation,⁶² although none of these method has yet to emerge as a panacea for both of these pore-space engineering issues.

In light of this increasing interest in vehicular hydrogen storage and its increasing body of candidate materials, it is crucial that the potential applications of a technique as versatile and powerful as NMR are not overlooked for hydrogen storage studies. As discussed in the previous section, NMR has now been used widely in adsorption and surface studies for several decades (Turov and Leboda⁶³ have written an extensive review of such work in carbon-based materials). However, there is a complete lack of instances where H₂ has been utilized as the NMR probe molecule. In fact, H₂ is rarely even used for [non-NMR] surface area determination due to a low condensation point of 20.28 K, which is experimentally required for application of the Brunauer-Emmett-Teller (BET) theory.⁴⁵ For this same reason, it is also excluded from experiments designed to measure PSDs for any type of material. Despite a general lack of experimental precedent, H_2 is the adsorbate species in this case and thus it would be advantageous and quite appropriate to use it to probe the nanostructures of these materials. Despite their familiarity, the traditional probe molecules (N2, CO2, etc.) may not be able to explore fully all of the H2relevant pore structures and surfaces due to issues such as differences in accessibility and molecular dynamics. Further, the lower limit of pore size where the BET approach is applicable for determining pore size distributions is uncertain; some have suggested this to be as large as 7.5 nm.⁶⁴ Given that this regime is of utmost importance to H_2 storage,^{51,65,66} a method better equipped for probing the smallest of pores is needed. Recently, ¹H and ²H NMR was used to evaluate the hydrogen storage properties of carbon nanotubes.²³ in which adsorption isotherms based on the NMR intensity were obtained but no method for calibrating the absolute quantities was proposed. Such isotherms, properly converted to units of mass, would be a useful alternative to volumetric and gravimetric isotherms. Furthermore, in carbonaceous samples, chemical shifts arising from the ring-current effect⁶⁷ could potentially allow the H₂ occupying intergranular macropores to be distinguished from H₂ residing in smaller pores, providing valuable information about nanostructures that the other methods for producing isotherms are not able to give. In addition to the uptake of the smaller pores, the binding energies associated with their surfaces also may be determined from this information, both of which are important parameters for the application of hydrogen storage with a DOE 2015 target value⁵⁰ of 9 wt% for the uptake and 15 kJ mol⁻¹ (or possibly as high as 20-40 kJ mol^{-1})⁶⁸ for the binding energy. It is crucial that candidate materials can be engineered to have optimal pore sizes and structures if physisorption is to be a viable option for vehicular storage.⁶⁹ The information about the structure provided by the NMR method will prove to be valuable feedback for the chemists and material scientists synthesizing the samples.

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CHAPTER TWO

EXPERIMENTAL SETUP

Of primary interest in hydrogen storage studies are the binding energies and storage capacities (or uptake) of the relevant gas-surface systems. The critical experimental variables necessary for investigating these characteristic properties via adsorption/desorption isotherms are temperature and pressure. The binding energy E_b of H₂ on graphitic surfaces is normally dominated by van der Waals interactions, typically resulting in values in the range of 4-7 kJ mol^{-1.1} For this range of binding energies, the isotherm of the H₂-graphitic system will be linear below 10 MPa at room temperature (RT, ~290 K), as can be seen in (e) of Figure 2.1. Here, the Langmuir model of adsorption is used to describe n_{ad} , the number of adsorbed molecules, and is given by²

$$n_{ad}(P,T) = n_{\infty} \frac{bP}{1+bP}; \ b = \frac{\sigma}{v_0 \sqrt{2\pi m_{H_2} k_B T}} \exp(\frac{E_b}{k_B T})$$
 (2-1),

where n_{∞} is the saturation coverage, σ is the area occupied by a H₂ molecule on the surface (about 0.16 nm² based on the commensurate filling measurement of a graphite plane),³ v₀ is the attempt frequency of about 10¹³ Hz, m_{H_2} is the mass of H₂, and k_B is the Boltzmann constant. These conditions are crucial when designing the experiment, as they correspond well to the technical targets the DOE has set forth for the maximum delivery pressure and operating temperature for on-board vehicular H₂ storage.⁴

In order to observe a characteristic adsorption curve in the isotherm below 10 MPa that can be distinguished from components behaving as free gas, it is beneficial to take measurements at lower temperatures in addition to RT. This advantage can be readily observed in the simulated adsorption curves for T = 80, 100, 120, and 160 K in Figure 2.1. In most cases saturation will occur at or below 10 MPa at these temperatures, which is easily obtained by implementing a nitrogen-flow cryostat from Oxford Instruments ([a] in Figure 2.2). It was determined that 100 K was the optimal low temperature for both physical (see above) and practical (temperature stability and probe functionality) reasons. Hereafter, "low temperature" and "LT" should be taken to mean 100 K unless otherwise specified. In general, both RT and LT measurements were performed for the hydrogen storage studies.



Figure 2.1 Langmuir adsorption isotherm simulations of hydrogen storage for $E_b = 5 \text{ kJ} \text{ mol}^{-1}$ at (a) 80 K, (b) 100 K, (c) 120 K, (d) 160 K, (e) 290 K. Parameter fitting of the characteristic curve for data below 10 MPa is difficult in (d) and nearly impossible in (e).





The pressure control component of the experiment was designed so the pressure could be varied from 100 Pa to 10 MPa in-situ without otherwise disturbing the system, which is crucial for producing reliable isotherms. Referring to Figure 2.2, a methane or hydrogen source [b] is connected to a titanium coupler [c] within a 200 MHz (4.7 T) superconducting magnet [d] via an arrangement of Autoclave medium pressure stainless steel tubing [e] with a 0.109" inner diameter (ID), a 0.250" outer diameter (OD), and a pressure rating of 20,000 psi (~138 MPa). Swagelock valves with the same pressure rating are incorporated in order to increase the pressure from the gas source [f] or decrease the pressure by releasing gas into a branch [g] connected to a BOC Edwards turbo-pump [h] capable of vacating the system to less than 1 Pa. Three pressure gauges were used to accurately cover a range from 0.13 Pa to 12 MPa. A high pressure gauge [i], accurate from 50 kPa to 12 MPa, is connected to the main gas line, while another gauge with a range from 0.13 Pa to ~133 Pa [j] is situated in the branch leading to the vacuum and is primarily used for monitoring the turbo-pumping. A gauge accurate below 50 kPa, located alongside the low-pressure gauge, bridges the range gap between the others but was present only in later experiments. Lastly, the sample holder [k], which is composed of a cylindrical sapphire tube (open on one end; 3 mm ID) bonded to a titanium neck with Emerson and Cuming StyCast Black Epoxy, is connected to the pressure system via the titanium coupler. The final closed system has been extensively checked for leaks at both 10 MPa and under vacuum.

Perhaps the most important components of the experimental setup are the NMR probe, spectrometer, and processing software, which enable meaningful data to be obtained in the first place. Within the custom-built probe is a saddle coil [m] with a

tuning circuit that can be tuned to resonance (here, f = 200.0835 MHz) at both RT and LT, along with a thermocouple [n] for accurate temperature monitoring in the sample region. This is connected to a TecMag Apollo spectrometer [o]. TecMag's interface and processing software, NTNMR, is used to control the experiments [p]. The susceptibility shift of the H₂ molecules within the porous graphitic materials provides a wealth of information, so a basic free-induction decay (FID) pulse sequence is used for obtaining isotherms of the frequency-domain spectra (via a Fourier transform of the FID, which is in the time-domain) in the all of the hydrogen storage experiments. While the susceptibility shift is technically distinct from the chemical shift, the latter will be used in place of the former hereafter since chemical shift is the more familiar concept of the two within the field. In a few instances, T_1 saturation recovery, T_2 spin-echo, and 2D-exchange sequences are used to supplement the FID data.

In all of the hydrogen storage experiments, the sample was dynamically evacuated at RT for 12 hours to less than 1 Pa using the turbo-pump before the initial loading of hydrogen. NMR spectra were taken during the initial pump down and the removal of Hcontaining contaminants, mainly H₂O, adsorbed on the sample was observed. After pumping down, a background spectrum was obtained; this was later subtracted from the isotherm spectra with H₂ gas present. After recording the background spectrum, a spectral isotherm up to 10 MPa was measured at RT. The system was then lowered to 100 K while still under pressure. Once the 100 K had been maintained for a minimum of 15 minutes, the pressure was readjusted to 10 MPa and another isotherm was acquired, this time decreasing in pressure. A background spectrum was taken once the system had been dynamically pumped an average of 15 minutes.

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CHAPTER THREE

NMR OF HYDROGEN IN MICROPOROUS CARBONS

It is rather useful to begin with a discussion of the general features that might be expected to arise in the NMR spectra of gaseous molecules interacting with a microporous carbon. There are three key assumptions: 1) the surfaces are at least partially graphitized; 2) the contribution of the micropores accounts for a significant amount of the overall porosity; and 3) the geometry of the micropores can be approximated as slit-pores. Whether or not these criteria are met will be discussed on a per-case basis in later chapters. As mentioned in Chapter 1, the majority of methods of porous media characterization by NMR focus on measuring relaxation times T_1 and T_2 , and then draw correlations between these parameters and features of the volumes and surfaces within the material. However, the valid regime of the established theory excludes size-scales on the order of nanometers or less,¹ making similar applications of NMR to studying microporous media difficult, if not impossible. Due to confinement and adsorption, local interactions between the gaseous molecules and the pore walls predominantly determine the NMR features within the micropores. Therefore, in order to accurately characterize materials which are largely comprised of micropores via NMR, the ability to measure the phenomena of this shorter length scale is needed. NMR is excellent for measuring variations in the local magnetic field throughout the sample. A brief overview of this aspect of the NMR experiment is in order.

3.1 Review of the Chemical Shift

These variations often arise from magnetic shielding of the nuclei due to their local chemical environment and appear as a shift in the frequency-domain spectrum away from the resonance frequency v_0 of an unshielded nucleus. Thus, the term "chemical shift" is most often used to describe the x-axis of NMR spectra, and is defined as $\delta = (f_{loc})$ $-f_{ref}/f_{ref}$ and measured in relative units of ppm (10⁻⁶). Here, v_{ref} is an experimentally-set reference frequency and is not necessarily v_0 , since the shift is a relative measurement. Although not used here, the shift of the standard reference compound of tetramethylsilane, Si(CH₃)₄ (TMS), is set to zero for ¹H NMR. The chemical shift convention assigns ¹H nuclei resonating downfield (to the left) of TMS positive values and regards those as less shielded while nuclei resonating to the right of TMS are considered more shielded or diamagnetic and given negative chemical shift values. NMR shifts downfield to TMS have been observed for ¹H nuclei associated with C-H bonds, in chains, aromatic compounds, etc. with ¹H associated with alkane chains being located between 1 and 2 ppm and the proton line of benzene at 7.26 ppm.² It was Pople³ who first invoked an induced ring current extending along the benzene ring and involving the π electrons to explain the difference in chemical shift between the ethylenic and aromatic protons. In this case, the protons are located in the plane of the benzene ring and the ring current effect affords an additional downfield shift that adds to the ethylenic (or local) contribution.³ In the case of liquids and gases, some experimentally determined values of the chemical shift are 0.4 ppm for H_2O vapor, 4.8 ppm for H_2O liquid, and 6.9 ppm for free H₂ gas.

Armed with an idea of how the chemical shift of nuclei fixed relative to their immediate surroundings behaves, one can approach what a characteristic shift of nuclei that are dynamically exploring a variety of environments looks like, as is the case of gas in porous media. There are three important differences to consider between the cases of fixed and gaseous nuclei. First, there needs to be a basic understanding of the effect the surface of the host material will have on the spatially-varying local magnetic field that the gas is exploring. Second, an averaging effect arises from the considerable distance that the highly-mobile gaseous species will travel within the material during the timeframe of the NMR experiment, which is on the order of 3 ms. These two factors alone will allow some rather useful generalizations to be made and will provide a basis for interpreting the results in later chapters. Finally, the possibility of variations of the surface throughout the sample raises the question of how extensively these generalizations can be applied and must be duly addressed.

3.2 Susceptibility Shift of Molecules Near a Graphitic Surface

In contrast to the chemical nature of the NMR shift of nuclei stationary relative to their surroundings, the shift associated with a gaseous molecules in a pore will arise from a gradient-like variation of the susceptibility within the pore space, which, for a slit-pore geometry, can be adequately described as a function of the distance z of the molecule from the surface that is causing the deformation in the magnetic field profile. In this sense, this is technically a susceptibility shift and the NMR spectrum is a reflection of the distribution thereof. However, since the chemical shift is the more familiar term of the

two, it will be predominantly used to describe any shift in the spectra. Initially, σ will be used to discuss the susceptibility shift, but will be replaced by δ once the appropriate generalizations have been made.

Since a precondition placed upon the porous material is that the surfaces is at least partially graphitized, the aforementioned ring current effect (RCE) of the aromatic rings will provide a general frame-work for understanding the distribution of local fields produced by placing the surface in the external magnetic field of the NMR experiment. In stark contrast to the fixed planar hydrogen of the benzene ring described above, a hypothetical ¹H nucleus located above the center of the benzene ring would show a diamagnetic response due to the ring current and the resonance would be shifted upfield, the ¹H nucleus being more shielded (see Figure 3.1). Consequently the chemical shift for a hydrogen molecule adsorbed on graphene and located above the plane of the aromatic rings is expected to be strongly diamagnetic. This enables shifts that are upfield of TMS to be clearly distinguished from nuclei in conventional C-H bonds. Today the Pople – Langston – Pauling approach of invoking ring currents has been replaced by *ab initio* quantum mechanical computations. However, the intuitive picture of the extended ring current and induced dipole moment giving rise to a local field at the probe nucleus is still useful⁴ and is invoked here in a phenomenological approach.



Figure 3.1 a) An external field is aligned along the principle axes of a molecular grouping with a susceptibility tensor that is axially symmetric around the *z*-axis. The chemical shift in each case is graphically depicted and is dependent on the probe molecule's position in the *x*-*z* plane, delineated by *r*, the radial distance of the probe molecule from the center of the grouping; θ , which is the angle between the *z*-axis and the location of the probe molecule in the *x*-*z* plane; and χ_{\perp} and χ_{\parallel} , which are the molar magnetic susceptibilities of the grouping perpendicular and parallel to the *z*-axis, respectively. b) When the probe molecule is located above the graphene plane, $\theta \sim 0^{\circ}$ and $r \sim z$.

Given the axially symmetric nature of aromatic rings and graphitic surfaces, it is natural to start by referring to semi-empirical formulae for the chemical shift tensor components produced by a molecular grouping with such susceptibility symmetry in a magnetic field aligned along its principal axes (see Figure 3.1a):⁵

$$\sigma_{xx} = \frac{1}{4\pi} \chi_{\perp} (3\sin^2 \theta - 1) \frac{1}{r^3}; \sigma_{yy} = -\frac{1}{4\pi} \chi_{\perp} \frac{1}{r^3}; \sigma_{zz} = \frac{1}{4\pi} \chi_{\parallel} (3\cos^2 \theta - 1) \frac{1}{r^3}$$
(3-1).

Here, θ is the angle between the *z*-axis and the location of the probe molecule in the *x*-*z* plane, *r* is the radial distance of the probe molecule from the center of the grouping, and χ_{\perp} and χ_{\parallel} are the molar magnetic susceptibilities of the grouping perpendicular and parallel to the *z*-axis, respectively. As previously described, H₂ probe molecules adsorbed above a graphene plane will experience a noncontact chemical shift due to local magnetic fields caused by induced ring currents. For this specific geometry with $\theta \sim 0^{\circ}$ and $r \sim z$, eq. (3-1) simplifies to

$$\sigma_{xx} = \sigma_{yy} \cong -\frac{1}{4\pi} \chi_{\perp} \frac{1}{z^3}; \quad \sigma_{zz} \cong 2\frac{1}{4\pi} \chi_{\parallel} \frac{1}{z^3}$$
(3-2)

This first generalization is useful for describing the susceptibility gradient of the pore space as a function of the surface (χ) and the distance from the surface (z). However, it is only applicable in the static case, and averaging due to molecular dynamics must be considered as well.

3.3 Effects of Molecular Averaging on the NMR Timescale

For H₂ stationary over the NMR timescale of ~ 3 ms, and with a constant value of z, the random (isotropic) distribution of orientations of the slit pores with respect to the external magnetic field in the laboratory frame will give rise to the well-known powder pattern spectrum. This is shown in Figure 3.2a⁶ below the physical situation to which it corresponds. However, spectral features observed in the experiments relevant to this dissertation are much more narrow and symmetric than would be anticipated of a powder

pattern. This is a strong indication that the NMR spectrum has been narrowed through motional narrowing. The observed spectra are consistent with H_2 that, during the NMR timescale, explore many slit pores with random orientation within a grain with respect to the applied field. This situation is depicted physically and spectrally by Figure 3.2b. Therefore, the observed chemical shift is given by averaging the three tensor components of eq. 3-2:

$$\delta = \frac{2}{3} \frac{1}{4\pi} (\chi_{\parallel} - \chi_{\perp}) \frac{1}{z^{3}}$$
(3-3).

Here, the quantity $(\chi_{\parallel} - \chi_{\perp})$ is also known as the total anisotropy of the susceptibility χ_{Tot} , and has been experimentally determined⁷ to be approximately -4.4 x 10⁻⁹ m³mol⁻¹ at T = 100 K for graphite. For convenience, a new quantity is defined $\lambda \equiv \left| \frac{2}{3} \frac{1}{4\pi} (\chi_{\parallel} - \chi_{\perp}) \right|$,

so eq. 3-3 may be written in the simpler form:

$$\delta = -\lambda \frac{1}{z^3} \tag{3-4}.$$



Figure 3.2 a) Due to a random orientation of the slit pores with respect to the external magnetic field, an NMR experiment based on stationary H_2 molecules would produce a characteristic powder pattern. However, since the NMR timescale is on the order of 3 ms, each H_2 molecule will explore many different slit pores (b) essentially sampling all orientations and producing a Gaussian (or nearly Gaussian) spectral shape centered at the average of the contributing susceptibility tensors.

3.4 General Interpretations of the NMR Spectra

Using this phenomenological approach Tabony⁸ estimated the chemical shift observed by molecules adsorbed on graphite at z = 0.3 nm to be -35 ppm. This is consistent with his experimental value of -37 ppm determined for protons of aromatic compounds adsorbed above a graphitic plane at low coverage and measured with respect to the value found in the respective liquid. However, for H₂O adsorbed on graphite, Tabony⁸ measured an upfield shift of approximately -15 ppm with respect to water in intergranular pores. While the actual observed chemical shift caused by the anisotropic susceptibility of graphite may vary with the specific adsorbate, it is clear that even in the case of partial graphitization adsorbed molecules will have a negative and significantly large chemical shift with respect to their free gas counterparts. Thus, at least two distinct peaks can be predicted to appear in the spectra, which will be labeled "Peak A" and "Peak B." The shift experienced by molecules in regions whose populations are dominated by free gas (those defined as contributing to Peak A) are expected to reflect only the constant bulk susceptibility of the material. Since the molecules that experience near-surface susceptibility effects (those contributing to Peak B) also experience the bulk susceptibility, the bulk component can be treated as an offset. Thus, if the shift of Peak A is set to zero, the chemical shift will conveniently be a function of the near-surface effects alone. This was done for all the PEEK data sets where the behavior of the shift of the peaks provided additional insight into the structure of the material, while in the borondoped graphite TMS was used to define zero. Since Peak B represents molecules with shifts roughly following the form of eq. 3-4, it will have a negative shift relative to Peak A, and will be found upfield from (to the right of) Peak A in the NMR spectra.

The environment of the gaseous molecules within the porous materials can be divided into three regimes of pores per IUPAC technical standards:⁹ macropores (d > 50 nm); mesopores (50 nm > d > 2 nm); and micropores (d < 2 nm). The macroporous regime includes, and is largely comprised of, large intergranular pores that are not necessarily an intrinsic property of the sample itself and are related to the random

packing of the sample. The majority of the population of H_2 molecules in these pores and those contained in the small contribution of macropores within the sample itself will have no additional chemical shift and will behave like free gas, obeying the ideal gas law:

$$n_{fg} = P(V_{fg}/k_BT) \tag{3-5},$$

where V_{fg} is the free volume available to the gas. Any molecules adsorbed on the surface of these largest volumes will have a negligible contribution to the averaged, observed peak in the spectra, so it can be safely assumed that Peak A is wholly representative of gas in the macropores. Peak B, on the other hand, arises from those molecules in much smaller pores whose population is dominated by adsorbed and confined molecules. With a dynamic diameter of H₂ (~0.406 nm),¹⁰ comparable to the maximum micropore diameter (2 nm), Peak B can be assumed to encompass all H₂ molecules in this regime. As one might expect, the more difficult question is how the mesopores population will be spectrally represented. Assuming that a third, intermediate peak is not present in the spectra (which, in practice, turns out to be true in most cases), the H₂ in mesopores must appear in either one of the peaks, or some combination thereof. This will require a semiquantitative assessment of eq. (3-4).



Figure 3.3 Surface plots of the expected chemical shift due to the ring current effect of the graphitic surfaces, as a function of distance z from the left wall, for slit-pores with widths of a) 0.8 nm, b) 1.2 nm, c) 3 nm, and d) 5 nm. The spheres represent hydrogen molecules located on the pore wall (white) and in the middle of the slit pore (black). The minimum shift (black molecule) is appreciable for d = 0.8, 1.2 nm and has dropped to less than -1 ppm for d = 3 nm; by 5 nm it is roughly equal to that of a free hydrogen molecule. In the 0.8 nm slit pore there is little distinction between the two cases. In (e) the 1.2 nm pore is divided into discrete regions determined by the thickness of an adsorbed monolayer of H₂. Despite being a continuous function, the chemical shift in the pores can be well-approximated by a free region and an adsorbed region. For all plots, $\lambda = 0.25$ ppm nm³, or $(\chi_{\parallel} - \chi_{\perp}) \sim -9.5 \times 10^{-10}$ m³ mol⁻¹.

Given that a quite common pore geometry in graphitic materials is the slit-shaped pore,¹¹ it is appropriate to use it for modeling the chemical shift within the smaller pores. In this treatment, eq. (3-4) can be modified to take into account a second wall in a slit pore of width d:

$$\delta = -\lambda \left(\frac{1}{z^3} + \frac{1}{(d-z)^3} \right)$$
(3-6),

where z can be measured from the center of either of the walls. Figure 3.3 plots this function for four different values of d ranging from 0.8 nm to 5 nm. The black molecules represent the minimum shift produced by each slit-pore while the white molecules are "adsorbed" on the wall. In the narrower slit-pores of 0.8 and 1.4 nm (8a and 8b), the walls are close enough to produce an additive effect and thus their minimum shifts are considerably larger. On the other hand, slit-pores of 3 and 5 nm (8c and 8d) produce chemical shifts that are only significant near the walls and thus can be easily divided into two regions: on the wall (i.e., adsorbed) or not on the wall. Despite appearing to be a continuous function, the chemical shift can also be treated in a similar fashion for the narrower pores. In Figure 3.3e, the 1.2 nm slit pore is divided into discrete regions based on the monolayer thickness of H₂. As in the case of wide pores, treating the shifts of the molecules as either adsorbed on one of the walls (δ_{ad}) or in the free space excluded by the adsorbed monolayers (δ_{fg}) is a good approximation. The notation fg is used again, since the behavior of the H₂ in the middle region of the pore is expected to be similar to a free gas, in agreement with grand canonical ensemble Monte Carlo simulations of the particle density in a slit pore performed by Rzepka, et al.¹² Without more knowledge of the explicit value of λ , it is difficult to critically assess the boundary between pore sizes contributing to Peak A and Peak B. However, visual inspection of Figure 3.3 shows that the chemical shift contribution of confined molecules becomes negligible between diameters of 1.2 and 3 nm. This is concomitant with an increasingly significant contribution from the confined H₂ to the total pore population, thus exacerbating the trend

towards a negligible total observed chemical shift of the resident species. It would seem then that the boundary between mesopores and micropores is a good approximation of the boundary between the two peaks. In general, the term micropore will be hereafter used to describe the population of Peak B, an assumption that will later be evaluated when more information about the nature of λ can be experimentally determined.

3.5 Brief Discussion of "Invisible Micropores"

Since the near-surface effect is dependent on the surface being graphitized, it could be argued that some micropores could have zero graphitization and therefore be "invisible" to NMR and not included in Peak B. However, it is unlikely that any significant number of micropores would not be represented by Peak B. If the entire amount of carbon comprising a particular micropore was not graphitized, it might be expected that the chemical shift it would produce would be indistinguishable from Peak A. However, as mentioned above in Section 3.3, there is an averaging process that arises from the H₂ exploring many different micropores, with a range of orientations, widths, and degrees of graphitization (amongst other properties). A single probe molecule's observable chemical shift is taken to be an averaged value of all these factors, which is representative of a semi-localized neighborhood of pores. In other words, if a molecule is in a micropore with zero graphitization at a given point in time, it is much more likely to be found in another micropore (most likely with a non-zero degree of graphitization) within the next small time interval than in an intergranular pore. For a micropore to be truly "invisible" to the NMR method, a molecule would have to be able to spend the vast majority of a time span of ~ 3 ms in either exclusively invisible micropores and/or intergranular pores. However, micropores will be much more highly correlated with other micropores (with varying degrees of graphitization) than with intergranular pores, so it is highly improbable that H_2 probing a non-graphitized pore would not be shifted up-field. A 2-D NMR experiment of one of the Activated-PEEK samples (Steam-9-35) at 10 MPa and RT showed no cross-peaks, verifying that H_2 in the two regions exchanged very little on the NMR timescale. Further, if there were indeed any micropores not represented by Peak B, their existence would be obvious in the form of Peak A appearing in spectra below 0.1 MPa where only H_2 molecules adsorbed in the pores contribute, regardless of their chemical shift. Thus, in theory they would be experimentally observable under these conditions. The non-existence of these "invisible micropores" has been consistently confirmed in every hydrogen storage experiment performed to date.

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CHAPTER FOUR

HYDROGEN STORAGE IN BORON-DOPED GRAPHITE

Van der Waal interactions between the H₂ molecule and the typical pore wall alone are not able to produce a sufficiently strong binding energy for the purposes of practical hydrogen storage, on the order of 5 kJ mol^{-1} . It is thus important to identify, investigate, and incorporate alternative mechanisms into materials with micropore structures and high surface areas. The NMR approach is particularly well-suited for studying materials believed to have successfully incorporated such mechanisms. The molecules interacting closely with the surfaces of a material can be isolated via the NMR spectrum. In addition, other properties of their environment to which NMR is sensitive can be further used to differentiate and characterize surfaces that have been successfully enhanced from those that may have not been enhanced. Several different mechanisms have been identified as having the potential to significantly increase the binding energy of a materials adsorption sites. In certain metal-organic frameworks (MOFs) at low loading levels (i.e. low pressures), an enthalpy of adsorption has been experimentally observed to be in the neighborhood of 10 kJ mol^{-1,1} This enhancement is believed to be due to the H₂ molecules directly binding to unsaturated metal ion site. Alternatively, the challenge can be approached first from a theoretical perspective that can then guide the synthesis of a prospective material. In particular, it has been suggested that an enhancement in binding energy similar to that in MOFs may result from substitutionally doping fullerene (C_{36}) with boron (resulting in $C_{35}B$).² It is predicted that an H₂ molecule would bind non-dissociatively with the boron and experience an elongation of the H-H bond. The expected partial charge transfer between the σ -bond of the H₂ molecule and the empty localized p_z orbital of boron has been calculated to result in a significantly enhanced binding energy of 19.2 kJ mol^{-1,2} However, the storage of hydrogen in borondoped fullerenes is ultimately impractical. First it is not possible to produce them in bulk quantities, which would be necessary for commercial applications. Second, as revealed by a quick back-of-the-envelope calculation, the theoretical maximum of the hydrogen storage capacity of such a system would be less than 0.5 wt%, an order of magnitude smaller than that which would be economically viable. This brings up the question of whether it would be possible for the advantage produced by such an enhancement to be retained while the geometry of the system is altered towards one that is better suited for commercial hydrogen storage. Although there are yet to be any studies into the resulting binding energy of similar but planar systems, it is possible to substitutionally dope boron into a graphitic matrix on a production scale much larger than that of fullerene. Via a thermodynamic route, boron can be doped into graphite up to a maximum of 2.35 at% to produce a highly ordered material.³ However, there are significant quantum mechanical differences between the planar and spherical structures. There is also little reason to believe that the phenomenon that gives rise to the enhanced binding energy in the latter case—the molecular localization of the wave function—will be present in the former. A better simulation of the $C_{35}B$ system would be a disordered B-doped graphitic carbon (B/C) whose localized electronic states arising from the disordered structure would be more likely to produce the desired enhanced binding energy at the boron site.

Collaborators within the Hydrogen Sorption Center of Excellence at the Pennsylvania State University have developed a non-thermodynamic synthesis route that will produce just such a disordered material.⁴⁻⁶ This is naturally of great interest to apply our NMR methods to investigate the real-world implications it may have for hydrogen storage, namely whether it exhibits enhanced binding energies in the range of interest for a hydrogen economy. It should be noted that since the resultant material is expected to be similar to un-doped graphite in many aspects, it is inferred that it meets the three criteria mentioned in Chapter 3: surface graphitization, microporosity, and slit-pore geometry.

4.1 Sample Preparation

The B/C studied here was prepared from the polyaddition adduct of phenyldiacetylene and BCl₃ that provides the basic conjugated aromatic framework. After initial polymerization at 60°C, the sample was subsequently carbonized at 800°C producing a dense disordered graphitic carbon material with a BET surface area of 54 m^2/g . A complete description of this process can be found in the relevant literature.⁶ The expected graphitic structure of the granular material was confirmed by X-ray spectra and transition electron microscopy (TEM). Figure 4.1 shows an image of the sample acquired using a scanning electron microscope (SEM). By studying the exposed surface area of the granules in this image, it was estimated to have an external surface area of less than 2 m^2g^{-1} . This implies that the measured SSA of 54 m^2g^{-1} based on liquid N₂ BET is associated with pores produced during synthesis. These pores result from the chosen precursors and their reaction path; thus, their production is preconceived and is part of the

material design.⁶ The boron content of the sample is 1.5 wt% as determined by ¹¹B NMR and further confirmed by prompt Gamma-ray activation analysis.



Figure 4.1 A scanning electron microscopy (SEM) image of the B/C studied was used to estimate an exposed surface area of less than $2 \text{ m}^2\text{g}^{-1}$.

4.2 Measurement of the Binding Energy at Room Temperature

For the room temperature isotherm measurement, a capillary of known volume was placed inside the sample holder and then surrounded by the sample itself. This resulted in a distinct peak (Peak C in Figure 4.2) appearing in the spectrum, which was used for calibration of the spectral intensity in terms of the mass and/or number of H_2 molecules. Since the volume of the capillary within the NMR coil region was known (0.027 cm³), a conversion factor α could be easily calculated from the isotherm of Peak C via the ideal gas law, with the appropriate units of mg H [1k scans]⁻¹. This can be further converted to units of number of H_2 or wt%, if so desired. For this experiment, the zero shift was set to equal that of TMS, although the data was acquired with an observing frequency of 200.0835 MHz.

Three peaks are clearly visible in Figure 4.2, which is the spectrum acquired with an FID pulse sequence at a pressure of 10.2 MPa. This can be well fitted by three lines, with the line-shape of Peaks A and C being Lorentzian and that of Peak B being Gaussian. These all have chemical shifts that are independent of the pressure, as is evident in Figure 4.3. As noted, Peak C, at 7.70 ppm, is associated with H₂ gas in the capillary. This assignment was confirmed by the absence of Peak C when the capillary was removed from the sample holder (see Section 4.4, for example). As was expected, Peaks A at 5.87 ppm and B at -1.36 ppm are upfield shifted from the capillary peak. Peak A will experience a shift corresponding to the bulk magnetic susceptibility that arises from the same phenomenon that produces the upfield shift of Peak B. The sample is a powder of packed grains of several microns in size (see Figure 4.1). H₂ gas residing in the void space in between grains is the primary contribution to Peak A. Peak B corresponds to the micropores within the grains. These micropores account for the difference in external surface area and the measured total SSA. The lack of exchange between these two regions on the NMR timescale (~3 ms) was confirmed by a 2D exchange NMR experiment.



Figure 4.2 The ¹H spectrum of B-doped graphitic carbon exposed to H_2 gas at 290 K and 10 MPa. The black line is the experimentally obtained spectrum while the colored lines are the three components that fit the spectrum very well: the two expected peaks representing H_2 in large voids (A) and H_2 in micropores (B), in addition to H_2 in the calibration capillary (C).


Figure 4.3 Three different perspectives of the spectra of the H_2 in the B/C at 290 K (room temperature) as it evolves with pressure. Peak B is dominant at low pressures while Peaks A and C are dominant at higher pressures. It is also shown that the chemical shifts of the peaks do not evolve with pressure.

In Figure 4.3, the spectra at the various pressures of the isotherm are displayed. At low pressures (P < 1 MPa), Peak B is larger than Peaks A and C. Above 1 MPa, the spectra are dominated by the latter two components. The apparently linear relationship with pressure of A and C is consistent with the interpretation of these peaks as gaseous components in macroscopic spaces. For Peak B the approximately linear relationship with pressure at lower pressures and a trend towards saturation at higher ones agrees with the notion that those molecules are in a confined space and are possibly interacting with a surface binding energy that is significant within this pressure range at 290 K. It is actually rather surprising to see any indication of saturation under these conditions for microporous carbons in general, as the isotherms produced by the typical binding energies (4-8 kJ mol⁻¹) of such materials are still in the linear regime below 15 MPa at room temperature. This initial assessment is encouraging as it appears that the binding energy in the pores has indeed been enhanced beyond the range of those arising from van der Waal interactions.

For a more involved quantitative analysis, isotherms for the three individual components were produced by the integration of the area of their respective Lorentzian or Gaussian fits from the spectra at each pressure. The isotherm of the intensity of Peak C was first used to calculate the appropriate conversion factor α , which was then subsequently applied to the isotherms of the intensities of Peaks A and B. Finally, the mass of the sample in the coil region was used to calculate the corresponding wt% H₂ uptake values. Figure 4.4 displays the individual wt% uptake for all three peaks plotted as a function of pressure.



Figure 4.4 The room temperature isotherms derived from the integrated intensities of Peaks A, B and C of Figures 10 and 11. Peak B exhibits a non-linear relationship with pressure, which can be fit as a Langmuir adsorption curve, in contrast to Peaks A and C, which obey the linear ideal gas law.

As predicted by the visual analysis of Figure 4.3, the isotherms of Peaks A and C are linear. In Figure 4.4, the slope is indicative of the amount of the free volume that those components occupy. The uptake of Peak B at 10 MPa is approximately 0.17 wt%, which is much smaller than what will be needed for practical vehicular applications. However, when one considers the fact that materials with SSAs as high as 5640 m²g⁻¹ have been observed to have total uptake capacities of less than 1 wt% at the same temperature,⁶ it is rather remarkable that this sample achieves nearly a fifth of that

capacity with 1% of the available surface area. Further, this is strong evidence that surface area alone accounts for the H_2 storage capacities of this class of materials.

The binding energy experienced by the constituents of Peak B can be extracted from the isotherm by assuming that the Langmuir model of adsorption is sufficiently accurate in the region of interest. Fitting the data with eq. 2-1, it is revealed that the H_2 in the micropores have a binding energy of 9.2 kJ mol⁻¹, validating the hope that the doping of boron would enhance the binding energy significantly. Additionally, it is of interest to calculate the surface area that the fitting of the data implies (keeping in mind that this is not an exact method for determining this value). If the fit of the isotherm is extrapolated to its asymptotic region where the micropore surfaces would be completely saturated, one arrives at 1.6 10^{20} H₂ molecules, corresponding to an estimated SSA of 180 m²g⁻¹ (taking the surface area occupied by each molecule to be 0.16 nm^2). This is significantly higher than the 54 m^2g^{-1} measured by the nitrogen BET measurement. It is quite possible that there exists a significant population of micropores (or micropore access points) that are too narrow for the N₂ molecules to penetrate but are still accessible to the H₂ molecules. This underscores the advantage (and perhaps necessity) of using H_2 as the probe molecule, noting that a similar measurement by N2 would have potentially resulted in uptake and surface area values a factor of three times too small.

4.3 Further Separation of Components via T_1 Measurements

The characteristics of the micropores in the B/C thus far derived from studying Peak B are representative of the *averaged* value for all micropores across the sample. However, the substitution of boron into a disordered carbon rarely results in a homogenous material, if ever. For example, it should be expected that the distribution of boron within the micropores will be heterogeneous, even with some micropores possibly containing no boron atoms at all. Therefore, the binding energy derived from the intensity of Peak B does not truly reflect the effect the doping has on the surface, which is of primary interest in this case. Fortunately, NMR provides a nice array of techniques for probing materials and through relaxation measurements further details about Peak B can be revealed. The spin-lattice-relaxation time T_1 of H₂ gas is dominated by the transfer of angular moment via inter-molecular collisions, while that of confined and adsorbed H₂ is significantly affected by collisions with various surfaces within the material. Thus, measuring the T_1 of the three peaks in our spectra will provide important information about the local environment to which each corresponds, as well as allowing multiple components that might have identical chemical shifts to be further resolved. The general form that has been established to quantitatively describe T_1 of H₂ gas is⁷

$$T_1^{-1} = \omega^{\prime 2} \tau_c / \left(1 + \omega_0^2 \tau_c^2 \right)$$
(4-1).

Here, $\omega_0/2\pi$ is the Larmor frequency of 200 MHz, and τ_c is the correlation time associated with the lifetime of the quantum state $|1m\rangle$ determined by H₂-H₂ collisions. Since increasing pressure results in a higher frequency of collisions, and thus a shorter τ_c , the relationship between the two can be described as $1/\tau_c \propto P$. The term ω'^2 is a known constant related to dipolar and rotation-induced effective fields at the proton and is given by the Bloembergen-Schwinger formula:⁸

$$\omega'^{2} = 2\gamma^{2} \left[\frac{{}_{1}}{{}_{3}}B'^{2} J(J+1) + \frac{{}_{3}B''^{2} J(J+1)}{(2J-1)(2J+3)} \right]$$
(4-2)

All of the variables in eq. 4-2 are known: γ , the gyromagnetic ratio of the proton; *B*', the effective field at the position of the proton due to molecular rotation (2.7 mT); *B*", the dipolar field produced at the position of one proton by the other (3.4 mT); and for our purposes all of the molecules can be assumed to be ortho-hydrogen (J = 1), giving $\omega'^2 = 3.4e10 Hz^2$. Furthermore, for gaseous hydrogen at P = 1 MPa and room temperature, τ_c is on the order of 0.3 ns,⁹ so in this regime $\omega_0^2 \tau_c^2 \ll 1$ and eq. 4-1 can be approximated as

$$T_1 \cong \frac{1}{\tau_c} \omega'^{-2} \to T_1 \propto P \qquad (4-3).$$

Spectra of saturation recovery measurements obtained concomitantly with the RT isotherm measurement, from which the measured nuclear magnetization, M(t), for all three peaks were plotted in the form $[M_0 - M(t)]/M_0 = \exp(-t/T_1)$, where M_0 is the magnetization in equilibrium. Both Peaks A and C exhibited a singular linear dependence on the recovery time *t*, indicating a high degree of homogeneity in those environments. In contrast, the plot of M(t) for Peak B at P = 7.5 MPa in Figure 4.5 exhibits double-exponential behavior, implying that there is bimodality within the microporous region. Since the data could be fit to determine not only both values of T_1 but their relative intensities as well, it was possible to produce an isotherm for each component.



Figure 4.5 The saturation recovery curve of the magnetization of Peak B at P = 7.5 MPa showing the characteristics of double-exponential decay.



Figure 4.6 The values of T_1 plotted as a function of pressure for Peaks A and C, and the two components of Peak B, B1 and B2.

In Figure 4.6 the observed values of T_1 for A, B1, B2, and C are plotted as a function of pressure. Both Peaks A and C had very similar values and were linear with pressure. The conclusion, via eq. 4-3, that H₂ in the free gas state would exhibit T_1 with a linear *P*-dependence reinforces the earlier assessment that these two peaks represent H₂ in large spaces (i.e., the large intergranular pores and the calibration capillary, respectively). To further interpret this plot, a deeper understanding of the correlation time τ_c is needed. This parameter can be described in terms of the two primary processes, surface and intermolecular collisions, which work in parallel to determine the observed values:^{10,11}

$$\tau_c^{-1} = c_{surf} R_{surf} + c_{gas} R_{gas} \qquad (4-4).$$

Here c_{surf} and c_{gas} are determined by the effectiveness in altering the $|1m\rangle$ states by H₂surface and H₂-H₂ collisions, respectively, while R_{surf} is the *P*-independent H₂-wall collision rate and R_{gas} is the H₂-H₂ collision rate that is linearly dependent upon *P*. Still assuming $\omega_0^2 \tau_c^2 \ll 1$, eqs. 4-3 and 4-4 give

$$\frac{T_1}{{\omega'}^2} = c_{surf} R_{surf} + c_{gas} R_{gas}(\mathbf{P})$$
(4-5).

The first term is what gives rise to the offset at P = 0, which is most apparent in the case of B2. For Peaks A and C, where the molecules are in relatively open spaces, surface collisions have a negligible impact on τ_c , which is consistent with the observed absence of an offset. The second term gives rise to the linear increase of T_1 with P, which already has been established as the source of linearity in Peaks A and C. However, it does prove insightful for determining what B2 represents. Since the average distance between gas molecules at P = 1 MPa is around 1.6 nm, the contribution of H₂ collisions with walls is significant in determining the lifetime of $|1m\rangle$ in micropores of a few nanometers. This indicates that B2 is H₂ confined within micropores, but does not spend an excessive amount of time interacting with the pore walls, which hints at a weaker binding energy. On the other hand, the behavior of T_1 versus P for the long- T_1 component B1 is drastically different than B2, most notably in that it is orders of magnitude longer. This shows that this component is dominated by adsorbed H₂.^{12,13} The effect of gas-like H₂ is very small and is perhaps only noticeable at high pressure where the amount of confined H₂ gas becomes non-negligible for spin-lattice relaxation. This indicates that the pore size associated with the long- T_1 component is most likely of the order of 1 nm or smaller. Similar behavior has been previously observed in adsorbed methane and ethane inside 1.4 nm diameter carbon nanotubes.¹⁰

Figure 4.7 is the isotherm of the two components of B. When B1 is fit with a singular Langmuir component, an interestingly high binding energy is revealed: $E_b = 11.4$ kJ mol⁻¹. This fit also reveals that when the surface is saturated and the uptake within these pores is properly calibrated via the capillary peak, a 0.1 wt% storage capacity at 10 MPa is obtained, which on a per-surface area basis gives 0.9 wt%/500 m²g⁻¹. Likewise, when the B2 component was fit with just one Langmuir component, the resulting binding energy was $E_b = 8.6$ kJ mol⁻¹. This value indicates that the surface energy of the B2 pores has been enhanced as well, just to a lesser degree than that of those corresponding to B2. This is not contrary to the T_I results above. The lower binding energy decreases the amount of time the H₂ molecules spend on the surface, which results in an increased frequency of relaxation events, as well as behaving somewhat similar to a free gas under these conditions. While it is hoped that the micropores are evenly doped with boron, this analysis of our results suggests that B2 may be corresponding to those micropores that

have little or no boron, while B1 may be representative of H_2 in micropores that have been effectively doped.



Figure 4.7 Isotherms of the two components of Peak B, as identified by T_1 measurements. B1 is associated with the long- T_1 component and B2 is associated with the short- T_1 component. Here both lines are fit with only one Langmuir adsorption term, although using the binding energy determined for B2 plus an ideal gas term will give a nearly identical fit for B1.

An alternative interpretation of the multi-exponential T_1 behavior is that the micropores have a bimodal diameter distribution, but both sizes are narrow enough to not result in a difference in the chemical shift. This perspective would imply that the boron had been evenly incorporated into the surface; thus, B1 would have the same binding

energy of $E_b = 11.4$ kJ mol⁻¹. If the B1 isotherm is fit with a Langmuir adsorption component using this binding energy, an ideal gas component is necessitated. The presence of this ideal gas component implies that the micropores associated with B1 contain both adsorbed as well as a fraction of gas-like H₂, which would be expected of even a slightly larger pore size. This view is also consistent with the evolution of T_1 with pressure, which has been previously discussed, since ¹H spin-lattice relaxation of H₂ is more efficient in the gas phase than adsorbed due to the decreased number of wall collisions.

An implication of both elucidations is that there is little exchange between the two different regimes on the NMR time-scale; otherwise the two T_I components would have averaged out. It is not fully understood whether this is the case. In general, the path of any given probe molecule is expected to explore a wide variety of environments (see Sections 3.3 and 3.5), even if unusually high binding energies are involved. It is possible that similar micropores (with respect to boron content and/or pore diameter) are clustered together within the sample and the molecules involved in the exchange between each adjacent pair of unlike regions that experience this time-averaging effect represent only a small fraction of the total H₂ population within the micropores.

4.4 Low Temperature Kinetics

In addition to the RT isotherm measurement, it was of interest to investigate the behavior of the H_2 -B-doped graphite system at lower temperatures, namely 100 K. For the LT experiment, the calibrating capillary was removed, so only Peaks A and B were expected to appear in the spectra. Initially, the hydrogen was loaded with 10.0 MPa H_2 at

RT before the temperature of the system was lowered to 100 K. Upon lowering the temperature to 100 K, the system pressure dropped to 7.5 MPa. Figure 4.8 shows the NMR spectra taken at 100 K as a function of decreasing pressure. As expected, Peak C is absent. What was unexpected, though, was that Peak B did not decrease with pressure and only showed a small intensity reduction when the sample was dynamically pumped for 1 hour. On the other hand, the intensity of Peak A decreased linearly with pressure, just as is expected for free H_2 occupying the intergranular regions of the sample, verifying that the surprising results were not just due to experimental error. However, once the system was allowed to warm to 160 K, the H_2 associated with Peak B was quickly removed under dynamic pumping.



Figure 4.8 Low temperature spectra of boron substituted graphitic carbon exposed to H_2 gas. The sample is first exposed to 10.0 MPa H_2 at room temperature and then cooled under pressure to 100 K (the pressure is reduced to 7.5 MPa due to the cooling). The pressure is then further reduced at 100 K and ¹H spectra are taken at each new pressure. Inset: Spectrum when the sample is cooled under dynamic vacuum to 100 K and is subsequently exposed to 10.0 MPa H_2 gas. Here, Peak B is absent (C is also absent because no capillary was used in this case).

If the H₂ is unable to leave the micropores at LT due to slow kinetics, then the converse should prove to be true. If it were due to chemisorption, it would be expected to still be able enter the pores. To determine which mechanism was at work, the sample was dynamically pumped while at RT (as opposed to being under 10.0 MPa) and throughout the cooling process. Once 100 K was reached, the vacuum pump was turned off and an isotherm of increasing pressure was acquired. The inset of Figure 4.8 shows the spectra at 10.0 MPa and 100 K. In this case, Peak A is the lone feature of the spectrum, and Peak B is entirely absent. Furthermore, Peak B is still not present after being exposed to the high hydrogen pressure for a period of 10 hours. It is clear then that slow kinetics, and not chemisorption, is the mechanism responsible for this phenomenon. It should be noted that the uniqueness of our approach allows for such a dramatic and clear confirmation of the micropore kinetics, especially compared to the more common experiments that are similar in nature (gravimetric and volumetric isotherms, for example). This strong temperature dependence of the effect is a clear indication of an activated diffusion process with activation energy E_a , similar to that which has been observed in other microporous material such as zeolites.¹⁴ Here, the diffusion constant is described by $D = D_0 \exp(-E_a/RT)$ with $R = 8.314 \text{ J/K} \cdot \text{mol}$, while the pre-exponential factor D_0 depends on the details of the diffusion process. Comparing D_{160K} to D_{100K} , it is seen that their ratio, $\exp(-E_a/R \cdot 160 \text{ K})/\exp(-E_a/R \cdot 100 \text{ K})$, becomes very large for activation energies approaching the value of the observed binding energy E_b in the RT measurements. Its values are 9.5, 91, 868, and 8274 for $E_a = 5$, 10, 15, and 20 kJ mol⁻¹, respectively. The activation energy E_a is expected to be comparable to the binding energy

 E_b , and thus the strong temperature dependence of diffusion supports the previous assessment of an E_b that is in the range of 10-15 kJ/mol.

Once again, the LT observations raise an intriguing question regarding the exchange of H_2 within the micropores. In Section 3.3, it was predicted that an ensemble of H_2 molecules, which were not dynamically averaged on the NMR time-scale, would be spectrally represented by a Pake pattern. However, there is no indication that the LT Peak B is anything but Gaussian in nature. Since diffusion is thought to be slow enough in the micropores that there is negligible exchange with the external environment, even on the order of hours, it is curious that the line-shape of Peak B is indicative of significant movement of the H_2 within those pores, which is on the scale of microseconds. While there is not enough evidence available to give a clear indication of what is really happening, it is conjectured that there is enough orientational anisotropy of the micropores on the nanometer scale to allow for time-averaging despite the dramatically slowed diffusion.

4.5 Boron-doped Graphite Conclusions

The intent of this particular set of experiments was to determine whether or not doping of graphite with boron would lead to a significant enhancement in the binding energy, as was alluded to by calculations for boron-doped fullerenes. The value which was observed by our NMR approach was 11.4 kJ mol⁻¹. This represented a significant step forward in reaching the Hydrogen Program ultimate target range of 15 - 20 kJ mol⁻¹. In contrast to the vast majority of porous carbons, including others that have been studied in this work, the room temperature isotherm of B-doped graphite is nonlinear in nature.

At 100 K, severely restricted exchange between the micropore and intergranular pore environments was directly observed in the NMR spectra. It is suggested here exclusively that if the energy costs of changing the operating temperature of the hydrogen storage apparatus could be overcome, a practical route to vehicular hydrogen storage might be to load and unload the H_2 into the micropores at ambient temperatures and then take advantage of the low temperature entrapment to store them without the need for maintaining a high external pressure.

The room temperature uptake at 10.0 MPa of the sample was found to be 0.1-0.17 wt%, which is small due to its small surface area of 54 m² g⁻¹. However, when one recalls that surface area is the primary determinant of the total storage capacity,¹⁵ this value might be considered disproportionately large (0.9 wt%/500 m²g⁻¹) and has the potential to be a viable solution to the H₂ storage challenge. Currently mobile cryogenic storage tanks based on activated carbon as a storage material (SSA 3300 m² g⁻¹, 5.6 wt% at 77 K) are being designed on the assumption that surface area and capacity are sufficient for engineering purposes. While boron-doped graphite currently does not simultaneously have the surface area and total capacity to effectively compete with the current materials, it is possible that these issues may be overcome in the future. If the observed binding energy were to be maintained in boron-doped graphite while the surface area were increased to 3300 m² g⁻¹, it would have roughly 6 wt% storage capacity at ambient temperatures, which is something that no other prospective material can currently boast.

Finally, while not directly related to the target goals for hydrogen storage materials, the NMR approach covered several topics of general scientific interest. First

and foremost, it confirmed that it is reasonable to expect two peaks in the NMR spectra of H_2 in a porous carbon (Peak B), one corresponding to the micropores and the other attributed to mesopores and intergranular pores (Peak A). This has the clear (and intended) advantage of providing the ability to exclusively study H_2 within the regions of interest, which can be further coupled with other NMR measurements. Here, a T_I relaxation measurement was used to distinguish two regimes of micropores and measure their respective binding energies and storage capacities. It was also demonstrated that it was possible to directly observe the confinement and exclusion of H_2 within the micropores at lower temperatures, further establishing the approach as a powerful technique for the application of studying potential hydrogen storage materials. The intriguing observation of significantly slowed H_2 dynamics within the micropores was contrasted with the assumption that in such a case a Pake pattern would be appear in the spectra instead of the observed Gaussian line-shape, a question which at present remains unresolved.

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CHAPTER FIVE

HYDROGEN STORAGE IN ACTIVATED PEEK

Of primary interest for those concerned with producing a viable hydrogen storage material via physisorption is the spatial engineering of candidate materials. Porous carbons comprise a large portion of these particular materials, and microporous carbons in particular are especially well suited for H₂ uptake due to their ability to achieve high SSAs while maintaining relatively small pores sizes. As mentioned in the Introduction, it has proven to be a non-trivial task to simultaneously achieve both the large surface areas and the micropore diameters necessary for optimized H₂ storage.¹ Many approaches have been taken in hopes of realizing such porous materials, notably activation² and inorganic³ or organic⁴ templating. However, no material has mastered both a large surface area and a small pore diameter. Additionally, a disadvantage associated with most of the templating procedures is that they suffer from dangerous template removal conditions³ and very narrow production conditions, making large-scale production impractical.^{4,5} Initial results indicated that CO₂ treatments of poly(etheretherketone), or PEEK (Figure 5.1), may produce a porous carbon with attributes desirable for H_2 storage, as implicated by Cansado et al.⁶ There are several immediate advantages to this approach: the method is simple, robust, and does not require the removal of any template or the use of any dangerous chemicals. The creation of well-defined pores is via the oxidization of the PEEK structure. The work here is aimed at investigating the H₂ storage capabilities of PEEK and the key factors that are relevant to the optimization of the parameters (surface area, pore size, binding energy) that are crucial for maximizing uptake. An independent study of PEEK⁷ indicated that materials produced by this process will be predominantly microporous with a slit-pore geometry. The pre-activation step effectively carbonizes the polymer⁸ and a partially graphitized surface is expected, thus fulfilling the criteria set forth in Chapter 3. Therefore activated PEEK is an excellent choice of material to investigate with our NMR approach.



Figure 5.1 PEEK in an alumina combustion boat (a) before and (b) after thermal treatment under CO_2 (steam produced a very similar product). (c) The chemical structure of one subunit of PEEK. (d) A post-treatment PEEK-CO₂-9-80 is used to display a typical TEM image in which small diameter pores are evident.

5.1 Sample Preparation

Collaborators within the Hydrogen Sorption Center of Excellence at Duke University prepared all the activated PEEK samples studies here. Full details can be found in the paper they published summarizing their overall PEEK results.9 A brief version of the sample preparation is shared here. PEEK was loaded into a 1 inch quartz tube furnace and flushed with argon. The temperature was raised from room temperature to the reaction temperature (900 °C) at a rate of 10 °C min⁻¹ and allowed to carbonize at 900 °C for 30 minutes under an argon flow of 700 sccm. The purpose of the preactivation step was to carbonize the material while the activation's role was to develop the microporous structure by attacking the weak bonds in the carbonized PEEK created by the first step. After carbonization, the gas was changed to either CO₂ or steam and allowed to react for a predetermined amount of time under 700 sccm of the chosen gas. After completion, the gas was changed back to argon and the system was allowed to cool back to room temperature. Once the activation step was complete, the sample was removed and ground with a pestle and mortar. Its final mass was then determined before being stored under vacuum desiccation until further analysis could be performed. The burn off (BO), relative to the mass after the pre-activation step, was calculated assuming that the carbonization yield was 51%.⁵ The sample nomenclature is *activation method-9* (for the activation temperature of 900°C)-percent burn off. For example, PEEK, which was steam-activated at 900°C with 70% BO, is labeled Steam-9-70. Table 1 lists the nine samples studied in this work along with their mass filling the NMR coil detection region $(V = 0.174 \text{ cm}^3)$, the corresponding packing density, and BET surface area, the latter having been measured at the National Renewable Energy Laboratory.9

Sample	Mass (mg)	Density (g cm ⁻³)	BET SA $(m^2 g^{-1})$
CO2-9-1	138.3	0.795	524
CO2-9-26	81.3	0.467	1027
CO2-9-59	65.1	0.374	1986
CO2-9-80	41.3	0.237	3103
Steam-9-20	109.6	0.630	1294
Steam-9-35	86.8	0.499	981
Steam-9-47	56.9	0.327	1207
Steam-9-70	50.6	0.291	1956
Steam-9-95	19.8	0.114	2802

Table 5.1 Activated PEEK samples characterized by NMR in this study.

The shift of the free H_2 gas peak observed for each specific sample is used as the shift reference in ppm (as opposed to TMS or a capillary), the reasons for which will be discussed later. Isotherms for CO2-9-59, and Steam-9-20, -47, -70, -95 were measured over the full pressure range, while CO2-9-1, -26, -80 and Steam-9-35 were probed between 0.1 and 10 MPa. The activated PEEK samples appear remarkably clean based on their proton background. Samples with BO larger than 35 % do not show a proton background measurable by NMR. All background spectra taken after completed isotherm measurements were identical to those taken in the pumped state at the beginning of the experiments indicating that no permanent H bonds were formed during the hydrogen exposure of the samples. The general procedure for acquiring the isotherm spectra was followed as described in Chapter 2. After recording the background spectrum, a spectral isotherm up to 10 MPa was measured at RT. In the case of

Activated PEEK, this was primarily for the purpose of calibrating the LT data. The system was then lowered to 100 K while still under pressure. Focusing primarily on the desorption isotherm at 100 K can be justified since hysteresis effects are expected to be minimal so far above the critical temperature of molecular hydrogen. All samples exhibited fast kinetics even at 100 K, and an equilibrium pressure was reached in 20-30 seconds or less after changing the system pressure. The average time available for the system to approach equilibrium between measurements ranged from 52 to 165 seconds, making non-equilibrium scenarios unlikely.

5.2 Spectral Fitting and Calibration

In general, the spectra had two peaks; however, resolution between the two peaks was incomplete. This required that they be decomposed to allow for further detailed quantitative analysis. The line-shape of Peak B appeared to be very similar to that of a Gaussian with a slight tail on the downfield side (following the nomenclature used with B-doped graphite, Peak A is on the left side of the spectra while Peak B is on the right side). Unfortunately, this is not easy to fit mathematically. In order to retain this characteristic of the line-shape in the fitting, a "template" spectrum taken at sufficiently low pressure and 100 K was scaled and shifted as necessary to match the upfield peak of the spectrum being decomposed. This was justified since Peak A is negligible below 0.1 MPa. Once the matched component was subtracted from the spectrum, the remainder was taken to be an accurate decomposition of Peak A. Figure 5.2 shows the breakdown for Steam-9-35 at 100 K and 10 MPa.



Figure 5.2 Steam-9-35 spectrum at 10 MPa and 100 K demonstrating the method of using a 0.1 MPa spectrum to decompose Peaks A and B. The 0.1 MPa spectrum (a) is scaled (b) and shifted (c) to give a good approximation of Peak B. Subtracting this from the full 10 MPa spectrum (d) gives Peak A.

Converting the arbitrary units of the spectrometer was achieved by using known volumes in conjunction with the ideal gas law. In two separate instances, RT spectra of an otherwise empty sample holder filled with 10 MPa of H₂ were taken. The total intensity in each case was then found by integrating over the entire spectrum. For 1024 (1k) scans, a conversion factor, α , was calculated to be 4.59 10⁻⁷ mg H [1k scans]⁻¹, which

can easily be converted to moles or total number of molecules per 1k scans. This value was consistent for both measurements of the empty sample holder, but it still needed to be valid when the sample holder was filled with a graphitic material. The constancy of the conversion factor at RT was tested by inserting a capillary of known volume into the sample holder along with several of the PEEK samples, in the same manner as with the B-doped graphite. Figure 5.3 compares the spectra of Steam-9-35 with and without the capillary, as well as a quarter-scale spectrum of the empty sample holder. The intensity of the capillary was determined by integrating only over the area of the spectrum indicated in Figure 5.3. In all three cases, α appeared to be accurate within 6% error (2.8 10^{-8} mg H [1k scans]⁻¹). This value was further verified upon surveying the total collection of data acquired with this particular experimental set-up.

Using α to calibrate the spectra was only valid for data taken at RT, so at low temperatures the spectra was calibrated indirectly via the hydrogen in the intergranular pores (Peak A), since this volume is unchanged at low temperatures and their population is virtually all free H₂ obeying the ideal gas law. A 100 K conversion factor, β_{sample} , was calculated for each individual low temperature run because tuning the circuitry in the probe was more difficult under those conditions:

$$\beta_{sample} = \alpha \frac{c}{d} \frac{T_{RT}}{T_{Low}}.$$
(5-1)

Here *c* and *d* are the slopes derived from the isotherm of the intergranular components (in the arbitrary units of the spectrometer) at RT and low temperature, respectively. For all temperatures, the intensity was multiplied by the proper conversion factor to arrive at units of [mg H₂]. In some cases the slope was approximated by dividing the intensity at 10 MPa by the value of the pressure: c (or d) \approx I_{10MPa}/(10 MPa).



Figure 5.3 Steam-9-35 NMR spectra with and without capillary, and spectrum of empty sample holder containing only hydrogen, all acquired at room temperature under 10 MPa of H_2 . The arrows indicate the regions corresponding to known volumes.

5.3 General Results

The ¹H NMR spectra at 100 K of CO2-9-59 as they evolve with pressure are shown in Figure 5.4 (not all pressures are represented here for the sake of clarity). Two distinct peaks, A on the left and B on the right, are clearly resolved and evolve very differently as the pressure is varied, similar to what was observed in the RT spectra of B-

doped graphite. Peak A increases linearly with pressure, consistent with the behavior of a free gas, and is not clearly visible until around 0.3 MPa. In contrast, Peak B is present even at 100 Pa but eventually approaches saturation at higher pressure, consistent with Type I mono-layer surface adsorption. In Figure 5.5 the chemical shifts of Peak B can be observed moving closer to Peak A as the pressure is increased, a behavior that is even more obvious when the position of Peak B is plotted versus a log scale of the pressure (inset). An intriguing trend appears when the varying chemical shift is plotted for all nine samples (Figure 5.6): the strength of this pressure-dependence increases with the amount of BO but is absent below 35% BO. This suggests that the NMR method is sensitive to changes in the structure of these materials. This can provide information useful for engineering them for optimal hydrogen storage.



Figure 5.4 Evolution of the NMR spectra as a function of pressure for CO2-9-59 at 100 K. Peak A on the left evolves linearly with pressure and does not have a significant contribution at low pressures while Peak B is present even at the lowest pressure and approaches saturation at higher pressures.



Figure 5.5 Spectra of H_2 in CO2-9-59 at 100 K demonstrating a pressure dependence in the chemical shift of Peak B. The maximum of Peak B is indicated by each spectrum's respective marker, ranging from about -10 ppm at the lowest pressures to approximately -6 ppm at 10 MPa. The chemical shift is plotted against pressure with a logarithmic axis (inset) to emphasize this dynamic behavior.



Figure 5.6 Chemical shift of the micropore peak versus pressure at 100 K. A noticeable change in shift with varied pressure is expected only in samples whose average pore size is larger than ~1.2 nm. All nine samples appear to have the same low pressure limit of about -10 ppm, indicating little variation in the degree of graphitization of the adsorbent surface. The error of the shift is approximately ± 0.2 ppm and is represented by the size of the data points.

5.4 Determining a Critical Pore Size

Since the NMR timescale is too long for these sub-populations to be resolved in the spectrum, the fast exchange between the adsorbed and free species will give rise to an observed shift δ_{ob} of Peak B that is the weighted average of the chemical shifts of each region:

$$\delta_{ob}(P) = \frac{\delta_{ad} n_{ad}(P) + \delta_{fg} n_{fg}(P)}{n_{ad}(P) + n_{fg}(P)}$$
(5-2).

Here, the *ad* and *fg* notations refer to the adsorbed and free gas populations/regions within the micropores, respectively. If the populations of these two regions evolve differently with pressure, an effect similar to that seen in Figures 5.5 and 5.6 will appear. Following the ideal gas law, n_{fg} should be linear with pressure and proportional to the "free volume" (the micropore volume less the adsorbed monolayers), while the Langmuir model of adsorption (eq. 2-1) describes n_{ad} . The adsorbed shift δ_{ad} is simply eq. 3-4 with the appropriate value for *z* of an adsorbed H₂ molecule. This distance can be estimated by using the Lorentz-Berthelot mixing rules to calculate the fluid-solid Lennard-Jones (LJ) interaction parameter σ_{fs} . For hydrogen, the fluid-fluid LJ parameter is taken to be $\sigma_{ff} =$ 0.296 nm,¹⁰ while the value for the solid-solid LJ parameter of carbon is taken from Steele¹¹ to be $\sigma_{ss} = 0.34$ nm, producing a value of 0.318 nm for σ_{fs} . For current purposes, it will suffice to say z = 0.32 nm, so

$$\delta_{ad} = -\lambda \left(\frac{1}{(0.32nm)^3} + \frac{1}{(d - 0.32nm)^3} \right)$$
(5-3)

The molecular density is very close to homogenous in the free gas region,¹² so it is assumed that an H_2 molecule within this region has equal probability to be found at any

point between the two adsorbed layers. To account for possible variations of the chemical shift across this region, the averaged value of eq. 3-6 is calculated:

$$\delta_{fg} = -\lambda \frac{\int_{w}^{d-w} \left(\frac{1}{z^{3}} + \frac{1}{(d-z)^{3}}\right) dz}{\int_{w}^{d-w} dz} = -\lambda \frac{d}{w^{2}(d-w)^{2}}$$
(5-4),

where *w* is the effective thickness of the pore wall excluded by the adsorbed monolayers, ~0.6 nm. For pores of width much larger than the monolayer thickness $(d \gg w) \delta_{fg}$, the chemical shift for gas within pores approaches 0 as 1/d. Therefore, the observed chemical shift $\delta_{ob}(d,P)$ will change with pressure from $\delta_{ad}(P=0) \sim -10$ ppm and approach $\delta_{fg}(d, P = 10 \text{ MPa})$ according to eq. 5-2 because at 10 MPa, $n_{fg} \gg n_{ad}$ in large pores.

While it is useful to have explicit expressions for the parameters of eq. 5-2, fitting the data in hopes of extracting a value for d is complicated by the fact that there is an inhomogeneous distribution of pore sizes, and this left for an in-depth treatment at a later time. Comparative analysis of Figure 5.6 for Steam-9-70 and CO2-9-59 shows that they have strikingly similar evolutions, so it is suggested that their average pore widths are equal within experimental error, and they have very similar pore size distributions (this has been independently shown to be true).⁹ Steam-9-20 and CO2-9-26 show potential to have identical trends, but the CO2-9-26 data is too sparse to verify this.

Despite currently being limited to qualitative analysis, eq. 5-2 can still be utilized to interpret the implications of an unchanging chemical shift. If there is no free volume within the pores, the free gas population n_{fg} will equal zero for all pressures and eq. 5-2 will reduce to $\delta_{ob}(P) = \delta_{ad}$, which is assumed to be constant. It is very practical then to calculate the critical average pore size at which $\Delta \delta_{ob}(P) \neq 0$ (i.e. a change in the chemical shift would first be observed); those materials that exhibit only one chemical shift for Peak B across the pressure range can be taken to have an average micropore size smaller than this d_c . A region distinct from the adsorbed H₂ could develop as soon as the average pore width increases beyond that of two close packed monolayers of H₂, and should be fairly well-defined once the pore width is equivalent to three monolayers. Following the adsorption studies of Bhatia and colleagues¹³⁻¹⁵ using simulations based on LJ interactions, we define a critical pore diameter range as

$$2l_{H_2} \le d_c \le 3l_{H_2} \Longrightarrow 2.9\sigma_{fs} \le d_c \le 3.9\sigma_{fs}$$
(5-5),

where l_{H_2} is the monolayer thickness of H₂ and σ_{fs} is the fluid-solid LJ interaction parameter calculated earlier. Note that the latter half of eq. 5-5 is generalized and can be used to calculate d_c for any adsorbent-adsorbate system with monolayer adsorption studied by NMR. Inserting σ_{fs} = 0.32 nm from above into eq. 5-5, we find (roughly)

$$0.9 \le d_c \le 1.2 \text{ nm}$$
 (5-6).

Returning to Figure 5.6, it is noted that CO2-9-1, Steam-9-20, and CO2-9-26 all appear to have $d \le d_c$, while the slight downfield trend of Steam-9-35 suggests that it is just beyond the critical boundary. In general, it is probably more accurate to quote the higher value of 1.2 nm as the critical diameter.

5.5 Relative Pore Diameters

It is tempting to directly compare the magnitude of the shifts at a given pressure to infer the relative pore diameters of the nine samples, but in general this proves to be unreliable since it cannot be assumed automatically that the value of λ is the same for any two given materials. It is fortunate in this case that in the low-pressure limit, where $\delta_{ab} \sim \delta_{ad}$, the shift of Peak B in Figure 5.6 consistently approaches -10 ppm, which also indicates that the degree of graphitization is dependent only on the argon pre-activation step. This is true even in the highest case of BO, Steam-9-95. With the value of λ experimentally verified to be unchanged for all the data sets, the respective shift of each sample at a well-chosen pressure can be accurately used as a relative measure of pore size. A pressure of 0.1 MPa at 100 K was selected because the lack of a significant contribution from Peak A at those conditions simplified determining the value of the pore shift, as well as the fact that these data were available for all of the samples. As can be deduced from eq. 5-4, a larger absolute shift indicates a smaller pore diameter (very roughly, $d \propto -\delta^{-1}$). Figure 5.7 plots the 0.1 MPa shift as a function of BO. Both methods produce a trend of increasing *d* with increasing BO, which should be expected.



Figure 5.7 Chemical shift of the micropore peak at 0.1 MPa and 100 K versus burn-off. The pore diameter is approximately inversely proportional to the absolute value of the shift.

5.6 Upper Limits of Pore Size Associated with Peak B

Thus far a lower limit and a relative comparison of the pore widths above that limit have been established. What is now needed is an approximate upper limit on which micropores Peak B can represent to put Figure 5.7 into context, and this can be based on the resolution of the two peaks in the spectra. In order to be able to distinguish H₂ in micropores from the H₂ in intergranular pores, the micropores must be able to produce a shift large enough for Peak B to be resolved from Peak A. Our criteria for resolution will be that the absolute value of $\delta_{fg}(d_{max})$ be on the order of (or greater than) the Half-Width-Half-Max (HWHM) of Peak A. For the CO₂-activated samples, $\overline{HWHM}_A \equiv \Delta_A \cong 1.75 \, ppm$. Combining this with eqs. 3-4 and 5-4 gives

$$|\delta_{fg}(d_{\max})| = |\delta_{ad}| \frac{z \cdot d_{\max}}{(d_{\max} - z)^2} \ge \Delta_A$$
(10),

where the free gas region has intentionally been extended to include the entire pore space, w = z = 0.32 nm. The shift of an adsorbed molecule δ_{ad} can be determined from the low pressure limit of Figure 5.6, where the shifts for all nine samples have already been established as converging near -10 ppm. Numerically evaluating eq. 10 with $|\delta_{ad}| = 10$ ppm and $\Delta_A = 1.75$ ppm indicates that the largest micropores that can be reliably resolved as a separate NMR peak are around 2.4 nm. Due to the averaging process of the molecular dynamics, it is possible that slightly larger pores may be included in Peak B, but 2.4 nm is the largest *average* pore size expected to produce a resolved second peak. It is clear that even with the range of distinguishable pore sizes extending slightly beyond the micropore regime, the ability to differentiate between H₂ in intergranular pores and H₂ in pores with diameters on the nanometer scale makes NMR a rather useful tool when it is beneficial to be able to restrict the region of interest to the micro/nanopore domain. The general ability to resolve the two components produced by the samples in this study is demonstrated by Figure 5.8, which displays the high pressure/low temperature spectra of all nine samples. The lone exception here is Steam-9-95, which will be discussed in more detail later. Two lines are observed for H₂ in all but one sample indicating that H₂ in micropores do not exchange on the NMR time scale with H₂ in intergranular pores. A 2-D exchange experiment of Steam-9-35 at RT did not show any exchange peaks and extended the time over which no exchange between the two H₂ reservoirs occurs to 10 ms.



Figure 5.8 Non-normalized NMR spectra for all nine samples at 10 MPa and 100 K. All but Steam-9-95 clearly exhibit a Peak A and a Peak B.

5.7 Uptake and Binding Energy at 100 K



Figure 5.9 High pressure (0.1-10 MPa) isotherms at 100 K for seven of the nine samples, with Langmuir adsorption fits.

While the intensity of the NMR signal is directly proportional to the number of protons being probed, an exact empirical relationship does not exist between the two.¹⁶ By decomposing the two peaks and properly calibrating the signal to units of H_2 mass as described in Section 5.2, information that is significantly more useful can be accessed. Isotherms of the weight percent (wt%) uptake of the micropores were derived from calibrated, integrated intensities of Peak B for seven of the samples and plotted in Figure 5.9. Incidentally, the NMR derived capacities are in agreement with volumetric measurements done on the same samples.⁹ For all samples, a maximum uptake is observed for CO2-9-59. This is clearer in Figure 5.10 where the uptakes at 0.2 and 10

MPa are plotted versus BO. This maximal behavior is reflected at the lower pressure as well, which is a decent approximation of the traditionally reported excess uptake. For both activation methods, samples with BET surface areas of approximately 2000 $m^2 g^{-1}$ exhibited the highest uptakes. Since the specific surface area is expected to be the main determinant of uptake, 17,18 it is somewhat surprising that CO2-9-80 with ~3000 m² g⁻¹ is inferior in this respect. The real discrepancy between the surface area and uptake can be explained partially in terms of the structure of the material. The upper limit of the surface area of an exclusively slit-pore geometry is the maximum theoretical surface area of both sides of a graphene sheet, $2630 \text{ m}^2 \text{ g}^{-1.19}$ Above this, the surface area must be created by deformations of the structure, which in real materials will start to appear long before $2630 \text{ m}^2 \text{ g}^{-1}$ of surface area has been produced. The breakdown in the slit-pore geometry at higher BO will produce the twin effects of reducing the effectiveness of the NMR method while increasing the mobility of the H₂ between regions. The latter is more significant as the small population of micropores, which are in close proximity to the intergranular pores, have an increasing chance of contributing to Peak A rather than Peak B. The former is a limitation of the experiment itself, since it is possible that the higher BO samples have a sizable fraction of pores that are wider than 2.4 nm but still contribute to the overall uptake. Nonetheless, several theoretical studies have predicted that the pore sizes that are optimum for H_2 storage are much narrower than this, ^{12,13,20} and so Peak B represents H₂ that can be stored efficiently from a volumetric perspective and the maximum in its gravimetric uptake as measured by NMR at 59% BO can be viewed as a balance between these two metrics of storage capacity.


Figure 5.10 H_2 uptake of the micropores versus burn-off at 100 K for 10 and 0.2 MPa. CO2-9-59 shows the highest uptake at both pressures, despite not having the largest SSA. This is thought to be a result of the limitations of the NMR method and an increase in the mobility between regions in the material.

The isotherms that had data for pressures below 0.1 MPa indicated that two distinct adsorption sites were present, most likely arising from a bimodal distribution of pore sizes with the lower binding energy site (~5 kJ mol⁻¹) being dominant. These isotherms were fit with two Langmuir terms in the form of eq. 2-1 and a small ideal gas term, since Peak B represents all of the H₂ in the micropores and not just the excess adsorption. The relevant pressure range for the lower binding energy at 100 K is 0.1 - 10 MPa, which was available for all seven samples above. In this case, a decent approximation for the fit could be made by replacing the Langmuir term with a constant offset without much loss in accuracy.

The results of the isotherm fittings are shown in Figure 5.11. Since the degree of graphitization of the adsorbent surface is altered very little by the activation process, the trend of decreasing binding energy is most likely due to the widening of the pores. This is consistent with the expectation that molecules in narrower pores are more likely to interact with two walls instead of just one,²¹ leading to enhanced binding energies with decreasing pore width. Assuming that the two binding energies arise from two micropore sizes, the weaker binding energy would be assigned to the larger micropores and the stronger binding energy to pores that are very likely what Dubinin²² called ultramicropores (d < 0.7 nm), due to the proximity to both walls, which would be required to enhance the binding energy by several kJ mol⁻¹. Smaller pores are more responsive to this effect, which is why the higher binding energies are more sensitive to the amount of BO than the lower binding energies.

To fit the data without pressures below 0.1 MPa, the second Langmuir term was approximated by a constant since the higher binding energy sites would be nearly saturated at that pressure. The insets of Figure 5.12 show that the substitution of the constant term allows for the determination of the lower binding energy from the limited data sets, as the extracted values in both cases are equal within less than 2.5% error. For Steam-9-20, the ratio of total sites with lower binding energy to those of the higher binding energy $n_{\infty,low}/n_{\infty,high}$ is 2.06 for the high pressure fit and 2.02 for the full-range fit. In the case of CO2-9-59, these ratios are 3.89 and 3.61, thus these parameters are consistent within 8% error as well and further support the claim that the high pressure fits of the isotherms can accurately provide values for the lower binding energy. Finally, the uptake data for Steam-9-47 exhibited signs of experimental error and a full isotherm could not be reliably produced, while data for Steam-9-95 could not be properly calibrated due to issues with resolving Peak B from Peak A at high pressures.



Figure 5.11 Binding energies extracted from high pressure isotherms (estimated 5% error) and full pressure-range isotherms (estimated 2.5% error), versus burn-off for seven of the nine samples. The trend of decreasing binding energy with increasing burn-off can be correlated to the increasing widths of the pores in both cases; this is more noticeable in the higher binding energies associated with the narrower pores.



Figure 5.12 Fitting of Steam-9-20 (a) and CO2-9-59 (b) isotherms for extracting binding energy using the entire pressure range and just the high pressure data (insets). This illustrates that the higher binding energy Langmuir term can be approximated to be saturated at 0.1 MPa and therefore replaced with a constant, allowing for the lower binding energy to be determined from partial data sets.

5.8 Structure of Pores at High Burn-Off

Figure 5.13 shows the pressure-dependent spectral evolution of Steam-9-95. Peak B is distinct and clearly shifted upfield at low pressures, while at high pressures any components present in the spectra cannot be easily distinguished. Without the ability to properly decompose the spectra, it was not possible to calibrate the intensities with confidence, and therefore an isotherm for the micropore could not be produced. In the intermediate range of 1.0 to 4.4 MPa, two distinct peaks are clearly present, although they would be rather difficult to accurately resolve. This indicates that the average pore size is in the neighborhood of the upper limit (2.4 nm) of what our method can reliably distinguish from free gas. In the pressure regime where Peak A becomes significant, there is a contribution to the spectrum between the two expected peaks, which appears to be an average of their intensities and shifts. This indicates a considerable amount of exchange happening between the two regions on the NMR timescale. It is an exceptional case to see evidence of such exchange as even the sample with the second highest BO that was studied, CO2-9-80, did not show signs of exchange in its 1-D spectra (see Figure 5.13). When the ¹H spectra for those two samples are plotted versus a common shift reference, the dominant peak of Steam-9-95 appears between peak A and B of CO2-9-80 (Figure 5.14). This difference points to the structure of activated PEEK having a limiting effect on the inter-region exchange of the H_2 molecules, with any perceptible inter-region exchange occurring only when its structure becomes largely disorganized in the latest stages of the burn-off process. However, without an accompanying increase in intraregion mobility, the inter-region exchange would be limited primarily to micropores that are directly connected to the intergranular pores. Qualitatively speaking, in Figure 5.13 it appears that a large number of both species participate in the exchange process, which is indicative of intercalation of the micropores throughout the sample and not just on the grain surfaces.



Figure 5.13 Pressure-dependent evolution at high pressures (a) and low pressures (b) for Steam-9-95 at 100 K. Peak B is clearly distinct in (b) but cannot be resolved at all in (a) indicating that the average micropore size is \sim 2.4 nm (or larger), the experimental upper limit of Peak B. Above 1.0 MPa (a), a component due to exchange between the two regions appears between Peaks A and B. This was not observed in any of the other samples.



Figure 5.14 When plotted relative to the same reference shift (200.0835 MHz), a comparison of the 10 MPa, 100 K spectra of CO2-9-80 and Steam-9-95 shows that the position of the dominant peak in the Steam-9-95 is very near the midpoint between Peaks A and B of CO2-9-80, an indication of significant exchange present only in samples with very high BO.

5.9 Activated PEEK Conclusions

The NMR approach has been employed to characterize the hydrogen storage capabilities and pore structures of a series of CO₂- and steam-activated PEEK samples with various amounts of burn-off. As with the boron-doped graphite, the ability to distinguish between H₂ molecules occupying intergranular pores and those in micropores has enabled focused study of the H₂ interaction with those pores of interest. For Activated PEEK, it was estimated that Peak B corresponded to H₂ in pores with diameters less than ~2.4 nm, only slightly larger than the technical upper limit for micropores, 2 nm. Unlike the boron-doped graphite, the chemical shift of Peak B was seen to evolve with pressure for certain samples, offering a new avenue of sample characterization. This pressure-dependent behavior of the chemical shift of Peak B was shown to arise from the different pressure dependences in populations of H₂ adsorbed and gaseous H₂ in the micropores, which each experience a difference chemical shift due to the spatial dependence of the ring-current effect. This allowed for critical information about the average micropore diameter to be inferred, most notably whether it is less than an adsorbate-dependent critical diameter. No pressure-dependent shift was observed in samples with less than 35% burn-off, indicating that the average widths of their micropores were less than 1.2 nm, and that the transition to pores wider than this occurs between 35-47% burn-off during activation. Values for the more common parameters of hydrogen uptake and binding energies were also extracted from 100 K isotherms. The degree of graphitization of the adsorbing surface appeared to be unaffected by the activation process and thus variations in binding energy were attributed solely to micropore width. The adsorption appeared to be bimodal, which is thought to be a

bimodal distribution of pore sizes rather than two different adsorption sites dispersed heterogeneously on the sample surface. Although it was not possible to accurately determine the value of the higher binding energy for samples without low pressure data, those which could be analyzed ranged from 7 to 9 kJ mol⁻¹. The two binding energies are thought to be due to the aforementioned bimodal micropore size distributions, with the higher binding energy corresponding to ultramicropores. At 100 K, maximum uptakes of 2.3 wt% at 0.2 MPa and 6.2 wt% at 10 MPa were observed for the CO₂-activated sample with 59% burn-off. Increased inter-region exchange due to structure breakdown and the upper limit of resolvable pore sizes are believed to account for the apparent drop in measured uptake despite increased surface area in samples with higher burn-off. This breakdown was evidenced by the exchange between the peaks in the 10 MPa/100 K NMR spectrum for the steam-activated sample with 95% burn-off. From a methodological point of view, this work has further established the NMR-H₂ approach as a valid technique for characterizing microporous graphitic materials. Most notably it has been demonstrated that the pressure evolution of the chemical shift can be correlated to spatial characteristics of the micropores. In future work, it may be possible to take the current phenomenological and qualitative analysis of the phenomenon and transform into a more powerful quantitative form based upon recently developed alternative firstprinciple calculation of the magnetic shielding tensor—i.e., the chemical shift.

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CHAPTER SIX

HYDROGEN STORAGE IN ZEOLITE-TEMPLATED CARBONS

The key role of spatial engineering in developing suitable hydrogen storage materials was pointed out during the discussion of Activated PEEK. A drawback that activated carbons with high surfaces area tend to suffer from is the creation of unwanted mesopores, as micropores are the most efficient means of storage.¹ An alternative approach is the template method, which allows for a more controlled means of producing pores of a desired geometry and dimension.

Since first being synthesized by Kyotani and co-workers in the mid-1990s,² zeolite-templated carbons (ZTCs) have found a place in a wide range of potential applications, such as double layer capacitors,³ fuel cells^{4,5} and in gas storage^{1,6-11} Their attractiveness lies primarily in their ability to obtain high surface area (up to 4000 m².g⁻¹) in addition to having long-range periodic structures, most notably those which originate from zeolite Y.¹²⁻¹⁶ In general, ZTCs have very sharp pore-size distributions¹¹ and, thus, they can be designed as having a minimal mesopore volume.

ZTCs are produced by filling the regularly-structured channels of zeolites with a carbonaceous precursor, followed by carbonization via pyrolysis creating a zeolite/carbon composite material. The composite is then rinsed with HF, removing the zeolite and leaving behind only the carbon material. During this process, the resulting ZTC inherits

the structure of the zeolite pore space. Figure 6.1, illustrates how the pore structure of the parent zeolite (zeolite Y in this case) is transferred to the solid structure of the resulting ZTC.



Figure 6.1 Diagram illustrating how a ZTC acquires the inverse pore structure of its zeolite Y parent (reprinted with permission from Ref.17).

The primary motivation of the current study was to replicate P7(2)-H, a ZTC produced from zeolite Y, and to independently determine if it exhibited enhanced H_2 due to confinement at 34 MPa and 300 K, as had been previously reported.¹ In that particular study of P7(2)-H, there was indication that confinement effects at these pressures could enhance the H_2 storage capacity of the material beyond that which is expected from the surface area alone.^{1,18} The material produced for this study is referred to as ZTC-23.



Figure 6.2 Structural model of ZTCs, which features an unsaturated cubic lattice (a) comprised of buckybowls (b) and containing various functional groups (d). A nano-cage pore structure is seen in the large-sized molecular model(c), which is constructed with the buckybowl units(b) in the structure of the cubic lattice (a). The inset of (b) shows the structure of the buckybowl sub-unit (reprinted with permission from Ref. 17).

It is important to have a basic understanding of the pore structure and chemistry expected for ZTC-23 and P7(2)-H. In Figure 6.2 several aspects of the structural model of ZTC are illustrated. The structural models were discerned from a comprehensive

analysis of experimental data and computer modeling of a material nearly identical to P7(2)-H.

The micropore system of zeolite Y has a diamond-like structure. Because of the unique complementary symmetry of the voids in this form, the produced ZTCs have a tetrahedral diamond-like structure as well (see Figure 6.1).¹⁷ It is important to note that the vertices of this structure is not composed of singular carbon atoms, as modeled in Figure 6.2(a), but rather a structure consisting of buckyball fragments (known as buckybowls), which are comprised of a singular graphene-like sheet (inset of Figure 6.2). These buckybowls are then connected to other such subunits by two to three common carbon atoms (Figure 6.2(b)).¹⁷

To bring the idealized model in closer agreement with experimental data (Figure 6.2(d)) the model is modified by the addition of various O-containing functional groups. Overall, the pore structure is comprised of super-cages with a diameter of 1.0-1.7 nm. The super-cages are then connected by narrower pore necks (Figure 6.2(c)).

A basic assumption in the interpretation of the NMR characterization of B-doped Graphite and Activated PEEK was that they had a slit-pore structure (see Chapter 3). Figure 6.2 show that ZTC has completely different pore geometry; it is of interest to see how this difference is manifested in the line-shape of the NMR spectra. The other two basic premises of partial graphitization and a significant micropore population remain valid. This is the first such NMR investigation of a highly-ordered, non-amorphous carbon material. A brief overview of the findings of this work is provided here for easy reference and to provide an overall context for each individual experiment. The reproduced sample is found to have multiple phases due to an unexpected variation in the synthesis temperatures. The multi-phase nature of ZTC-23 allows for the pore structure and magnetic behavior to be examined more closely.

ZTC-23 is observed to have a local paramagnetic environment within the sample while being diamagnetic in bulk form. The evolution of the chemical shift with pressure at 100 K indicates that anomalous short-range paramagnetic behavior, which is observed within the material, is associated with the edge sites of the buckybowls rather than topological defects due to its curved surface. This result demonstrates that NMR is wellsuited for studying the local paramagnetic and ferromagnetic properties of carbon-based materials.

An adsorption isotherm at 100 K was acquired to examine the adsorption properties of ZTC-23. These results were used to predict the adsorption behavior at 300 K and 34 MPa to allow for comparison with the published measurements on P7(2)-H. This extrapolation, which is based solely on the Langmuir model of adsorption, agrees with the previously published measurements on P7(2)-H.

The preliminary implication is that the surface area of the material accounts for the all of H_2 uptake in ZTCs and any confinement effects are negligible.

6.1 Sample Preparation

ZTC-23 was prepared by collaborators at General Motors Research (GMR) by following the methods for synthesizing P7(2)-H found in the literature.¹ Dried zeolite Y (Na-form, SiO₂/Al₂O₃ = 5.6) in powder form was impregnated with furfuryl alcohol under vacuum at 19 °C. First, the resulting composite was washed with mesitylene. Then, under gaseous N₂ flow, the following steps were performed: the furfuryl alcohol within the zeolites channels was polymerized by baking the sample at 150 °C for 8 hours. The temperature was then raised to 700 °C at a rate of 5 °C min⁻¹. At 700 °C, chemical vapor deposition (CVD) of propylene (7% in N₂) was performed for 2 hours. After CVD treatment, the composite material was baked at 900 °C for 3 hours. Finally, the zeolite template was removed by dissolving it in a 47% aqueous solution of HF. The remaining carbon was then rinsed with a generous amount of water and then baked at 150 °C under vacuum for 8 hours.

The only known major variation with respect to the preparation process of ZTC-23 compared to that of P7(2)-H is that in the latter case a vertical furnace was used. Each P7(2)-H particle was suspended in the gas flow resulting in even CVD exposure and heating throughout the sample, while ZTC-23 was baked on a wire mesh in a horizontal tube furnace. It will be shown that the different heating technique has a significant impact on the resulting structure of the material. The measured BET surface areas for the two materials are 3800 m² g⁻¹ and 3417 m² g⁻¹ for P7(2)-H and ZTC-23, respectively.

ZTC-23 very quickly adsorbs a wide range of gaseous species; therefore, it is important that the sample be properly evacuated of guest molecules adsorbed during its

handling before acquiring any H_2 adsorption spectra. This was accomplished by baking the sample under vacuum sequentially at 100, 150, 200, and 250 °C for 2-3 hours per step. It was baked in-situ in the sapphire sample holder with a ceramic fiber heater. However, it was necessary to wrap the portion of the holder outside of the heater with silver wire in thermal contact with an ice bath to protect the epoxy that secures the holder to the high-pressure system from degradation.

The density of the ZTC-23 was low enough (~0.11 g cm⁻³) such that sharp changes in pressure could result in the creation of macroscopic empty spaces within the packed sample. A snug-fitting capillary, which was open on both ends, was packed with glass wool and inserted into the sapphire tube to hold the sample in place, while still allowing H₂ to freely access it. While pressurized, the sample was visually examined by removing the probe to see if any voids had been created. In the few instances where this void was formed, it was duly noted and was remedied by gentle tapping of the sapphire tube until the sample was evenly redistributed and no voids remained.

NMR isotherms of the baked sample were acquired at H_2 pressures ranging from 0.05 to 9.7 MPa at RT and 360 Pa to 9.7 MPa at 100 K. In contrast to the Activated PEEK and B-doped Graphite experiments, where the 100 K isotherms were taken while desorbing, here they were exclusively adsorption isotherms. In both cases, background spectra were acquired as described in Chapter 2. Measurements of the T_1 and T_2 relaxation times were taken at RT and 9.6 MPa.

After all the desired data was acquired for the baked sample, the system was opened to the atmosphere and the sample was allowed to freely adsorb N_2 , O_2 , and water

vapor for 5-120 minutes. The amount of adsorbed gas did not exhibit any time dependence on the scale of the experiments. A background spectrum was taken while the system was still exposed to the external atmosphere. Another isotherm was then acquired at RT for the exposed sample, and a T_2 measurement taken at 9.7 MPa.

To test the repeatability of the general results of the ZTC-23 experiment, the original sample was removed and replaced with a fresh batch that was baked under vacuum as before. Another RT isotherm was obtained, and then two additional exposure experiments were performed. A void within the sample was created during the first exposure run. Its volume occupied 6.6 ± 0.5 mm of the length of the sample holder, or 46.7 ± 3.8 mm³. The number of H₂ in the void was calculated from the ideal gas law and an initial calibration factor was determined via comparison to the intensity of its corresponding spectral component (in essence, this is just a variation of the capillary method used for B-doped Graphite). The sample was restored to its original packing and pumped before being re-exposed to the atmosphere.

When re-exposing the sample to H_2 , the pressure was quickly increased to 9.6 MPa and a spectrum was acquired. Spectra were then taken periodically over the following 16 hours, tracking the dynamics of the system as the high-pressure H_2 displaced adsorbed species within the sample. In all of the experiments reported here, the observation frequency of 200.0835 MHz was set as zero ppm. Exponential line broadening of 30 Hz was applied to all spectra prior to analysis.

6.2 Features of the Spectra at 290 K

As made clear by Figure 6.3, the ¹H NMR spectra of ZTC-23 changes with pressure at RT, this material is fundamentally different in nature compared to the other microporous carbons studied in this thesis. At high pressures at least four discernable features—labeled A, B, C, and D, moving from left to right in the spectra.



Figure 6.3 Evolution of the NMR spectra as a function of pressure for ZTC-23 at 290 K. Above 1.5 MPa, at least four features become apparent, in contrast to only two peaks observed in the B-doped Graphite and Activated PEEK samples.

For comparison, the spectra of both Activated PEEK and B-doped Graphite contained only two broad features: a downfield peak representing the intergranular gas and a peak shifted upfield corresponding to the H₂ confined and adsorbed in micropores. The broadness of these peaks was attributed to the heterogeneity of the local magnetic field due to the random orientations between individual micropores and the external magnetic field. In contrast, the narrow features in ZTC-23's spectra indicate that there are large regions within the sample with a homogenous magnetic susceptibility. This is evidence of the high degree of structural order that should be expected from a templated material.

The proper identification of the spectral features is a vital endeavor; however past experience provides little assistance in the matter. It is by no means obvious which one is the intergranular peak, so there is no *de facto* reference for the chemical shifts of the other peaks. Adding to the difficulties associated with interpreting this previously unobserved type of spectral shape is the apparent overlap of the features. In previous studies, such lack of resolution could be attributed to fast exchange between H₂ in intergranular pores and those in a pore region dominated by mesopores, resulting in a single spectral feature. Here, there exist multiple distinct features that do not have enough separation in their chemical shifts to unambiguously separate them.

The pressure dependence of the features does not clearly indicate to which physical regions they correspond. When the spectrum at each pressure is integrated and the resulting intensity is plotted as a function of pressure (the RT isotherm), the resulting relationship is linear within error. Therefore, the intensity of the individual features will most likely be linear as well, and in this aspect they will be indistinguishable. More information beyond spectral pressure dependence and chemical shift is necessary to properly interpret the ZTC-23 spectra.

6.3 The T_2 Measurement at 290 K

The first feature to be identified by alternative methods is the one that corresponds to the molecules in the intergranular pores. It is reasonable to assume that these pores will constitute the largest free volume in the system. For gaseous H₂ in macroscopic voids, inter-molecular collisions are much more frequent than collisions with the surface of the material (or with the walls of the sample holder). Since the former is a relatively ineffective relaxation mechanism for both the recovery of the magnetization aligned with the external field (T_1) and the decay of the coherence of the spin populations (T_2), the peak associated with the intergranular space is expected to have the longest relaxation times of all of the features.

A T_2 measurement was taken at 9.7 MPa and RT in order to identify this specific feature. At long 2τ , the length of time the coherence is allowed to decay before a spectrum is acquired. The intensities of features with shorter T_2 times will be negligible, leaving only an approximation of the intergranular peak in the spectrum. Upon examination of Figure 6.4, where the spectra for selected values of 2τ have been normalized by the intensity of their respective Peak D, it can be seen that Peak D is the intergranular peak ($T_2 \sim 6$ ms).

111



Figure 6.4 The 9.7 MPa at 100 K spectrum as it decays with 2τ , scaled relative to Peak D for comparison of decay rates. Peak D has a longer T_2 than the other peaks and appears to have a powder pattern line-shape.

An immediate consequence of this analysis is that the other features, assumed to be originating from H₂ within the sample, are shifted downfield rather than upfield from the intergranular peak. An unrelated NMR study of H₂ encapsulated in a fullerene molecule¹⁹ showed that the shielding effect of the cage produced a significant upfield shift, most likely originating from the ring-current effect (RCE).²⁰ The buckybowl structure assumed for ZTC-23 should have a similar effect on the local magnetic environment within the sample, so there must be a competing paramagnetic phenomenon that produces the net downfield shift. This is the first such observation by NMR of a strong paramagnetic effect within microporous carbons. This is consistent with the ferromagnetic behavior expected to arise from isolated clusters in ZTC samples prepared in a manner similar to ZTC-23.²¹ Above the ferromagnetic $T_C \cong 30$ K measured in Ref. 21, the ZTC will exhibit paramagnetic behavior, as seen at 290 and 100 K.

It is now possible to get a better idea of what the remaining features of the spectrum look like. In addition to its position, the T_2 spectra provide information about Peak D's line-shape, which cannot automatically be assumed to be Gaussian or Lorentzian. It is deduced from Figure 6.4 to have the asymmetric powder pattern line-shape observed in spectra of H₂ in the empty sample holder (see Sections 3.3 and 5.2). Such a spectrum, which was previously acquired at 10 MPa and RT, fits the experimental data well. An initial deconvolution of the spectrum is achieved by subtracting Peak D from the original spectrum. The two components of the 9.7 MPa are plotted in Figure 6.5, along with the T_2 values for all the peaks, which were found by fitting the intensities at that specific point with eq. 1-8a. Another distinct peak is revealed to be residing in the upfield shoulder of Peak D ("Peak E"), bringing the number of identified features to five.

The spectrum cannot be resolved any further by the T_2 data. It is seen in Figure 6.5 that Peak D has a sizable contribution to the intensity at Peaks C and E, and, to a lesser extent, Peak B. The T_2 value found for Peak A is the only one which is taken to be completely accurate. However, once the influence of the slow-decaying Peak D is accounted for in the T_2 analysis, the actual values for Peaks B, C, and E are found to be very close to that of Peak A, if not the same. Given that Peak A has the shortest T_2 value observed here, it is assumed its corresponding H₂ environment is the confining nanostructures within ZTC-23.



Figure 6.5 The 9.7 MPa, 100 K spectra decomposed into two components, with the T_2 values of the identifiable peaks, including a "hidden" Peak E. The significant contribution to the intensities of most of the other peaks by Peak D is shown.

6.4 The Expected NMR Line-shape of H₂ in Ordered Materials

Before dissecting the spectral features any further, it is worthwhile to discuss what line-shapes are expected to arise from H₂ in a microporous carbon with long-range order. The discussion presupposes that an anisotropic magnetic susceptibility is present within the ordered structure. As discussed in Section 3.3, if $\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz}$, an asymmetric double-peaked powder pattern will appear, while $\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$ gives rise to a triply-peaked line-shape.²² In amorphous carbons, there is little correlation between the orientations of σ_{zz} with respect to the external magnetic field (characterized by the Euler angle β) of adjacent micropores. As a probing H₂ molecule explores many randomly oriented micropores during a single NMR measurement, only an average of the local susceptibility is measured, resulting in a single broad peak.

In the opposite scenario of materials with long-range (i.e., highly-correlated) pore structures, each crystal-like particle will share a single characteristic β value. The majority of the H₂, which are in a given particle at the beginning of an individual measurement, will remain there throughout the duration thereof (~3 ms), and thus their chemical shift will NOT be averaged out. Instead, it will be determined by the local anisotropy and the β value of that specific particle. When the entire population of similar particles is considered, the resulting line-shape will be a powder pattern. Despite the expected cubic symmetry of the super-structure of ZTCs produced from zeolite Y, it is likely that the susceptibility tensor is anisotropic. Therefore, it is expected that the longrange micropore structure of ZTC-23 will manifest itself in the NMR spectra as an asymmetric powder pattern.

6.5 The T_1 Measurement at 290 K

The validity of subtracting Peak D from the spectrum was confirmed by a T_1 measurement performed under the same conditions as the T_2 measurement. Within the material, frequent collisions between confined H₂ and the pore walls is expected to be the most effective means of relaxation in the overall system. This population will therefore have the shortest T_1 values. The frequency of the H₂-wall collision has an inverse relationship with the characteristic dimension of the confining volume.²³ The measured T_1 values, therefore, give an order-of-magnitude estimate of the size of the space.

At short τ , the length of time the *z*-magnetization is allowed to recover before acquiring a spectrum; features with the shorter T_1 times appear in the spectrum first, revealing those that arise from the smallest confined spaces. Figure 6.6 is a plot of the spectra for various τ and each spectrum is normalized by the intensity of their respective Peak A. At the shortest τ value (25µs), the only feature absent is Peak D, which confirms that Peak E is a real spectral feature. Figure 6.7 compares the short τ spectrum to that obtained by subtracting Peak D, showing that the positions of the four peaks are consistent between the two approaches.



Figure 6.6 The 9.7 MPa at 100 K spectrum as it recovers with τ , scaled relative to Peak A for comparison of recovery rates. All peaks except D are present at short values of τ , including the previously obscured Peak E.



Figure 6.7 Comparison of the spectral features of Peaks A, B, C, and E at 9.7 MPa and 290 K as arrived at via T_1 (red) and T_2 (green) filtering methods. All peaks are present in both and have corroborating chemical shifts.



Figure 6.8 The vertically zoomed $\tau = 25 \ \mu s$ spectrum reveals at least three additional features with relatively low intensities.

The T_1 spectrum at $\tau = 25\mu s$ reveals that there are numerous chemical environments that have very similar geometries and dimensions. Once again, when the recovery of Peak D is taken into account, all of the features present at $\tau = 25\mu s$ have indistinguishable T_1 values. Close inspection of Figures 6.4 and 6.6 strongly suggest that Peak B is actually two peaks with small chemical shift separation. In addition to Peaks A, B1, B2, C, and E, at least three additional peaks are revealed on the fringes of the spectra (see Figure 6.8). Thus, there are currently a minimum of eight features detectable by NMR that are identified as representing H_2 confined within the sample; yet each one of these represents a different chemical shift environment. Furthermore, these environments must be isolated from each other to such a degree that exchange between any two regions has a very limited averaging effect. Why so many unique environments are present is outlined in the next section.

6.6 The Creation and Characterization of a Multi-phase Sample

The unusually large number of spectral features is strong evidence that ZTC-23 has multiple phases. P7(2)-H is known to have a highly homogenous structure; therefore, the conclusion of Section 6.4 predicts that its single phase would produce at most three spectral features (corresponding to a susceptibility tensor within the structure where $\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$) in addition to Peak D. Per the same metric, ZTC-23 must have a minimum of three unique crystal structures. In light of this, the synthesis conditions of ZTC-23 were carefully reexamined.

A temperature profile of the horizontal tube furnace (see Figure 6.9) revealed that the thermal conditions needed for the three related synthesis steps were not equally achieved in the sample region. This explains why ZTC-23 is actually composite material. Additionally, ZTC-23's XRD pattern did not exhibit a noticeably sharp peak at $2\theta = 6.4^{\circ}$ corresponding to long-range structure in the {111} plane, which was present in XRD pattern of P7(2)-H.¹ This confirms that ZTC-23 is not a fully successful replication of P7(2)-H, which was not known *a priori*.



Figure 6.9 Thermal profile of the horizontal tube furnace and the corresponding positions. A variation as high as 90 °C was observed at 900 °C.

Almost paradoxically, the creation of a multi-phase sample has created the opportunity for a more informative study than if a single-phase sample had been produced. By identifying the source of the multi-phase nature of ZTC-23, phases with varying degrees of paramagnetic behavior and pore structure can be tenuously linked to the variations in the sample preparation that may have led to them. Long-range order was shown to have no effect on P7(2)-H's ability to store hydrogen.¹ Otherwise, ZTC-23 should have more than enough commonalities with P7(2)-H to allow for meaningful conclusions to be drawn in regards to H₂ storage.

6.7 Behavior of the Chemical Shifts Relative to H₂ in a Large Void

ZTC-23 exhibits internal paramagnetic behavior while its bulk magnetic susceptibility appears to be dominated by diamagnetism. A large void with a volume roughly the one third of the total sample space was created *in situ* via quickly lowering the pressure. The pressure was raised to 9.6 MPa and a T_2 measurement was performed. Since the void space is a few orders of magnitude larger than the intergranular pores, the former will have a noticeably longer T_2 value and can be clearly identified as the slowest decaying component in Figure 6.10. The measured T_2 values of several of the peaks are plotted in Figure 6.11. The dominant peak at ~ 2.5 ppm has the longest T_2 value of 8.6 ms, about 2 ms longer than any of the previously measured relaxation constants in this sample. The most downfield-shifted peak is still Peak D, as identified by its T_2 value (compare Figure 6.5 to Figure 6.11). The chemical shift of the large void peak can be considered a very good approximation of the natural zero shift of the spectrum. In other words, its position is the chemical shift of a hypothetical hydrogen molecule that is completely uninfluenced by the presence of ZTC-23. This test molecule's position in the NMR spectrum will experience a diamagnetic chemical shift to the right as it physically approaches the external surfaces of the material. However, as the molecule moves into the pore spaces within ZTC-23, its spectral component is shifted downfield into the paramagnetic regime.



Figure 6.10 Due to its long decay constant, the peak arising from the hydrogen in the gap is easily identified in the scaled decaying spectra from the T_2 experiment at 290 K and 9.6 MPa. Its appearance in the middle of the spectra indicates that ZTC-23 has bimodal magnetic susceptibility: paramagnetic internally and diamagnetic externally.



Figure 6.11 The experimentally determined T_2 values of select shifts, as found at 9.6 MPa and 290 K in the gapped sample. The far right is identified as Peak D by its T_2 value of ~6 ms, while the dominant middle peak has a decay constant 2 ms longer and must be the H₂ in the gap.

6.8 Temperature Dependence of the Overall Spectral Chemical Shift

It is assumed that the predominant means of producing diamagnetism in ZTC-23 is the RCE (ring-current effect), as it is in many microporous carbons. The overall diamagnetic shift of the spectra at 100 K is evidence of this. The 9.7 MPa spectrum acquired at 100 K is compared to its counterpart at 290 K in Figure 6.12 (the areas of both spectra have been normalized to unity). The two spectra are quite similar in their line-shapes, the most notable difference being the upfield shift of 1.952 ppm for *all* the features at 100 K. In line with the graphene structure predicted by the molecular model of zeolite Y-based ZTCs,¹⁷ this bulk shift is roughly a fifth of the difference in the observed bulk susceptibility of graphite at these two temperatures.²⁴ The effective

contribution of the RCE is limited by the size of the graphene clusters in ZTCs, the buckybowl $C_{36}H_9$ subunits.¹⁷ Therefore, the path of the current-producing π -electrons encompasses an area with a diameter of only a few benzene rings (0.9-1.3 nm). An experimental study of the relationship between the cluster size and mass susceptibility of a wide range of graphitized materials²⁵ predicts that the ratio of the mass susceptibilities of buckybowl-sized particles and those approaching pure graphite to be on the order of one fourth. Therefore, the RCE is the accepted dominant diamagnetic mechanism, as it accurately predicts the behavior of the bulk susceptibility of ZTC-23 at different temperatures.



Figure 6.12 Comparison of the 9.7 MPa spectra for 100 K and 290 K. There is a difference in their positions of 1.952 ppm, which is consistent with graphene particles the size of the buckybowls. Chemical shift aside, there are only minor differences in their respective line-shapes (spectra are normalized to unity).

6.9 Spectral Evolution at 100 K and Paramagnetism in ZTC-23

The entire 100 K spectra will shift downfield as the pressure is increased. This provides some insight into the close-range paramagnetic behavior in ZTC-23. Recently there has been an ongoing discussion in the carbon community about the origins of anomalous ferromagnetic behavior in carbon-based materials, graphene in particular.²⁶⁻³¹ As mentioned in Section 6.3, ferromagnetic behavior is observed in samples very similar to ZTC-23²¹ due to isolated graphene clusters (buckybowl subunits). The presently observed paramagnetism is possibly due to this phenomenon, only at $T >> T_C$. Topological defects,^{32,33} namely the three pentagons in the curved buckybowl structure, along with zigzag edge sites,^{29,34,35} are two possible explanations as to how this behavior might arise in the ZTCs. The pressure dependence of the chemical shift provided insight into near-surface susceptibility effects in Activated PEEK due to adsorption on the surface. Similar behavior in ZTC-23 should prove equally informative.

Spectra acquired at 100 K and a representative range of pressures are displayed in Figure 6.13; also plotted is the shift of the point in each spectrum with maximum intensity versus the pressure. Peak D apparently shifts with the rest of the spectrum as the pressure is varied. It is unlikely that the concentration of H_2 within the sample has an impact on the bulk susceptibility. This would indicate that a large portion of the intergranular H_2 population is able to exchange with H_2 on the outer edges of the particles thus coupling Peak D's chemical shift to the general behavior of the shifts within the sample.

ZTC-23@ 100 K



Figure 6.13 Normalized spectra of ZTC-23 at 100 K illustrate the equal effect of pressure on the position of all the spectral features (top). The peak of the maximum intensity in each spectrum is plotted versus the logarithmic pressure scale to depict this relationship (bottom).
By itself, the direction of the pressure dependence is indicative of whether paramagnetic or diamagnetic effects dominate on the surface of the ZTC-23 pores. At low pressures, the majority of the H₂ population will be surface-adsorbed molecules. The chemical shift in this lower pressure limit is reflective of the susceptibility close to the surfaces. Being limited by surface saturation, the relative density of adsorbed molecules will decrease as the pressure increases, compared to the density of those within the pores but excluded from the surface monolayer. The surface effects will diminish in favor of the susceptibility elsewhere in the pores. The trend in Figure 6.13 goes from diamagnetic to paramagnetic as the pressure increases, which suggests that the RCE dictates the chemical shift of near-surface molecules. Yet the paramagnetic behavior attributed to the buckybowls is localized, indicating, more likely, the phenomenon is occurring along the three-dimensional zigzag-like edges.

Future investigations of the magnetic properties of graphene/graphite edge sites would be well-suited for study by gaseous NMR. Currently, there is an abundance of theories about edge site phenomena, but progress in this area is being hindered by the lack of experimental evidence.²⁹ In addition, the predominant method for studying magnetization in materials is limited to measuring the bulk properties of a sample. Since the molecules employed in gaseous and liquid NMR essentially act as localized probes of the magnetic field on a sub-nanometer scale, it is curious that there has been no previous work similar to the present experiment. The preliminary results presented here demonstrate that NMR can potentially play in important role in understanding ferromagnetic behavior in carbon materials.

126

6.10 Pore Blocking via Exposure to Atmosphere at 290 K

In order to identify to which phases of ZTC-23 Peaks A, B, C, and E correspond, it is necessary to know more about the pores. An experimentally convenient way to further explore this multi-phase pore structure is to expose the baked sample to the ambient atmosphere. This will allow the sample to adsorb larger molecules with stronger affinities for the graphitic surfaces (N₂, O₂, and H₂O vapor). If the connecting pore necks are narrow enough, it is possible that these species will restrict H₂ from fully accessing the interior pores spaces. With the exception of a small contribution from water vapor, the proton background should have the same spectral intensity. To account for any possible differences between experiments in the tuning of the probe that might affect the amplitude of the NMR signal, all spectra in this part of the experiment was scaled such that their backgrounds matched that of the RT isotherm spectra of the baked sample.

The diminished intensity of certain peaks in the exposed spectra (Figure 6.14) is a direct result of the larger atmospheric molecules strongly adsorbing at the pore entrances and within the pores, sharply decreasing the H₂ molecules' access to the interior of those particular grains. By subtracting the exposed spectra from the baked spectra, approximate spectra of the blocked pores can be deduced (Figure 6.15). It is readily observed that the pores associated with Peaks B and C are most efficiently blocked. Peak D is not affected by exposure to the atmosphere, further supporting that this is the gaseous intergranular H₂. Peaks A and E seem to be virtually unaffected as well, particularly at higher pressures. If not for the T_1 and T_2 measurements, these peaks easily could have been mistaken for intergranular H₂. By simply blocking the pores and

observing the resulting spectral changes, the final key pieces of information needed for identifying the phases in the material is at hand.



Figure 6.14 Comparison of the isothermal spectra at 290 K of the baked sample and of the sample exposed to the atmosphere (to scale). The molecules adsorbed from the atmosphere clearly block access to a large number of pores. Peak D is unaffected as expected. Peaks A and E also are unaffected, which is not expected.



Figure 6.15 Evolution of the peaks excluded from the spectra by pore blockage.

6.11 Correlating Multiple Peaks with Multiple Phases

There are three primary phases, each one associated with a zone in the horizontal tube oven, identified as 1, 6, and 11 corresponding to their respective positions in Figure 6.9. In order to assess the potential effects of insufficient synthesis temperatures, literature that considers the separate effects of polymerization of the furfuryl alcohol (150 °C), the CVD step (700 °C) and the carbonizing heat treatment (900 °C) is referenced.¹⁴

Phase 1 is associated with Peak E. The temperatures at Position 1 varied the most from the set temperature of the furnace. It experienced consistently lower temperatures, off by 40 °C at 150 °C and 90 °C at both 700 °C and 900 °C. At each step in the sample preparation process it was the most adversely affected. Thus, it was most likely not to have reacted properly at any of these points.

The proximity of its chemical shift to that of Peak D suggests that it can easily exchange with the intergranular H₂ indicating a high percentage of mesopores. This property is exhibited in ZTCs prepared without the polymerized furfuryl alcohol step.¹⁴ This is also consistent with the results of the pore-blocking experiment, in that it has malformed pore structures with large voids that cannot be effectively blocked by surface molecules. Poorly formed structure could also be associated with failure in the CVD and carbonization steps.¹⁴

The shift of Peak E is upfield from Peak D, implying that the RCE is present but the structure responsible for the paramagnetic properties of ZTC-23 is not. It is assumed that less order is required of the chemical structure to produce the RCE than the paramagnetism. Also, the relative intensity of Peak E is smaller than the other major spectral features. If the zeolite channels are ineffectively filled during each step, the overall result will be the smallest amount of that phase being produced. The observed properties of Peak E are most consistent with the inefficient synthesis. This is to be expected of Phase 1.

Peaks B and C are correlated with Phase 6. In general, the temperature of this region was very close to what is required for proper replication of P7(2)-H. It is predicted that Peaks B and C, along with Peak D, will be the NMR spectral features observed in a single-phase sample. Their chemical shifts point toward the presence of both structures that produce paramagnetism and the RCE, indicating a balanced and consistent chemical structure. The pore-blocking results show that these peaks have the highest structural order within the sample, dually supported by the ability of the pores to be clogged by atmospheric species and also their approximate line-shapes in Figure 6.15. It is likely that the two peaks are actually one powder pattern, which was predicted in Section 6.4 for particles, such as P7(2)-H, that have high long-range order in their structures. These peaks also have the highest relative intensities, which is consistent with the very high microporosity that is only produced when all three preparation steps are maximally effective.¹⁴ Peaks B and C exhibit all the properties of a properly made sample that must be associated with the accurate synthesis temperatures of Phase 6.

Peak A arises from H₂ in Phase 11, in general representing a mixture of the successes and failures of Phases 1 and 6. During the polymerization step, Phase 11's temperature was close to the proper temperature ($\Delta T < 10$ °C). It is assumed that the variations are due to deviations in the temperature during the CVD and carbonization

steps. The unblocked pores associated with Peak A in Section 6.10 can be attributed to incomplete zeolite channel filling in either of the later two steps, as was mentioned earlier in the Peak E/Phase 1 discussion. In many aspects, the phases that could be assigned to Peaks A and E seem ambiguous, especially since they are both expected to correlate to those that are incomplete. However, it is the relative intensity and chemical shift of Peak A that leads to its association with Phase 11 and not Phase 1. The intermediate conditions of Phase 11 result in it constituting a larger proportion of the overall sample compared to Phase 1. This is reflected by the relative intensities of Peaks A and E, respectively. The higher order of chemical structure thought to be necessary for the strong paramagnetic effect is more likely to be produced in Phase 11 than Phase 1, leading to the association of the former with Peak A. However, it is not clear what would cause Phase 11 to produce an even more paramagnetic pore environment than Phase 6. Peak A has mixed characteristics exhibited by the other three Peaks, consistent with the intermediate deviations in synthesis conditions of Phase 11.

Associating peaks with different phases is not merely an intellectual exercise; these predictions can be experimentally proven or disproven. Single-phase samples representing each of the three phase zones in the tube furnace are currently being prepared for NMR and XRD characterization. It will be rather interesting to see how accurately the interpretation of the NMR data has predicted the structure of each phase.

The 9.7 MPa component of Figure 6.15 is combined with Peak D to produce a prediction for the 290 K, 9.7 MPa spectrum of a homogenous Phase 6 sample (Figure 6.16). Peaks B and C (peak "Phase 6") are expected to be noticeably narrower than indicated here and will, therefore, be more distinct in the real spectrum. Also, Phase 6

will have a larger relative intensity compared to Peak D, since Phases 1 and 11 will be absent.



Figure 6.16 Predicted spectrum of Phase 6 at 290 K and 9.7 MPa. The peak associated with H_2 within Phase 6 is expected to be narrower and have greater relative intensity than shown here.

6.12 H₂ Displacement of O₂ at 290 K

When the pressure was held constant for several hours during the pore-blocking experiment, a slight time-dependent decrease in the overall chemical shift was observed, naturally prompting a more focused investigation into what might cause this to occur. In general, the exposed spectra would appear downfield from the baked spectra and then slowly drift upfield with time. A time-dependent phenomenon observed for the chemical shift should be correlated with a dynamic process. It is assumed that the adsorbed atmospheric molecules can eventually be displaced by hydrogen molecules at sufficient H_2 pressures. Just such a dynamic process could explain the change in chemical shift.



Figure 6.17 Time evolution of the spectra of the exposed ZTC-23 at 9.6 MPa and 290 K. Note the initial loss in intensity of Peak D between the first two data points in addition to the upfield trend.

To test this correlation, an experiment was performed that focused on the timedependence of the spectra at constant temperature and pressure. A second batch of ZTC-23 was loaded into the probe and baked under vacuum as before. After checking the repeatability of the RT isotherm measurement, the sample was exposed to the atmosphere for approximately 2 hours. The system was then closed off and quickly pressurized to 9.6 MPa and initial spectrum was taken as soon as the pressure had stabilized (< 20 s). Spectra were then taken periodically over the next 1000 minutes. To prevent excessive smearing of the spectra due to physical changes during the acquisition time, this parameter was limited to 100 seconds for each data point. The time evolution of the spectra is shown in Figure 6.17. The time evolution of the integrated intensity and of the chemical shift of the dominant peak are plotted in Figures 6.18 and 6.19, respectively.

In Figure 6.17, an immediate drop in the intensity of Peak D is observed, accompanied by an increase in the other components. This is conclusive evidence that Peak D is the H_2 outside of the sample. Initially, very little hydrogen was found in the sample due to the pore blockage, so the initial spectra must represent the intergranular space to which the H_2 is confined until some pores have been flushed at least partially of the larger molecules. After just 10 minutes, a significant amount of exchange with the pores had already begun. The dynamics of this process were not fully appreciated until the evolution of the intensity was plotted (Figure 6.18), where a very clear trend was seen. The data can be treated as an exponential recovery, which is quite a reasonable physical representation of the blocked pores being opened up with time. Such a fit shows a 15% increase in the total spectra with a characteristic recovery time of 125 minutes. The magnitude of the recovered intensity corresponds to a rather large percent of the pores, as the spectra is dominated by integranular H_2 in low-density materials.



Figure 6.18 Time evolution of the total integrated intensity of the exposed sample. There was a \sim 15% increase of the period of 1000 minutes. In the inset, the increase is modeled as an exponential recovery process with a characteristic time of 125 minutes.

The chemical shift of the entire spectrum had very similar recovery dynamics as observed for the total intensity (Figure 6.19). In fact, their recovery time constants are virtually indistinguishable from each other ($\tau_{\delta} = 126$ minutes). The correlation between the two lies in the paramagnetic susceptiblity of molecular oxygen, as it is sure to be adsorbed from the atmosphere in significant quantities. None of the other expected atmospheric adsorbates have paramagnetic properties that could produce such a downfield shift.



Figure 6.19 Time evolution of the chemical shift of the spectra of the exposed sample, fit with an exponential recovery curve with a characteristic time of 126 minutes, identical within error to the value for the recovery of the intensity.

The shift of the spectrum can be considered a measure of the concentration of O_2 within the sample with which the H_2 is interacting. Therefore, what is being observed is the high pressure H_2 flushing out the oxygen (along with the other adsorbates) with a characteristic time of ~125 minutes at 9.6 MPa. This results in decreasing O_2 concentrations—manifested in the upfield shift of the spectra—concurrent with previously blocked nanospaces becoming accessible again. This is evidenced by the increase in total intensity.

6.13 Calibration of the NMR Intensity

Properly converting the NMR spectral intensity into units of mass or number of H_2 is not a straightforward task. In B-Doped Graphite, a capillary of known volume was used. In the Activated PEEK, the conversion factor α was taken to be constant at RT. This allowed the 100 K conversion factor β to be calculated via the intensities of Peak A, where the H_2 was gas-like in a constant volume at both temperatures. A capillary could not be used here due to packing issues associated with the low density of the sample. Without a well-resolved intergranular peak, the latter procedure was not an option. Since ZTC-23 contains a significant amount of protons, it was postulated that the background could serve as a means of calibrating the spectra, even if significant changes in tuning occurred.

There are two challenges associated with this method. The intensity of the spectral background does not usually correspond to the number of protons in the material because its FID signal will have already significantly relaxed (decayed) before the first data point is acquired due to an experimentally necessary dead time. The integrated intensity of the Fourier-transformed spectra of any FID signal is directly proportional to its value at this initial data point, so any truncation here will result in a FT spectral feature, which is reduced accordingly. In general, the relaxation of the H₂ introduced into the system is slow enough such that its FID signal does not experience any significant reduction in intensity during the dead-time and thus truncation is not an issue.

The fast-relaxing background is normally attributed to dipolar interactions, which are expected to have a Gaussian line-shape in the FID.³⁶ Thus, it is possible to fit the first

several data points to recover the initial value at the true t = 0 of the physical system. Rigorous error analysis of the present data indicates that the error associated with this method is 10-15%, so it is not expected to introduce abnormally large deviations in the data.

The dead time truncation problem for the fast-relaxing BG can be overcome by finding the ratio of the intensity of the experimental BG spectra to its real value. This value, θ_{BG} , can be calculated from the ratio of the first FID data point and the Gaussian intensity at t = 0 of the physical system. The Gaussian intensity at t = 0 can be determined by subtracting an approximation of any slow-relaxing component in the BG from the first three to five FID data points, and then fitting those points with a Gaussian curve. If the intensity of the BG differs between two runs with the same amount of sample present, they can be related to each other since the real intensity of the BG remains constant in both cases and can be calculated for both runs via their respective θ_{BG} values. This information can be used to attain a value for α in units of wt% if the mass fraction of H, w_H , in the sample is known for any given experiment with a significant proton background:

$$\alpha_n = \frac{w_H \theta_{BG}}{I_n^{BG}} \tag{6-1}$$

Here the *n* subscript denotes the specific experiment to which the calculation applies, and I_n^{BG} is the integrated intensity of the relevant spectral background.

This introduces the second issue with this method of calibration: obtaining a reliable value for w_H . In the case of ZTC-23 and similar materials, it is difficult to get a

precise value. It was measured to be 1 wt% in P7(H)-2,¹ however, with an implied uncertainty of \pm 0.5 wt%, it is possible to have an error of 50%. In other similar samples, w_H was found to be 2-3 wt%.¹⁴ A more direct measurement is needed; something similar to the capillary method would allow for a much more accurate value to be obtained. Unfortunately, a capillary complicates the entire NMR measurement in this case, as was mentioned above. However, this issue may be overcome if a large void of known volume exists in the sample space, as was the case in Section 6.7.

The conversion factor α can be determined via the large void in the sample that is acting as a capillary. Along with θ_{BG} and I_n^{BG} —both of which can be readily determined— w_H can be calculated by inverting eq. 6-1. The basic principle of the capillary method is to have a region in the sample holder with a known volume that is large enough for the H₂ to act as an ideal gas, and a spectral component that can be isolated by chemical shift and/or relaxation times. The large void discussed in Section 6.7 fits these requirements. Its spectral intensity was determined by fitting the long 2τ spectrum of the T_2 measurement with a powder pattern (previously acquired with 10 MPa of H₂ in the empty sapphire tube) and then scaled per its T_2 value to $2\tau \sim 0$, its contribution to the regular FID-derived spectrum. The corresponding value for m_H , the mass of the H₂ in the void, was then calculated from the ideal gas law and its measured volume, giving an experimental value for α_{void} . As mentioned, the inverted form of eq. 6-1 allows for easy calculation of w_H , which was found to be 1.9 ±0.3 wt% in ZTC-23, a significantly more accurate value than that found by elemental analysis of P7(H)-2. 6.14 The Calibrated 100 K Isotherm and Its Implications for P7(2)-H

One of the main purposes of this study was to reproduce P7(2)-H and verify the enhancement observed in its uptake at 34 MPa and RT. Pressures higher than 10 MPa are unattainable with the current experimental setup, so the adsorption of H₂ on ZTC-23 was studied at 100 K, where it is easier to characterize the adsorption behavior of binding energies in the range of 4-10 kJ mol⁻¹.

A good indicator of binding energy—the isosteric heat of adsorption—of P7(2)-H varies between 6 and 8 kJ mol⁻¹(depending on the surface coverage).¹ The isotherm at 100 K can be fit with a linear free gas term and a Langmuir adsorption term (Eq. 2-1), the latter of which can be used to predict the adsorption behavior expected at 34 MPa and 290 K. Comparing this to the published results for P7(2)-H can provide some insight into the whether the uptake is being enhanced by confinement effects in the ZTC nano-cages.

Figure 6.20 shows the spectra of ZTC-23 at 100 K and pressures 1.0 MPa and greater. None of the features saturate at high pressures, a characteristic commonly observed in the Activated Peek samples. Even after the surfaces have been saturated, there must be a considerable free gas population in the immediate vicinity with which it can exchange. For the expected pore diameters (1.0-1.7 nm), a material with a 1-D slit-pore geometry would most certainly exhibit saturation under these conditions. It appears that this is not the case for a 3-D super-cage/neck geometry, and it may be this higher-order topology that accounts for the deviation from the uptake predicted by the surface area of P7(2)-H.



Figure 6.20 The 100 K spectral evolution of H_2 in ZTC-23 at 1.0 MPa and above, showing that none of the features show signs of saturation.

A calibrated 100 K isotherm is achieved by first integrating the intensity of the spectrum for each pressure. For the 100 K isotherm, α_{100K} is calculated to be 3.78e-8 ±0.76e-8 wt% [1k scans]⁻¹. This value was used to calibrate the integrated intensities that were plotted against pressure to obtain an isotherm with units of wt% (Figure 6.21). When the isotherm is fit with a linear term and a Langmuir adsorption term, the Langmuir component gives a binding energy of 5.2 kJ mol⁻¹. This is lower than the isosteric heat of adsorption for P7(2)-H, but well within the range of binding energies expected for H₂ on a graphitic surface. Plotting the Langmuir fit (Figure 6.21) reveals a population that saturates around 3.5 MPa; no such saturation is observed in the spectra as noted above. The H₂ uptake of the saturated surface is 6.5 wt%, which, with $\sigma_{H2} = 0.16$ nm², corresponds to a surface area of 3131 ± 490 m² g⁻¹, a value comparable to the BET value of 3417 m² g⁻¹.



Figure 6.21 The calibrated 100 K isotherm gives a saturation uptake value of 6.5 wt%.

The results of the calibrated 100 K isotherm are compared to the calibrated 290 K isotherm derived from the spectra in Section 6.2 to check for consistency before extrapolating to 34 MPa. In order to predict behavior at higher temperatures, the linear and Langmuir terms determined by fitting the 100 K isotherm were replotted with their temperature adjusted from 100 K to 290 K. The calibrated experimental RT isotherm is plotted in Figure 6.22 along with the predicted total, linear, and adsorbed components as

indicated by the 100 K isotherm. Within the combined error of the separate calibrating processes at each temperature, ± 0.9 wt%, the total components are in agreement.



Figure 6.22 Predicted isotherm at 290 K and its components based on the fit of the 100 K isotherm, compared to the corresponding calibrated experimental values.



Figure 6.23 Comparison of the high pressure isotherm of P7(2)-H to the predicted uptake of ZTC-23 at 290 K reveals an excellent fit of the data (adapted from Figure 8 in Ref. 1, reprinted with permission). Despite not exactly replicating the structure of P7(2)-H, ZTC-23 appears to be nearly identical in terms of H_2 storage capacity and binding energy.

Finally, the extrapolation of the 100 K prediction of the adsorbed component is extended to 35 MPa at 290 K and compared to the isotherm of P7(2)-H taken under similar conditions (Figure 6.23). The ZTC-23 prediction matches the P7(2)-H data very closely. The ZTC-23 prediction has not been altered or tweaked to match the P7(2)-H data in the least. Given that ZTC-23 is known not to be an exact replication of P7(2)-H, such similar uptake properties were unexpected. As previously noted in the P7(2)-H study,¹ this confirms that the long-range order of the structure is not a dominant factor in the uptake process.

The agreement of the data does not support the idea of enhanced uptake due to confinement; however, the current data alone is not enough to conclusively disprove it either. On one hand, Figure 6.23 indicates that the uptake isotherm of P7(2)-H was an accurate measurement. On the other hand, it implies that its entire uptake behavior can be accounted for by Langmuir adsorption on the surface. In the Langmuir model, the uptake is entirely determined by the surface area and the binding energy. Since P7(2)-H has a BET surface area over 10% larger than that measured for ZTC-23, its increase should be roughly 10% larger as well—before any uptake-enhancing mechanisms are taken into account. There is no indication in the ZTC-23 results that enhanced confinement is a real phenomenon in ZTCs.

While a multi-phase sample has many properties, the different phases make it difficult to independently track their corresponding spectral components. Also, it is not ideal in the sense that it is not a completely accurate replication of P7(2)-H. Additionally, the Langmuir model is not the most sophisticated theory; its implicit assumption of a coverage-independent binding energy may lead to oversimplificaton of a complex system. Most importantly, inferences were made from an extrapolation; until direct observations at 34 MPa are experimentally possible, these results should be used primarily to guide future research into the matter.

A development of a pressure system that can achieve pressures near 70 MPa is currently underway. Extra precautionary steps in the preparation of the sample should ensure that forthcoming materials can accurately duplicate the structure of P7(2)-H. With the experience gained from this study guiding this expected future work, thouroughly reliable conclusions should be attainable.

6.15 ZTC Conclusions

The H₂ uptake and structure of a microporous carbon with a high degree of structural order has been characterized by the NMR method for the first time. The structural regularity, high surface area, and reported enhanced high pressure uptake of P7(2)-H, a ZTC synthesized and charcterized by Nishihara, et al., was hoped to be replicated in ZTC-23 for independent measurements. Although, no long-range order was confirmed in ZTC-23 by XRD, several spectral features appeared to have a powder pattern line-shape indicating that irregular long-range order was present. A spectrum with more than four peaks and an intergranular peak (Peak D) shifted upfield from the rest of features was observed. This was completely opposite of past observations where only two spectral features were present and the one downfield consistently represented the intergranular H₂.

ZTC-23 was found to have very different magnetic susceptibilities within and outside of its pores. This was consistent with ferromagnetic and paramagnetic properties observed at low temperatures in similar ZTCs. The entire spectrum was observed as shifting with pressure at 100 K and is understood to arise similarly from the pressure dependent distribution of the H_2 within the magnetic susceptibility gradients within the nanopores. The trend of this behavior from diamagnetic to paramagnetic with increasing pressure indicated that the paramagnetic phenomenon was located at the edges of the buckybowls and not on the surface. This implied that topological defects due to its tripentagonal and curved graphene structure was not the source of paramagnetic behavior. By exposing the sample to the atmosphere, dynamic flushing of the adsorbed species—namely O_2 —was dually observed by NMR, with both processes having a characteristic recovery time of 125 minutes. The spectra gave direct evidence that atmospheric species can efficiently block the pores of the phases associated with Peaks B and C, indicating the presence of well-formed pore structure. Peaks A and E experienced little pore blockage and are thought to be partially-graphitized phases that did not fully acquire the pore structure of the parent zeolite.

Spectral T_1 and T_2 relaxation measurements predicted that the material was actually a composite with multiple phases. This was confirmed upon inspection of the synthesizing conditions and XRD measurements. Based on the information determined about chemical shift mechanisms and pore structures, Peaks A, B, C, and E, were correlated with phases produced in different regions of a horizontal tube furnace that had a thermal profile. Peaks B and C were intrepreted as a single feature, which corresponded to a phase that accurately simulated P7(2)-H and was used to predict the spectra of a single-phase material. This is should be experimentally confirmed in the near future.

A temporary void in the sample volume allowed for calibration of the NMR intensity. By measuring the proton background in the spectra, it was determined that ZTC-23 contained 1.9 wt% of hydrogen in its structure. Langmuir adsorption with $E_b = 5.2$ kJ mol⁻¹ and saturation H₂ uptake of 6.5 wt% was seen in the calibrated isotherm at 100 K. The isotherm fit at 100 K was extrapolated up to 35 MPa at T = 290 K for comparison with the isotherm of P7(2)-H. The calibrations at the two temperatures for which NMR data was acquired were compared and they were in agreement within the

error of the calibration process. The isothermal prediction for ZTC-23 at 290 K was in agreement with the P7(2)-H data, confirming that long-range order was not a major determinant of uptake. The conclusion from the P7(2)-H study was that its 2.2 wt% uptake at 34 MPa could not have been due to surface saturation alone and therefore some confinement mechanism must have been present. However, the NMR study of ZTC-23 could not support this claim, especially since higher uptake would have been expected from the higher surface area of P7(2)-H from Langmuir adsorption alone. A predicted measurement under different conditions, however, does not conclusively disprove the theory of enhanced uptake in the nanocages of ZTCs. Further studies with extended pressure capabilities of single-phase samples with confirmed long-range order are needed to discern the potential for ZTCs in vehicular hydrogen storage.

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CHAPTER SEVEN

CONCLUSIONS AND FUTURE WORK

A variety of nanometer scaled materials have been studied by NMR. A large bulk of the relevant work was establishing a suite of both standard NMR techniques along with novel approaches (first reported here), which enabled the most robust characterization of the samples. Along with the establishment of methodological tools, considerable effort has been put into the interpretation of the spectral behaviors commonly encountered in such investigations. While the primary goal of the study was to investigate properties of these materials that directly related to the application of onboard hydrogen storage, many other topics were encountered along the way. Methods, which have been first introduced here, may yet find a place in broader fields.

The most scientifically valuable of these methods was developed in response to the observation of the chemical shift exhibiting a dependence upon the pressure at low temperatures. This was seen in two samples: Activated PEEK and a highly-ordered zeolite-templated carbon. In the first case, this behavior was related to the diameter and geometry of the pore and was useful for studying just that. In the latter case, it enabled some interesting conclusions regarding ferromagnetic and paramagnetic phenomena in the graphene-like material. Work is currently underway with collaborators at Wake Forest University to better understand the relationship between pore dimensions and the chemical shift via Converse-NMR calculations. It is expected that a more quantitative approach will expand the pressure-chemical relationship into a potentially commercializable method of acquiring pore size distributions in carbon-based nanomaterials, with a continued focus on the hydrogen storage community.

Recent developments have indicated that NMR has significant potential in carbon-based ferromagnetic studies. The pressure-chemical shift is at the heart of these methods, which are just in their infant stages. Given that most magnetization measurements observe only a material's bulk properties, the highly localized subnanometer scale that NMR can probe makes it a promising method for studying novel magnetic materials. The future looks bright; the future looks promising; the future looks exciting for the scientific endeavors to come that will be based on the work presented here.