**EFFECTS OF SURFACE CHEMISTRY
ON THE POROUS STRUCTURE OF COAL**

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ABSTRACT

In this report, ^{129}Xe nuclear magnetic resonance spectroscopy of xenon gas adsorbed in coal is used to describe some poorly understood features of coal microporous structure, particularly in establishing that a connected network exists, the type of connectivity, and its changes with the rank of coal. Micropore size scale and distribution are also considered. Two methods are developed which are new and versatile tools for the investigation of porous structure. Both utilize xenon gas that is in motion, while undergoing diffusion or exchange in coal, to describe the connectivity of the micropore structure of coal. Time tracking of the adsorption process by NMR, selective saturation, and saturation transfer techniques were used to obtain new information on the coal rank dependence of porous structure. In addition, an existing ^{129}Xe chemical shift-pore diameter model was used to calculate micropore diameters for coals, as well as for a microporous carbon, before and after pore-size alteration.

In the initial study performed, straightforward ^{129}Xe NMR spectra at equilibrium xenon adsorption at a series of pressures were acquired for a rank-varied set of six coals. Acquisition of the NMR signal as an echo was tested and found to improve spectral quality. The spectra were used to calculate micropore diameters for the six coals. These range from 5.6 to 7.5 Å and exhibit a minimum value for the intermediate coal rank. The smallest pores occur in coals of about 82-85% carbon; at both lower and higher coal ranks, the average micropore size tends to be larger. The changes in the spectra with coal rank and surface area were explored. Signal linewidths were found to decrease with increasing coal rank and were interpreted in terms of increasing chemical or physical homogeneity of the coal as rank increases. The packing density of powdered coal was found to alter the spectral appearance in a high volatile bituminous coal, which is preliminary evidence that exchange affects the chemical shift of xenon in this coal.

Coal microporosity can be better described without the ambiguities involved in interpreting the meaning of chemical shift alone, by using NMR methods that are sensitive to the motion of xenon atoms undergoing diffusion or exchange. The process of xenon adsorption up to equilibrium adsorption was monitored by acquiring ^{129}Xe NMR spectra as a function of the adsorption time. Tracking of changes in ^{129}Xe NMR

spectra during adsorption reveals whether xenon occupies different pore spaces during the approach to equilibrium than at equilibrium, and indicates whether xenon dissolves in the solid matrix before reaching the porosity. Thus, this method gives information on the route into the internal porosity from the external surface. For two particle sizes of an anthracite, equilibrium is achieved faster in the smaller particles than in the larger, but in either size fraction the equilibration time is slower than for the microporous carbon. This is an indication that the anthracite pore network is constricted. It is also consistent with more pore openings, or larger porosity due to fracture, in the smaller particles. The 'external' xenon signal, thought to originate from xenon outside the external surface or in macropores, is observed only for the larger particle size; it loses intensity as the signal from internally-adsorbed xenon increases. No intermediate signal suggestive of dissolution in the solid matrix is observed prior to equilibrium, which is consistent with a pore structure that is open to the external surface.

Selective presaturation and saturation transfer techniques were adapted in a unique way to the problem of pore connectivity and tested for use on xenon in coal. Selective low power presaturation of the adsorbed xenon signal for four coals produces a hole-burning effect in the spectra indicating that the signal is composed of a series of overlapped chemical shifts. The overlapped chemical shifts indicate in turn that there is a distribution of adsorption sites for xenon in coal that are not generally resolved as separate NMR signals. This distribution of adsorption sites is thought to reflect a distribution of pore sizes; a distribution of pore wall chemistry may also contribute to the dispersion of xenon chemical shift. Saturation transfer to the entire adsorbed xenon signal, and then to the external signal from xenon that is most likely in large pore spaces, is observed as presaturation time is increased. The saturation transfer is accomplished by the movement of saturated xenon atoms from the internal microporosity to the large pores, and occurs significantly faster in two low-rank coals than in two higher-rank coals. This indicates that the microporosity is more open to large pore regions, and is less constricted, in low-rank than in high-rank coals.

The time required for the equilibration of xenon in the bulk coal sample in the NMR tube, which was observed in the adsorption tracking experiments, is on the scale of hours. This greatly exceeds the time frame (ms to s) in which xenon adsorbed in the microporosity is observed to physically exchange with the xenon population from which the external gas signal arises. It is suggested that the external gas signal which is observed in spectra with 2-3 s recycle times arises from xenon adsorbed in macropores,

and that the exchange process observed in the presaturation/saturation transfer experiments is one that occurs across microporous domains within the coal particles, that are flanked by larger pores.

The overall picture of coal porosity that emerges from these experiments is that the porosity in coal is open and that it constitutes a constricted network. The degree of constriction or tortuosity in the micropore network is higher in coals containing over approximately 88% carbon. The microporosity in low-rank coals is quite accessible to the larger pores, as would occur in a continuum pore structure with larger pores providing the route of access to the micropores from the particle exterior. For higher-rank coals (over 88% carbon), the microporosity is much more isolated from larger pores; it is open to them via constricted, open micropores. There are indications that an anthracite has more open pore connectivity than a lower-rank medium volatile bituminous coal, and that smaller-particle-size anthracite has less constrictions in its porosity than larger particle size, which may be due to a greater number of external-surface pore openings. In addition, the absence of an external gas signal for xenon in small anthracite particles indicates that these may have fewer large pores or fractures than large particles.

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INTRODUCTION:

OVERVIEW AND STATEMENT OF PROBLEM

On the whole, there is wide acceptance of the following general model for the porous structure of coal; that "coals contain an interconnected pore network of high surface area, the slit- shaped pores having constricted openings of molecular dimensions...[and] coals contain both open and closed porosity" (Mahajan, 1991). This model is taken from the combined results of many analytical methods such as gas adsorption, x-ray diffraction, and mercury porosimetry, which have been applied to elucidating coal physical structure. Coal presents a formidable analytical challenge due to its irregularity and heterogeneity. No single analytical method is able, as yet, to present a full picture of coal physical structure. The micropore structure is additionally difficult to assess because these pores are less than 20Å in diameter - a size scale so small that many experimental methods are unable to evaluate them.

One method that is capable of assessing some properties of microporosity in coal is gas adsorption. A phenomenon that is characteristic of coal in relation to gas adsorption, and one which is quite significant to the interpretation of coal porous structure, is molecular sieving. Molecular sieving is the large difference in uptake by coal of gases having similar molecular dimensions. There are several critical reviews on the subject (Marsh, 1987; Mahajan, 1991). Molecular sieving effects by coal are considered evidence for the existence of microporosity in coal; paradoxically, these effects are also the basis of conflicting interpretations of whether the micropores are closed or part of an open network.

The primary area of conflict is in identifying the process by which one adsorbate may be excluded while another of very similar size is adsorbed. There are three possible scenarios; the pore is open and has a size close to that of the adsorbate molecules, the pore is open but smaller than the adsorbate molecules, or the pore is closed. The mechanism by which an adsorbate may be excluded from a pore opening of similar size is referred to as activated diffusion. There is an energy barrier to diffusion,

that is, diffusion is activated, through spaces of molecular dimensions, and its rate increases with increasing temperature, in contrast to most diffusion processes which are weakly dependent on temperature. This is supported by extensive experimental evidence that the rate of adsorption of gases in microporous materials is temperature-dependent (Maggs, 1958; Marsh, 1987). The mechanism by which an adsorbate can enter a too-small or closed pore, if at all, is through imbibition in the solid coal. In this case, it is not size but solubility in the coal that determines the rate of adsorption of a gas.

Larsen et al. (1995) found large differences in the uptake by coals of a series of adsorbates of very similar molecular area. They contend that the magnitude of this molecular sieving effect, along with the high fractal dimensionality of coal as determined by small-angle x-ray scattering, is inconsistent with an interconnected, bottlenecked micropore network model. Rather, they postulated that pores exist as isolated 'bubbles' in the solid matrix, and are reached by gas diffusion through the solid. This is a controversial conclusion. According to Walker and Mahajan (1993), these (1995) results and other results of the same group (Larsen and Wernett, 1988; Larsen and Wernett, 1992) do not eliminate activated diffusion, as opposed to closed porosity, as a cause of molecular sieving. Despite the quality of the reasoning that has been applied to this issue, conflict in this area persists. In order to interpret coal structure, there needs to be a way to directly show the difference in the route taken by a gas to reach its equilibrium adsorption site in the pore.

The method of ^{129}Xe NMR spectroscopy is extremely well suited to resolving the question of whether coal porosity is open or closed, as well as to the general problem of defining the connectivity of coal porous structure. The chemical shift of the ^{129}Xe NMR signal is sensitive to the dimensional and chemical features of its environment in a porous adsorbent. By the number and chemical shift range of the NMR signals, the spectra give an indication of what type of solid structure(s) xenon is located in when adsorbed in a porous solid. The gas in effect reports back information on its location within the range of void sizes in the solid, or even the solid matrix. This kind of information is impossible to determine by gas uptake measurements alone. Such ^{129}Xe NMR spectra can be utilized in several ways.

A direct correspondence of ^{129}Xe chemical shift to pore dimensions has been the subject of considerable research (Demarquay and Fraissard, 1987; Ripmeester et

al., 1988; Derouane and Nagy, 1987). The models that have been proposed have had positive results in some cases but nevertheless conflict with each other; in addition, they are by no means widely applicable. Many aspects of interpretation of ^{129}Xe NMR spectra are still being developed (DeDios and Jameson, 1994; Jameson et al., 1992). As a preliminary study, the method of Demarquay and Fraissard (1987) for determining micropore diameter from ^{129}Xe NMR spectra was applied to a rank-varied group of coals. This study also serves to identify the most workable experimental conditions to perform ^{129}Xe NMR of coal, and provides an overview of how the features of ^{129}Xe NMR spectra change with coal rank and with surface area. The pore diameter calculation technique is also used to determine whether it indicates pore size alteration in a microporous carbon subjected to oxygen chemisorption and desorption. This material is a more homogeneous carbonaceous solid than coal. The processes of oxygen chemisorption and desorption are known to be effective and controlled ways of modifying the diameter of its pores.

The ^{129}Xe chemical shift alone is insufficient to characterize pore structure, and further methods are developed to exploit ^{129}Xe NMR from a different perspective: that the NMR signals not only distinguish xenon populations adsorbed on physically or chemically different solid structural features; they do so while the gas is undergoing diffusion or exchange. Information can be obtained by NMR from the gas as it actively moves in the coal. The NMR signal intensity and chemical shift during diffusion and exchange processes are used to provide information on the *route* to the equilibrium location from outside the particle. Two ways in which ^{129}Xe NMR can provide information on the route into the internal porosity of coal are developed.

Observation of the NMR signal in a series of spectra during the adsorption process was performed on two particle sizes of an anthracite and on the microporous carbon. The time dependence of chemical shift and linewidth was compared to the time dependence of the pressure drop during adsorption. This has the dual purpose of testing whether features of the NMR spectra change differently (and thus provide different information from) the change in uptake, and giving specific information about the adsorption behavior of anthracite.

Selective presaturation and saturation transfer methods are developed and applied to four coals. Presaturation conditions resulting in hole-burning in the adsorbed xenon NMR signal were explored. Relative rates of saturation transfer from the

adsorbed gas signal to the external gas signal are used to identify the time frames of exchange between adsorbed xenon atoms and those that are outside the coal microporosity. The relative rate of xenon exchange for coals of different rank gives new information on how microporosity is connected to larger porosity within solid coal, and how the connectivity changes with coal rank.

Chapter 1

REVIEW OF ANALYTICAL METHODS TO ASSESS THE POROUS STRUCTURE OF COALS

1.1. Introduction

Coal is a heterogeneous organic rock formed from buried plant material subjected to varying degrees of heat and pressure as a result of burial. It is heterogeneous both macroscopically and microscopically. The macroscopically different components are classified as lithotypes. The microscopically distinguishable components are classified as macerals, which usually originate from plant tissues. The process by which plant remains are transformed into coal is called coalification. The chemical makeup of coal is highly complex and not amenable to straightforward analysis. Many analytical techniques have been applied, and the results from a broad range of methods are used to piece together an overall chemical structure (Van Krevelen, 1993). Coal has macromolecular character (quasi-polymeric chains and/or polyaromatic sheets depending on the particular type of coal) and there is a non polymeric component of small organic molecules embedded in the polymeric matrix.

The chemical changes that occur as the coalification process progresses are the loss of oxygen and hydrogen from coal constituent molecules, relatively enriching the carbon content, and increasing aromaticity. Coals from different geologic time periods and different geographic areas may differ in composition and physical properties. It is often desirable to classify coals into groups with broadly common properties based on the degree of coalification, referred to as rank. Coal rank is partly determined from the percent carbon in the elemental analysis of the dry, mineral-matter-free coal. Percent carbon increases with increasing coalification. Thus, for example, a high-rank coal of

90% carbon is older and has undergone more extensive chemical change than a low-rank coal of 75% carbon.

The focus of this study is in the area of physical structure of the coal porous network, particularly the microporosity. Porosity may be defined as void regions in a solid. These may be large relative to the atoms making up the solid pore walls, or small void regions of atomic dimensions. Coal pore sizes are classified as macropores ($>200\text{\AA}$), mesopores ($20\text{-}200\text{\AA}$) and micropores ($<20\text{\AA}$). Their geometry and connectivity has not been firmly established, but pores could potentially take a variety of possible geometric shapes such as cylinders, spheres or discs (slits). They may be connected throughout the solid in a network or be isolated. In this chapter the methods typically used to examine porosity in coal will be reviewed and the main results summarized.

1.2. Gas adsorption

In the analysis of solid surfaces by gas adsorption, a solid (adsorbent) is exposed to a gas (adsorbate) under conditions of controlled temperature and pressure. Gas that adsorbs on the solid 'sticks' reversibly to the solid surface through physisorption; gases and temperatures are chosen so that chemical bonds to the solid are not formed. The attractive forces in the adsorption process are London, or dispersion forces, and dipolar attraction in the case of polar gases and/ or solids. The amount of gas that adsorbs on the solid under the experimental conditions used is determined most often by monitoring the pressure differential following adsorption. Analysis of gas adsorption data is the most widely used method for the characterization of porous solids such as coal, and provides a major piece of evidence for the existence of coal microporosity. Three considerations are of particular importance in using gas adsorption to characterize a solid surface:

1. Accessibility of the surface to the gas;
2. Surface adsorption or dissolution;

3. Spatial coverage of the gas molecule, which encompasses both the physical state of the adsorbed gas and its molecular orientation on the surface.

All three of these considerations are currently incompletely understood in the case of microporous solids, despite their importance. Gas adsorption methods are generally a more successful technique to determine the surface area of nonporous, meso-, and macroporous solids; it is with microporous materials that the gas adsorption method is least accurate.

1.2.1. The adsorption isotherm and determination of surface area

The adsorption isotherm is a plot of the amount of gas adsorbed by a known amount of adsorbent material upon exposure to progressively higher relative adsorbate pressures at a fixed temperature. The relative pressure is the ratio of the gas pressure p to its saturation vapor pressure p^0 . The features of the isotherms of microporous and mesoporous materials have been reviewed by Gregg and Sing (1982). The Brunauer, Deming, Demming, and Teller (BDDT) classification method, **Figure 1.1**, lists six general isotherm shape types into which most real isotherms can be grouped.

The type II isotherm is that of a nonporous material. Type IV is characteristic of mesoporous solids. The rarer type III and V isotherms are convex to the pressure axis and indicate a weak gas-solid interaction with a stronger gas-condensed gas interaction, rather than a specific physical pore structure. Type VI isotherms are 'stepped'. Real microporous materials such as coal may have a composite of a type I and a type II isotherm which displays enhanced adsorption at low p/p^0 with a more sloped plateau.

The isotherm of an idealized microporous material is called type I. It shows steep initial uptake at low relative pressures ($p/p^0 \sim .01$), followed by a clearly defined plateau. The steepness of the uptake of gas in the low pressure region is due to enhanced attractive forces which are due to the proximity of the pore walls to each other, and it is referred to as the micropore filling region. Any pore wall has an attractive force that acts on an adsorbate within a certain distance to the wall. In

Figure 1.1. BDDT isotherm shape classes. Both adsorption and desorption branches (when different) are shown. From Gregg and Sing, 1982.

micropores, the highest attractive energy distances overlap within the pore space due to the proximity of the walls. The attractive force is thus greatly enhanced in micropores over flat or more widely spaced pore walls.

1.2.2. The BET equation

The isotherm can be quantitatively interpreted to obtain from it information such as surface area, monolayer capacity, pore volume, and pore size distribution. One of the best known and most widely used models is that developed by Brunauer, Emmett and Teller. The theory of Brunauer et al. (1938) was based on the Langmuir model. It describes adsorption as a process of monolayer coverage of the surface followed by multilayer formation. Dynamic equilibrium, where molecules condense on the surface at the same rate others desorb from it, is assumed. Lateral interactions between neighboring adsorbate molecules are ignored. The form of the BET equation is as follows:

$$p/V(p^0-p) = 1/V_m c + (c-1)p/V_m c p^0 \quad (1)$$

V = experimentally measured volume of gas uptake

p = experimentally measured gas pressure

p^0 = saturation vapor pressure

V_m = volume of gas needed to accomplish monolayer coverage

c = constant

The plot of $p/V(p^0-p)$ vs. (p/p^0) gives a line with slope $(c-1)/V_m c$ and intercept $1/V_m c$.

The region of the isotherm in which a monolayer of adsorbed gas is complete can be identified by a change in the slope of uptake vs. p/p^0 . Knowing how much gas covers the surface in a monolayer, and how much space each gas molecule occupies gives the surface area.

1.2.3. The Dubinin-Radushkevich equation

In practice, for microporous adsorbents the BET equation gives unrealistic surface area values, according to Dubinin et al.(1947), who asserted that the assumption of monolayer/ multilayer coverage does not hold in the micropores. They developed the theory that these pores are volume-filled. The mathematical treatment of the isotherm is based on the Polanyi theory of adsorption, that the adsorption potential equals the free energy of adsorption. Dubinin added the idea that the fractional filling of micropores is proportional to this adsorption potential (A):

$$A = RT\ln(p^0/p) = -\Delta G \quad (2)$$

The Dubinin-Radushkevich (D-R) equation is now generally used to determine micropore volume (from which surface area can be obtained).The equation has the following form:

$$\log W = \log W_o - R^2T^2k/2.303\beta^2 \log^2(p^0/p) \quad (3)$$

W = Volume of gas adsorbed at p
p = experimentally measured pressure
p⁰ = saturation vapor pressure at T
W_o = total micropore volume
R = ideal gas constant
T = temperature, K
β = adsorbate affinity coefficient
k = constant

The D-R equation is used to calculate micropore volume if the plot of log W vs. log²(p⁰/p) is linear. The line has slope - R²T²k/2.303β² and intercept log W_o, from which the micropore volume is obtained. The slope can be related to the micropore size (Dubinin, 1989; Stoeckli et al., 1993).

1.2.4. Nitrogen gas adsorption to determine pore size distribution

Nitrogen gas adsorption isotherms can be used to calculate pore size distributions. Nitrogen adsorption isotherms of coals that show a pattern characteristic of type II or IV (Figure 1) at $p/p^0 < 0.93$ indicate that capillary condensation of nitrogen occurs in the pores. Under these conditions the Kelvin equation is used to calculate a pore radius r corresponding to a point on the isotherm:

$$\ln(p/p^0) = -(2V\gamma\cos\theta)/rRT \quad (4)$$

p = experimentally measured pressure

p^0 = saturation vapor pressure at T

V = molar volume of liquid adsorbate

R = ideal gas constant

T = temperature, K

γ = surface tension

θ = contact angle between liquid and pore wall.

(The assumption is made that the liquid wets the pore walls and $\theta = 0$).

Gan et al. (1972) calculated the pore size distribution of a rank-varied set of coals using mercury porosimetry for the pores over 300 Å, and the nitrogen method for pores 12 to 300 Å. The micropore volume for pores under 12 Å was calculated from the difference between the mercury and nitrogen pore volumes, and the volume open to helium. The results are summarized in **Table 1.1**.

Gan's results indicate that low-rank coals (<75% carbon) are primarily macroporous, medium-rank coals (75-84% carbon) are macro- and mesoporous; and higher-rank coals (85-91% carbon) are primarily microporous. All coals have some macro- and microporosity. Mesoporosity falls off in the upper bituminous coal rank (83-89% carbon) range and reappears in anthracite (> 91% carbon).

Table 1.1. Open pore distributions in coals. V_T is the total pore volume open to helium; V_1 is the pore volume open to mercury (pore diameters $>300 \text{ \AA}$), V_2 is the pore volume from nitrogen adsorption at 77K (pore diameters 12-300 $\text{\AA}$), and V_3 , the micropore volume (pore diameters $<12 \text{ \AA}$), is the pore volume open to helium, but not nitrogen (77K) or mercury. From Gan et al. (1972).

Coal rank	%C (daf)	V_T cm ³ /g	V_1 cm ³ /g (% V_T)	V_2 cm ³ /g (% V_T)	V_3 cm ³ /g (% V_T)
lignite	71.7	0.114	0.088 (77.2)	0.004 (3.5)	0.022 (19.3)
h _v C bituminous	75.5	0.232	0.040 (17.2)	0.122 (52.6)	0.070 (30.2)
h _v B bituminous	76.5	0.105	0.022 (20.9)	0.013 (12.4)	0.070 (66.7)
h _v A bituminous	83.8	0.033	0.017 (51.5)	0.000 (nil)	0.016 (48.5)
MV bituminous	88.3	0.042	0.016 (38.1)	0.000 (nil)	0.026 (61.9)
LV bituminous	89.5	0.052	0.014 (27.0)	0.000 (nil)	0.038 (73.0)
anthracite	90.8	0.076	0.009 (11.9)	0.010 (13.1)	0.057 (75.0)

1.2.5. Experimental conditions to sample the entire surface in coal

The subject of a large body of coal research is whether the gas probes the entire surface or part of it. This issue has been reviewed recently by Mahajan (1991). The microporosity of coal is indicated experimentally by large differences in the amount of surface measured by gases having small differences in their molecular area. Determining which gas and temperature conditions accurately measure the entire surface is very important to identifying a reliable surface area and, by extension, to a reliable estimate of the amount of surface area that is due to micropores.

Coal, like other microporous materials, exhibits a phenomenon called molecular sieving. Molecular sieving is a marked degree of exclusion of certain adsorbate gases from adsorption in the micropores, while other gases close in size to the excluded gas can be adsorbed to a greater extent. This is a characteristic of microporous materials, in which the pore sizes are on the order of 20Å or less. For example, coals will adsorb significantly different amounts of N₂ and CO₂, although these gases are close in size, with diameters of 0.36 and 0.33 nm, respectively. While coals have relatively small surface areas of 2-40 m²/g measured by N₂ adsorption at 77K, their surface area determined by adsorption of CO₂ at room temperature is typically much larger (100-400 m²/g).

Molecular sieving is demonstrated by differences in the accessibility of a gas to particular parts of the surface - but there is both disagreement about and, in some cases, misunderstanding of the causes of this limitation. Molecular sieving may in some cases be due to the size of the pore opening alone, in that the pore is smaller than the adsorbate excluded from it. It may also be due, in other cases, to an energy barrier to diffusion into pores that are actually large enough to admit the adsorbate gas.

Nitrogen adsorption isotherms at 77K give a low surface area for coals, but give higher surface area when adsorption is carried out at higher temperatures. This was first noted by Maggs (1958). As temperature is increased, an increase in the amount of gas adsorbed at a particular pressure indicates that a barrier to N₂ adsorption exists that is overcome by increasing the gas energy (i.e., the temperature). The adsorption isobar for N₂ has a maximum at 196K (Marsh 1987). This temperature

dependence indicates that adsorption of gas into microporous materials is an activated diffusion process. Activated diffusion into coal micropores has been generally recognized since 1956 (Anderson et al., 1956). It complicates the issue of whether the size of the micropore can be inferred from the size of the molecules excluded from them. It is most likely that both size effects and activated diffusion effects are important in experiments that vary adsorbate size and do not critically examine the temperature used for each gas. A study on adsorbate size effects in which adsorption of a series of gases is carried out at temperatures where they each exhibit maximum adsorption would be valuable, but has not been done.

Studies to determine the most appropriate sorption system to completely measure the surface area of coals include that of Walker and Kini (1965) in which krypton at 195K, xenon at 273K and CO₂ at 195 and 298K were compared after analysis by the BET equation. The different surface areas obtained are shown in **Table 1.2**. The higher temperatures for CO₂ adsorption were chosen to determine whether activated diffusion effects could be eliminated. Xe and Kr were also chosen for this reason, as their high critical temperatures (ca. 300K) allow the isotherm to be obtained at relatively high temperatures. However, this also meant that the saturation vapor pressure was high, and the isotherm had to be obtained at high pressure, 33 atm for Kr and 43 atm for Xe. It is uncertain whether this pressure could deform the coal particle and affect the measurements. Walker and Kini (1965) found that CO₂ at either 195 or 298K, and Xe at 273K, measure essentially all the surface in coals, apparently since these gave the highest surface areas over all.

Marsh and Siemieniowska (1965) carried out an extensive study of CO₂ adsorption at three temperatures and analysed them using the BET, Dubinin-Polanyi (D-P) and Langmuir equations. This study confirmed the desirability of using CO₂ at 273 or 293K, and indicated that the D-P equation is the best theoretical treatment based on the closeness of the surface area to an "acceptable value". How the authors determined an acceptable value, at a time when the best probes of the surface were still being tested, is not properly clarified in this paper. The authors may have chosen them from similar higher temperature CO₂ studies by Lamond and Marsh (1964).

Table 1.2. Comparison of surface areas of several coals using different adsorbates and adsorption temperatures. From Walker and Kini (1965).

Adsorbate	Temperature (K)	sample 1 (m ² /g)	sample 912 (m ² /g)	sample 956 (m ² /g)	sample 885 (m ² /g)
N ₂	77	34	nil	nil	11
Kr	195	176	96	34	17
CO ₂	195	246	146	107	92
Xe	273	226	141	109	84
CO ₂	298	224	146	125	132

Gan et al. (1972) measured the surface areas of a rank-varied set of coals from lignite to anthracite using N_2 at 77K and CO_2 at 298K. The results are shown in **Figure 1.2**. N_2 surface areas are generally under $10 \text{ m}^2/\text{g}$; those that are greater tend to fall in the 76-82% C range, and coals with high N_2 surface areas generally have lower CO_2 surface areas. Coal CO_2 surface areas range from a low of 100 to high values of over $400 \text{ m}^2/\text{g}$. Most fall in $150\text{-}250 \text{ m}^2/\text{g}$ range. The trend in CO_2 surface area with coal rank falls in a band with differences between different coals of same carbon content of up to $80 \text{ m}^2/\text{g}$. The band exhibits a very broad minimum at about 76-88% C.

Figure 1.2. Surface areas of coals determined from CO_2 adsorption at 298 K (squares) and N_2 adsorption at 77 K (circles) as a function of coal rank. From Gan et al. (1972).

More recently, Larsen and coworkers (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992; Wernett, 1991) used the adsorption of gases systematically increasing in size, a series of cyclic hydrocarbons, and came up with a different interpretation of the nature of microporosity in coal. They contended that microporosity in coal is mostly isolated within a solid coal matrix. This challenges the view that the micropores exist as a connected network whose small apertures lead to molecular sieving due to activated diffusion. To support this position, the series cyclopropane through cyclohexane were adsorbed on a group of coals and compared the amount adsorbed vs. the molecular area. This was compared to results from the adsorption of N_2 , ethane, and CO_2 (**Figure 1.3**).

Figure 1.3. Log-log plot of amount adsorbed (n) vs. adsorbate cross-sectional area for Blind Canyon coal. Adsorbates used are CO_2 , N_2 , ethane, cyclopropane, cyclobutane, cyclopentane, and cyclohexane. From Larsen et al. (1995).

One of their major points was that ethane, CO₂, and cyclopropane have extremely close molecular areas (25.3, 25.1, and 25.2 Å² respectively as calculated by the Emmett-Brunauer (1937) method). However, their BET surface areas differ by 1 or 2 orders of magnitude. They contend that such extreme molecular sieving effects are not found in nature, and thus conclude that the solubility of the gas in the solid coal matrix must be the factor that determines the extent to which an adsorbate has reached all, or part of, the porosity in coal.

This conclusion is not well supported: activated diffusion could just as well explain the effects seen by Larsen and coworkers (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992; Wernett, 1991) as supported by much of the literature and as summarized by Walker and Mahajan (1993). These authors in addition note that the magnitude of discrimination demonstrated by some of the coals could indeed be found in nature. For example, 5A zeolites, which do not imbibe hydrocarbons, exhibit uptake differences of the same magnitude for n-butane and isobutane, which only differ in minimum dimension by 14%.

1.2.6. Molecular state and orientation on the surface

There are aspects of the study by Larsen and coworkers that bring out a deficiency in the coal literature in the attention paid to the amount of space really occupied by adsorbed molecules, which is related to the state, solid-like or liquid-like, of the adsorbed layer. This issue has been considered in the coal literature up to a point, but not as extensively as in the carbon literature. Walker and Kini (1965) discuss the density difference of solid vs. liquid state CO₂, because it is not known whether the adsorbed layer is packed like a liquid or a solid. They examined the effect of correcting the molecular area used in the BET equation in the treatment of their CO₂ data at high (298K) and low (195K) temperatures. If the surface areas were brought into agreement by using the solid density at 195K and the liquid density at 298K, there would be a positive indication of the state of the adsorbed layer. In fact the experiment indicated that the CO₂ density was probably intermediate between the two values.

An interesting approach to the question of the physical state of adsorbed nitrogen was used more recently in a NMR study by Bonardet et al. (1994) in which ^{15}N adsorbed in ZSM-5 zeolite was examined using ^{15}N NMR spectroscopy. Both the partial pressure of nitrogen and the temperature were varied. The spectra indicate the presence of two states at 77K, the most widely used temperature for nitrogen isotherms; a liquid state and another more motionally restricted state that is unlike solid nitrogen. The development of the restricted phase was found to be gradual.

Often, the importance of having a correct value for the space occupied is effectively glossed over, for instance in the study of Larsen et al. (1995). They used a method developed in 1937 to determine molecular area from liquid density. Although the adsorbates used were assymetric molecules (that is, they differed in length and width), no mention was made of the possibility of looking at the minimum dimension of these gases. This could be a serious oversight when the issue at hand is the size dependence of the uptake.

Other possible reasons were not given for why the cyclic hydrocarbons apparently did not fit into the pores (assuming these are open). Entropy loss by the adsorbate, for example, appears not to be directly discussed by anyone in the coal literature. Consider the different uptakes of CO_2 and ethane in Larsen and coworkers' study. They are close in both size and shape, but ethane adsorbs less at 195K. Ethane is also capable of more types of molecular motion than CO_2 , in that the C-C and C-H bonds twist about their axes in the free gas, in addition to tumbling of the whole molecule, as CO_2 would also experience. It is reasonable to suggest that there may be more entropy loss with ethane in the process of adsorption than with CO_2 , and this could contribute to the difference in uptake of these gases by coals.

An additional complicating factor is that the molecular area changes as the density of adsorbate changes due to variations in the molecular orientation of the adsorbate. A very interesting study by Bottani et al. (1994) on the thermodynamic properties of CO_2 on graphite is pertinent to both the interpretation of coal adsorption isotherms and the validity of the assumptions employed in the theoretical treatment of data. Using Monte Carlo simulations of a model of CO_2 on the graphite basal plane, these authors compared the calculated adsorption characteristics with experimental data. These coincided very well, supporting the validity of the model. The results from the simulation give much information about the makeup of the adsorbed layer(s). Of

particular interest are their findings that the molecular area is a function of temperature and coverage, that the second and higher layers form before completion of the monolayer, and that BET theory does not give the monolayer capacity. In terms of molecular area, CO₂ may lie flat on a surface, taking up $\sim 15.7\text{\AA}^2$ (which coincides with generally used values and with x-ray diffraction results at low temperature) or may lie perpendicular, for which the area is $9.3\text{\AA}^2$. Between these a range of tilt angles are possible. The favored low coverage orientation is parallel to the surface. Tilt towards perpendicular increases with coverage. Perpendicular orientation is favored at higher temperature, so that the area per molecule would decrease with increasing temperature. Taking into account greater spacing of the molecules at higher temperature, it appears that CO₂ takes up close to $17\text{\AA}^2$ on graphite at room temperature.

The size scale of a micropore system can affect the phase transition behavior of adsorbates in the micropores. Consider that a gas molecule in a micropore on the order of its own diameter is in a three-dimensional system overall, but it may only pack two-dimensionally with other molecules of its kind in the very restricted space. It is interesting to consider that the atoms' access to like neighbors, for actually forming a liquid or solid, may change the nature of the phase and/or the temperature and pressure conditions at which a phase transition occurs. Exploration of the fundamental behavior of adsorbates in microporous solids would be interesting in its own right; it would certainly be valuable for better understanding adsorption as a tool to evaluate the nature of microporous surfaces.

1.2.7. Gas diffusion in coals

Nandi and Walker (1966) measured the activation energy for diffusion of argon in coals of different rank (**Figure 1.4**). The diffusion parameter, $D^{1/2}/r_0$, where D is the diffusion coefficient and r_0 is the characteristic diffusion distance, ranged from 1.92 to $1.41\text{ cm}^2/\text{s}$. The apparent diffusion coefficients were found to vary with particle size. It was suggested that this is because r_0 is not related to the size of the particles but rather to the average micropore length. The activation energy for argon diffusion was determined from the temperature dependence of the diffusion parameter ($\log D^{1/2}/r_0$ vs. $1/T$). As a function of coal rank, activation energy showed a maximum at 85-90°C.

Figure 1.4. Activation energy for argon diffusion vs. coal rank. (Higher volatile matter content corresponds to lower rank. Maximum is at 27% volatile matter or 87% carbon.) From Nandi and Walker (1966).

The activation energy for diffusion of methane in coals (Nandi and Walker 1970) was found to be lower for anthracites than for bituminous coals, suggesting that the pores in anthracites are larger than those in bituminous coals or that pore constrictions are less pronounced in anthracites. The values for bituminous coals were constant at about 7 kcal/mol; they decreased to about 3.5 kcal/mol for anthracites. These authors concluded that chemical gas/surface interaction, as opposed to an interaction dominated by pore sizes, comes more into play during methane adsorption in bituminous coal.

Nandi and Walker (1970) also note that the specific volumes for anthracites, determined from helium densities, do not vary with particle size, but that there is an increase in surface area with decreasing particle size if N_2 or neopentane is used as the adsorbate. The area increase is more marked than could be explained by "increased

geometric area of particle with decrease in size." The authors suggest that grinding the sample produces macro cracks. Such cracks could increase the surface area by increasing the external or geometric surface (relative to particles of the same size without cracks), and/or by opening regions of porosity that were previously closed to the adsorbates under the experimental conditions used.

1.3. Electron microscopy

Electron microscopy (EM) has the potential advantage of directly showing pore shape and connectivity features. However, in practice, the required sample preparation of thin sections may alter the pore features, and the three dimensional connectivity of the pores cannot be seen. Another limitation is the resolution obtainable, 2 nm (20Å) at best for transmission electron microscopy; this means that only macro- and mesoporosity, from >300 to 20Å, is accessible by these methods. Microporosity, in general, is either inaccessibly small, or at the limits of the methods.

Harris and Yust (1981) examined an Illinois No.6 coal and a Kentucky coal using analytical electron microscopy (AEM). They obtained images of the smallest porosity available in the literature. In the Kentucky coal, large irregularly shaped pores and some tubular channels were observed in the maceral exinite, and a uniform distribution of fine porosity was observed in vitrinite. Vitrinite porosity appears to be highly interconnected. Coarse porosity from granular inertinite was observed at the exinite/vitrinite boundary. In the the Illinois No.6 coal, a broad range of pores, 40-500 nm, were observed in the inertinitic and exinitic granular constituents. Areas of interconnected porosity were observed in the vitrinite bands. Overall, the finest porosity was observed in vitrinite, with a size scale of 2 to 20 nm with most at the lower end. Regions of high porosity also showed high connectivity. The greatest porosity was observed in inertinite, a granular material with a broad range of pores of 5-50 nm. The least porosity was in the maceral exinite. Minerals were noted to be deposited parallel to the coal bedding plane. Examples are the clay minerals kaolinite and illite, both aluminosilicates with Na or K. Many of the fine minerals were found to be randomly oriented.

Scanning electron microscopy (SEM) was also used to image the pore space, for example using Woods Alloy (Cody and Davis, 1991) in a suite of coals ranging from lignite to anthracite. The coals were impregnated with the low-melting-point metal, which was then quenched. The polished samples were examined by SEM to image the pore space filled by the alloy. The SEM micrographs showed two types of porous structure depending on coal rank: (a) topologically rough, approximately cylindrical pores in subbituminous coal and lignite; and (b) smooth microcracks in bituminous and higher-rank coals on the order of 200-50 nm. The observable pores in the low-rank coals were concentrated at the outer surface of the particle. The observed roughness of the surface, considered along with evidence from SAXS that low-rank coal surfaces have a fractal character, suggest that these macropores are actually a fractal external surface. The microfractures observed in bituminous and higher-rank coals are considered by the authors to be secondary features, caused by sample handling.

1.4. X-ray diffraction studies and small-angle X-ray scattering

X-ray wavelengths are $1-2\text{\AA}$, of the same order as interatomic spacing in solids and liquids. X-ray scattering can thus be used to map the relative differences in electron density in a solid. When X-rays strike a solid sample, a portion is scattered in a different direction without a change in wavelength. The dependence of their intensity on the scattering direction is used to elucidate the solid structure. The scattering angle θ caused by structures with size characteristics 'a' can be determined from the following inequality:

$$0.1 < ha < 10 \quad (5)$$

h = scattering wave vector $4\pi/\lambda(\sin \pi/2)$, λ = x-ray wavelength

a = a size feature of the solid structure

θ = scattering angle

Early X-ray diffraction studies by Hirsch (1954) identified three types of rank-dependent structures for coals. These are the open structure, liquid structure, and anthracitic structure. The open structure of coals under 85% carbon consists of amorphous material and randomly oriented pores. Coals with between 85-91%C display evidence of greater structural order, or the existence of crystallites, embedded in the amorphous material which acts as crosslinks. Porosity is low. The crystallites are lamellae of one to three layers. They are randomly ordered relative to each other. The anthracitic structure is seen in coals over 91%C. The crystallites are larger, consist of more layers, and display orientation relative to each other. Crosslinks of amorphous material are absent. Porosity in high-rank coals is thus of a different type than in low-rank coal. These structural models proposed based on X-ray data are still widely accepted and are generally consistent with many other indicators of coal physical structure.

Structures in the solid that cause electron density variations over the size scale 4-2000Å cause x-ray scattering of under about five degrees. The technique of small angle X-ray scattering (SAXS) is the analysis of the intensity of X-ray scattering at these angles. A typical SAXS intensity vs. scattering angle plot for coal is shown in **Figure 1.5**.

SAXS studies can be used, with varying degrees of reliability, to calculate a surface area, identify the size scale of structural features causing scattering, estimate pore size distribution, and determine fractal dimensionality. Setek et al.(1984) discuss the use of SAXS in combination with gas adsorption to (1) verify that there are voids in the material, and (2) provide a test for pore geometry assumptions that must be made to calculate surface area from SAXS data. They arbitrarily varied the pore geometry used in the calculation of surface area from x-ray data, in order to determine which geometries resulted in agreement with surface areas determined by gas adsorption. The pore shapes least deviant from gas adsorption data were flat large-diameter discs (which amount to slit-shaped pores), or long filaments, in Victorian brown coal.

Bale et al. (1984) report an interesting result: the macropore- and mesopore-specific surface areas obtained from x-ray data agreed with N₂-determined surface area of the same coals. This correlation supports the idea that N₂ adsorption at 77K only penetrates pores of mesopore size or larger. It illustrates that Bale's SAXS data did not

provide information on microporosity (although it theoretically could, because size features as small as $4\text{\AA}$ can be identified and the micropores are under $20\text{\AA}$).

Lin et al. (1978) reported SAXS data that indicated scattering sources in a vitrinite on the size scale of 100 and $250\text{\AA}$. They correlated these with TEM observation of both minerals and pores in the same sample. Approximately spherical mineral deposits were imaged, with 70 to $120\text{\AA}$ diameters that are mostly kaolinite $[\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_6]$. The micropores were $20\text{-}30\text{\AA}$ and the meso- to macropores were $200\text{-}500\text{\AA}$ (**Figure 1.6**).

Figure 1.5. A typical SAXS curve for a low-rank coal (lignite). From Bale et al. (1984).

Figure 1.6. Size distribution curve for predominantly micropores (peak 1), microminerals (peak 2), and mesopores (peak 3) in a vitrinite. From Lin et al. (1978).

Both Bale et al. (1984) and Setek et al. (1984) treat the scattering sources as being due to porosity. However, Lin et al. (1978), in a study combining SAXS with TEM, were able to attribute one of three size features identified in the coal to small mineral deposits. Both coal-mineral matter and coal-void electron density differences are comparable according to these authors (1978). This complicates the interpretation of scattering data as being due to porosity alone.

Larsen et al. (1995) analyzed the fractal dimensionality of coal using SAXS data. Fractal dimensionality is a way of quantifying the roughness of a surface (Mandelbrot, 1982). Adsorption of gases with different molecular cross-sectional areas on a fractal surface will give different surface areas. Thus, the surface of coal is a fractal surface. In SAXS experiments there is a power-law relationship between the scattering intensity I and the scattering wave vector h :

$$I = h^{-(6-D)} \quad (6)$$

Larsen et al. (1995) assert that the SAXS dimension D equals the fractal dimension. The fractal dimension of the coals measured in their study, in which the scattering angles represented a length scale of 30 - 1000 Å, varied between 2.35 and 2.87. This demonstrates that coal surfaces are fractal surfaces. The fractal dimension did not correlate closely to coal rank, although the two low-rank coals in the sample set had the lowest fractal dimensions. Severe molecular sieving effects were also reported for all the coals studied, particularly for the lignite, which is inconsistent with its relatively low fractal dimension. This contrast was used to support the argument advanced by these authors that the coals do not have a pore network.

1.5. Mercury porosimetry

Mercury porosimetry (Washburn, 1921; Gan et al. 1972; Gregg and Sing, 1982; Friesen and Mikula, 1988) is used to obtain pore volume distribution based on the pressure of mercury required to fill pores of successively smaller sizes. Since mercury does not wet the coal surface, the surface tension of mercury limits the size opening it will penetrate at a given pressure. The minimum pore radius filled by Hg at a pressure P is given by the Washburn equation (Washburn, 1921):

$$P = -2\sigma\cos\theta/r \quad (7)$$

σ = surface tension of Hg

θ =Hg/solid contact angle, usually taken to be 140°

The volume of mercury taken up as a function of increasing pressure is incremented is a function of the pore size. Pores are most often assumed to be cylindrical. The pores filled are those accessible from the external surface. The volume-pressure relationship can thus be related to the pore size distribution. Intrusion/extrusion hysteresis is often seen in mercury porosimetry of coal and is an indication that coal contains narrow pores with access to larger spaces, also called aperture-cavity or “ink-bottle” pores. Gan et al. (1972), among others, determined macropore volumes for a series of coals using mercury porosimetry (**Table 1.1**).

At mercury pressures over 10 MPa, particle compression can occur. Friesen and Mikula (1988) attempt to differentiate when compression, or both compression and pore filling, occur based on analysis of the volume-pressure plot. Mercury porosimetry works if the particles are not deformed or broken during pore filling, and if assumptions of the Washburn equation regarding mercury-pore wall contact angle and cylindrical pore geometry hold. Cody and Davis (1991) discuss the implications of non-cylindrical pores on mercury porosimetry data. In terms of particle damage at high mercury pressures, it is generally accepted that it does occur, and as a result the lower limit of pore size for reliable data from intrusion of mercury into coal is 30Å. Smaller pores are not analysed by this technique. In addition, according to Friesen and Mikula (1988), the cumulative pore size distribution that can be obtained theoretically from the Washburn equation can also be related to the fractal dimension of the coal surface.

1.6. Summary

Coal surface areas and pore volumes. Surface areas of coals determined by nitrogen adsorption are generally under 40 m²/g, while surface areas determined by carbon dioxide adsorption range from a low of 100 m²/g to high values over 400 m²/g. (Most fall in 150-250 m²/g range.) Surface area vs. rank correlation is a band with surface area differences between coals having the same carbon content of up to 80 m²/g. The band exhibits a broad minimum at about 76-88% carbon. Coals <75% carbon are primarily macroporous; coals at 75-84% carbon are macro- and mesoporous; and coals at 85-91% carbon are primarily microporous (Gan et al., 1972).

Pore geometry. Coal is too amorphous and too heterogeneous to obtain definitive information on its pore geometry from X-ray diffraction. Mercury intrusion/extrusion hysteresis is an indication of aperture-cavity, or ink-bottle pores. Victorian brown coal pores may be slit-shaped or filament-like based on SAXS data (Setek et al., 1984). There is also evidence (Cody and Davis, 1991) that low-rank coals have very rough approximately cylindrical pores, and that higher-rank coals have microcracks.

Pore connectivity. All vitrinite samples observed by TEM and AEM (Harris and Yust, 1981) contained large regions of interconnected fine porosity. Fine porosity and vitrinite content also correlate from gas adsorption data (Gan et al., 1972). Completely different types of porosity associated with different macerals exist side by side in coal samples examined by Harris and Yust (1981). By contrast, Larsen et al. (1995) propose that porosity in coal exists primarily as isolated bubbles, based on their interpretation of adsorption data using different gases, and coal fractal dimensionality obtained from SAXS data.

Rank-dependent trends in coal physical structure. The nature of the physical structure of coal changes significantly with rank. There are many indications that the stage of coalification at about 85-90% carbon is a structural turning point. For example, x-ray diffraction indicates that there is a significant increase in the number, size, and relative orientation of graphitic crystallites in coals at about 90% carbon (Hirsch, 1954). At this carbon content, helium density is at its minimum (Gan et al., 1972), the activation energy for argon diffusion is at its maximum (Nandi and Walker, 1964), and surface area is just past its minimum and is beginning to increase (Gan et al., 1972).

These and other rank-dependent trends (Van Krevelen, 1993) collectively support the following picture of structural changes with increasing degree of coalification. Porosity decreases in overall amount and in the size or tightness of apertures through ~88% C and then increases; in general, higher-rank coals have a higher proportion of microporosity. Microporosity in low-rank coals is attributable to spaces between chainlike polymeric coal constituents, but at high rank it is attributable to the spaces between ordered carbon crystallites.

General problems associated with the use of analytical techniques. The assessment of porous structure, and particularly microporous structure, in coal is a difficult task that no single analytical technique can accomplish. It has been approached analytically in

many ways. It is important to remember the limitations, inherent or in how they are applied, of the various analytical methods applied to coal porosity.

In using gas adsorption methods, the adsorption isotherm summarizes the experimental data relating to the adsorbent material, from which all further information about the adsorbent (solid) surface is *derived* by fitting the isotherm into a mathematical model. This will yield accurate information only if our understanding of the adsorption process, which is incorporated in the mathematical model, is correct. While adsorption data is routinely used in studies of porosity, the process of adsorption, particularly on heterogeneous microporous solids such as coal, is still not completely understood. This is a situation that is made worse when what generally *is* known is not properly incorporated into experimental design. For example, the issue of whether true equilibrium is attained is at times skirted in adsorption studies.

There are general drawbacks to several analytical techniques mentioned in this chapter. The pore geometries in coal are not well defined, yet it is necessary to assume pore geometry in mercury porosimetry and SAXS (although in the SAXS technique, there are advantages to calculating surface area with several test geometries). Some methods require sample preparation techniques that may alter pore structure, such as thin sectioning for microscopy. The assumption of the molecular area of adsorbed gas can be a problem in calculating monolayer coverage for surface area and in calculating pore size distribution from the nitrogen isotherm. Lastly, in SAXS studies, x-ray scattering sources in coal must be attributed to a structural feature. Some evidence indicates that scattering sources are minerals as well as pores.

Much has been gained through the use of various analytical methods to characterize porosity in coal; macro- and mesoporosity are reasonably well characterized. Microporosity, while being a substantial component of the internal surface of coals, remains the least well understood. The size scale of microporosity tests or exceeds the limits of many techniques for the description of porosity; a new approach, for which the size scale is not a detrimental factor, is needed.

Chapter 2

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: GENERAL THEORY AND APPLICATION TO XENON-129

2.1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a method to observe NMR active nuclei that is based on the magnetization of the sample by an applied magnetic field. This technique can sensitively detect the influence of electric and magnetic fields originating in the atomic-level environment of an observed nucleus. It is a powerful tool for molecular structure determination as well as a noninvasive probe of the time course of active physical or chemical processes. In this thesis the NMR of xenon gas is used as a probe of the surface structure of porous solids. The basic principles of NMR (reviewed in Freeman, 1988; Sanders and Hunter, 1993) apply in the same way to all NMR-active nuclei.

The NMR of ^{129}Xe adsorbed in porous solids differs from well known applications of NMR such as molecular structure determination using ^1H and ^{13}C in that there are no chemical bonds to xenon in the systems studied; rather, changes in the magnetic environment of xenon come from its contacts with the solid surface. The gas is usually mobile in the adsorbent/adsorbate system. The chemical shift of ^{129}Xe adsorbed on a solid reflects the different types of contact xenon makes with the solid. It should be pointed out that the interpretation of ^{129}Xe chemical shifts is the subject of ongoing debate and development. The NMR experiment is influenced significantly by the mobility of xenon on the time scale of the experiment, and ^{129}Xe NMR can be used to study the dynamics of xenon adsorbed on and within porous solids. This is a

strength of the technique since it does not suffer from the the ambiguity of chemical shift measurements alone.

2.2. Pulse sequences used in this study

The majority of the NMR experiments reported in this thesis utilize a 90° pulse followed by spectrum acquisition. Two other experiments have been utilized, low power presaturation, followed by a 90° pulse, and an echo sequence.

The echo sequence is based on the Carr-Purcell-Meiboom-Gill sequence used for T₂ relaxation measurements, written as follows:

$$\pi/2_x - (\tau_D - \pi - \tau_D)_n - \text{echo}$$

This pulse sequence utilizes phase cycling which shifts the phase of the π pulse and the receiver 90° per repetition which suppresses spurious signals from the instrumentation. A 90° ($\pi/2$) pulse is applied. Using a rotating frame vector analogy, this pulse places the magnetization into the xy plane. An evolution period, τ_D , follows during which the magnetization undergoes both chemical shift evolution and dephasing due to T₂ relaxation and to inhomogeneous magnetic field.

A 180° (π) pulse is then applied, which flips the x and the y components of the transverse magnetization 180°, for example, from the y axis to the -y axis. The magnetization vectors approach each other and rejoin at the end of the second evolution period. The effect in terms of detectable NMR signal is that the signal amplitude is strongest when the x and y components meet. The signal, called an echo, is acquired at the end of the second evolution period when the signal would be strongest. The only process which causes loss of the echo signal intensity is the true T₂ relaxation, and not chemical shift evolution or magnetic field inhomogeneity.

This method was developed to determine the intrinsic spin-spin relaxation time T₂. If the echoes are acquired at increasingly long evolution times, the intensity of the echo signal will decrease with exponential time constant T₂. The echo pulse sequence was used for a different purpose in this thesis to address a practical experimental

problem. The sample signal and an instrumental signal from the sample probe, or ringing, had been detected together, and this method was used to separate them (Chapter 3). The echo was acquired for the purpose of obtaining the signal at a greater time after the application of the pulse than is normally feasible without losing a significant portion of the signal of interest, thus allowing the unwanted ringing to decay to some extent before the echo was detected.

The selective low power presaturation pulse is used in the experiments reported in Chapter 5. The low power of the pulse, combined with the long pulse length, result in a narrow excitation bandwidth. It can excite nuclei that have a particular, narrow range of resonant frequencies, leaving other nuclei in the sample, which have different resonant frequencies, unaffected; thus it is selective. As used in this thesis, the pulse is intentionally applied long enough to result in the saturation of nuclei with resonant frequency in a narrow frequency band. A 90° pulse applied directly after presaturation will result in detectable NMR signals from all sample nuclei that were not saturated.

The angle α that the sample magnetization (initially on the z axis in the rotating frame vector analogy) is tipped by the B_1 pulse away from z depends on the duration t_p of the pulse, and on the B_1 intensity.

$$\alpha = \gamma B_1 t_p$$

A high power 90° pulse requires a short duration t_p ; a low power pulse can also tip the magnetization 90° , but requires longer duration t_p . The longer the pulse, the narrower the frequency range of its excitation bandwidth. Thus, progressively longer low power pulses, as used in Chapter 5, are not progressively wider; in fact, they become progressively narrower. The relationship between the pulse power, which is the rf intensity of B_1 , and the excitation band width is that B_1 approximately influences a frequency range $\gamma B_1/2\pi$ Hz from its center.

The frequency domain excitation function of a rectangular, low-rf intensity pulse can be approximated by the Fourier transformation of the pulse envelope. It illustrates the frequency range and the intensity of the excitation that can be produced by the pulse; its shape is that of a $\sin x/x$ function, **Figure 2.1**.

Figure 2.1. Frequency domain excitation pattern for a rectangular selective pulse. (a) calculated from the Bloch equations, and (b) the Fourier transform of the time-domain pulse envelope. From Freeman (1988).

2.3. Effect of exchange on the NMR spectrum

Exchange may be chemical, such as reversible proton exchange in alcohols, or physical, such as the movement of adsorbate gas atoms among different adsorption sites in a solid. Exchange between magnetically different sites by NMR active nuclei can be detected in the NMR experiment. The rate at which the nucleus changes magnetic environments determines the effect the exchange process has on the NMR spectrum. The quantitative description of exchange between two sites requires knowledge of the resonant frequencies for each site in the absence of exchange. The difference between these two frequencies ($\Delta\nu$) compared to the rate (k) of the exchange process gives the criterion for whether the exchange is fast, intermediate or slow on the NMR time scale. Fast exchange is defined as follows:

$$(\sqrt{2} \pi \Delta\nu)^{-1} = k^{-1}$$

Slow exchange gives well resolved resonances at each site. At intermediate rates the resonances are broadened. Broadening occurs due to the replacement of a precessing nucleus at one site with another precessing at a different phase, the overall result of which is to decrease the effective T_2 , increasing the natural linewidth $1/T_2$.

The chemical shift of the signals from the two sites approach a weighted average value as the rate approaches fast exchange. At fast exchange, there is one averaged signal.

2.4. Saturation transfer

Saturation transfer is an NMR technique used to observe exchange processes. The nuclei corresponding to a particular resonance or part of a resonance can be noninvasively labelled by selectively saturating that resonance. The nuclear motion to another site, or conversion to one form to another (such as if the observed nucleus is bonded to a molecule which undergoes conformation inversion), can be detected based on loss of intensity for other signal(s). This intensity loss corresponds to a transfer of saturation from the irradiated signal to another. Saturation is accomplished with a 'soft', low power pulse directed at a narrow frequency band corresponding to a particular resonance or part of a resonance. The effect on the other resonances in the spectrum can be monitored as a function of saturation time. This can be used to demonstrate exchange between the saturated nuclei at site X and those at another site A with a different resonant frequency. For signals from two sites to be distinguishable, the exchange of nuclei between them should occur at a rate that is slow compared to the frequency difference between the signals. It is also possible to measure rates of exchange with this technique.

The spin-lattice relaxation time limits the period of time during which the nuclei corresponding to the selected frequency will remain saturated. If there is no exchange, the saturated resonance (X) recovers by spin-lattice relaxation after irradiation is stopped. The second signal (A) is unaffected. If the relaxation rate is slow compared to the exchange rate, the A resonance undergoes intensity loss due to transfer of saturated nuclei to A. If relaxation and exchange occur at comparable rates, A loses intensity following saturation of X, then recovers via spin-lattice relaxation. These effects can be described quantitatively.

The rate of recovery of magnetization M_Z to its equilibrium value M_∞ when the nuclei in a system are exchanging between two sites A and X and relaxing with rate

constant $1/T_1$, can be described mathematically. In a relatively simple case, if T_1 is the same at both sites and the site populations are equal,

$$M_{\infty}(A) - M_Z(A) = M_{\infty}(A)[\exp(-\tau/T_1) - \exp(-\tau/T_1 - 2k\tau)]$$

$$M_{\infty}(X) - M_Z(X) = M_{\infty}(X)[\exp(-\tau/T_1) - \exp(-\tau/T_1 - 2k\tau)]$$

where k is the rate constant for exchange.

2.5. ^{129}Xe NMR spectroscopy

^{129}Xe is a spin-1/2 stable isotope, one of nine isotopes of the inert gas xenon, atomic number 54. Its natural abundance is 26.4% and its magnetic moment is -0.77247 nuclear magnetons (μ_N). Its nuclear magnetic resonance signal was first detected by Proctor and Yu (1950). It has been known since that time that the resonance frequency changes with the gas density. The chemical shift in the gas phase has been studied extensively (as reviewed by Dybowski et al, 1991). It can be represented by a virial expansion

$$\delta(T, \rho) = \delta_0 + \delta_1(T)\rho + \delta_2(T)\rho^2 + \delta_3(T)\rho^3 + \dots$$

where δ is the chemical shift, T is temperature, and ρ is gas density. The higher order terms (ρ^2 and above) are negligible at low pressures (Jameson et al., 1973). They become more important over 100 agmat, where 1 agmat is the density of an ideal gas at standard temperature and pressure. The temperature dependence of the second virial coefficient fits a fourth order polynomial in T (Jameson et al., 1973). It increases steeply with decreasing temperature below 300K and is relatively flat above it.

The density dependence of the chemical shift of bulk gas indicates that the chemical shift is influenced by collisions of the xenon atoms. Xenon has a spherically symmetric 4s outer orbital and is highly polarizable. Gas collisions are able to change the shielding of the nucleus by perturbing the electron orbitals.

2.5.1. Relationship of chemical shift to size of void space in microporous materials

The chemical shift of xenon in contact with zeolites has been shown to be related to the porous structure (Ito et al., 1984; Demarquay and Fraissard, 1987). The chemical shift of xenon adsorbed on solids can be expressed as a virial equation, an extension of the same type of characterization of the gas alone. Each term represents a xenon interaction with other gas atoms, or with the solid on which it is adsorbed, that may influence the chemical shift. Demarquay and Fraissard (1987) proposed the following form:

$$\delta = \delta_0 + \delta_s + \delta_E + \delta_{\text{Xe-Xe}}\rho_{\text{Xe}}$$

Here δ is the observed chemical shift, δ_0 is the reference (0 ppm), δ_s is the chemical shift due to the Xe-pore wall interaction, δ_E is due to electric field from cations (a similar term would be added for magnetic fields if there were paramagnetics in the solid); the last term, $\delta_{\text{Xe-Xe}}\rho_{\text{Xe}}$, is the chemical shift due to Xe-Xe collisions, which is related to xenon density ρ_{Xe} .

A correlation between chemical shift and size of the void space was obtained by Demarquay and Fraissard (1987) using zeolites of known pore structure. The ^{129}Xe signal in these zeolites represents a fast-exchange average of the intra- and extraparticle gas signals. The conditions used are intended to eliminate all but the Xe-pore wall interaction, as described by the virial equation. Extrapolation of the chemical shift-pressure dependence to zero pressure removes the Xe-Xe interaction term. Dealuminated zeolites were used, which allows the term for cation effects to be neglected. The cation effects are significant if the cations are divalent or greater when xenon can move freely in the pore system. When xenon is immobilized, any cation may have significant effect (Chen and Fraissard, 1992). The remaining determinant of chemical shift according to the model is then the Xe-wall interaction. The reciprocal of the extrapolated chemical shift was linearly related to the computer-simulated mean free path of xenon in the zeolites studied:

$$\delta_s^{-1} = \delta_a^{-1}(1 + l/a)$$

Here δ_s is the chemical shift extrapolated to zero pressure, l is the simulated mean free path of xenon in the pore, and δ_a^{-1} , defined as the reciprocal of the chemical shift of xenon on a dealuminated zeolite surface, is also the zero-mean-free-path value of δ_s (in practical application of this model, it is treated as a constant = 0.412ppm^{-1}), and the constant $a = 2.054\text{\AA}$.

From this correlation, the theory of Demarquay and Fraissard states that the mean free path of xenon in the pore can be calculated from the above equation. This calculation is specific to the linear region of chemical shift vs. mean free path, meaning mean free paths for xenon from $1\text{\AA}$ up to $\sim 6\text{\AA}$, or a pore size range approximately $5\text{\AA}$ up to $\sim 16\text{\AA}$. At larger values of mean free path, the relationship becomes increasingly nonlinear. Pore diameter can be calculated from the mean free path if pore shape is known. It is a drawback if the method is to be applied to a porous material with unknown pore shape(s), although estimations can be used.

Some important points to note about this model are that, first, the evidence presented and the model presented may need to be considered separately. Demarquay and Fraissard (1987) present empirical evidence that chemical shift is related to void space size, which is apparently true under the conditions used. They also present a theoretical model, parts of which assume free-gas-like behavior of adsorbed xenon in zeolite pores. This assumption has drawn some criticism (Ripmeester and Ratcliffe, 1995; Annen et al., 1990). Evidence is not presented to show that free-gas-like behavior is actually occurring, although it is known that xenon atoms are in motion as opposed to occupying a fixed adsorption site. In the Y zeolites at room temperature it is generally accepted that xenon in the pores is highly mobile, sampling several zeolite crystallites on the time scale of the NMR experiment (Dybowski et al., 1991).

Second, the formulation of the equation from which pore diameter can be calculated contains two constants, a and δ_a , which are characteristic of the interaction of xenon with the zeolite structure. These may actually turn out to contain information related to pore wall chemistry that *may not be the same constants* once the method is applied to non-zeolite materials. Indeed, this method has had mixed results when applied to other microporous materials (for example, Earl et al., 1994), and this could be part of the reason. In order to determine the values of these constants in a different material, a pore-diameter-varied set with independent evaluation of pore size is

necessary. In an amorphous material such as coal, where the microporosity is not well characterized, this is not possible.

The mean free path model is applied in this thesis to the problem of measuring micropore diameter in coal. There are other correlations of extrapolated chemical shift and void space structure; the use of the mean free path model does not imply that it is preferable. Due to its rather poorly understood pore structure, coal is not suitable for, and is not used as, a test material for available theories. There is considerable research currently in progress on precisely defining xenon shielding (DeDios and Jameson, 1994; Jameson et al., 1992), which may lead to a more definitive reference point from which to interpret chemical shifts. There are a number of studies addressing how the chemical shift of xenon in microporous spaces relates to the size of these spaces, and these will be reviewed here, first considering alternatives to Demarquay and Fraissard's mean free path model. Experimental evidence that is at odds with the mean free path model will be considered last.

Some workers have proposed ideas or made observations that while pertinent, have not been extensively used. Cheung et al. (1988) propose a method for determining void volume by low-temperature NMR: xenon atoms are treated as hard spheres and the number needed to fill the zeolite pore is used to determine pore volume. Johnson and Griffiths (1987) report experimental data for zeolites on chemical shift vs. surface-area-to-volume ratio which is linear with one outlying point. Others present more developed models, some of which can be directly used to calculate pore sizes from ^{129}Xe chemical shift data.

Ripmeester et al. (1988) obtained a relationship between the ^{129}Xe chemical shift and the size of the space xenon is entrapped in using clathrate hydrates and a clathracil sample. These results were used to address the validity of the mean free path model. There are two important distinctions from the work of Demarquay and Fraissard (1987) in the conditions used by Ripmeester et al. (1988). In the clathrate cage, the xenon is trapped, but in zeolites it is exchanging through open channels and between crystallites; in addition, the temperatures used in the latter study are much lower than in the former. The chemical shift of xenon in the clathrates and in solid xenon correlated linearly with the size of the free-space radius available in the cage or crystal lattice with slope $-5.147 \times 10^{-3} \text{ \AA/ppm}$, **Figure 2.2**.

Figure 2.2. Correlation of ^{129}Xe chemical shift to free space radius available in the enclosing structure: (1) solid Xe, 21K; (2) solid Xe, 160 K, (3) dodecasil-3C, small; (4) "structure I, small; (5) "structure I", large; (6) "structure II", large; (7) dodecasil-3C, large. From Ripmeester et al. (1988).

Smaller spaces correlated with chemical shifts further downfield.

Interestingly, at the temperatures used, the xenon gas is definitely frozen (solid xenon samples), or is likely to be frozen (clathrate hydrates), and as such would not be actively sampling the available space. Its normal freezing point at is $-112\text{ }^{\circ}\text{C}$, (161K), and may well be lower in very small spaces, for example as shown by Cheung et al. (1988), and discussed in Section 2.5.3. A problematic aspect of the experiments is that a variety of temperatures were used. The temperature is not specified for several spectra used in the plot of chemical shift vs. cage radius. The authors do not address the effects on chemical shift stemming from inconsistent temperatures within the data set. Since temperature affects the ^{129}Xe chemical shift to varying degrees, depending on the system studied, caution should be used in interpreting these spectra strictly in terms of cage dimensions.

A critical discussion of Demarquay and Fraissard's background theory is included in Ripmeester et al. (1988). The binary collision of xenon atoms is the dominant contributor to chemical shift in dilute gas, as shown by Jameson et al. (1973), with higher-order terms in the virial expansion becoming important at higher pressure. The mean free path model correlates chemical shielding to the number of

binary collisions in the cage. Ripmeester et al. (1988) predict theoretically that a binary collision model should give a cubic dependence of chemical shift on mean free path - which neither study shows experimentally to be the case. They conclude that the theoretical basis of the mean free path model is flawed. It is clear that there is a flaw in one or both of these theories, but there is no evidence that the theory of Ripmeester et al. (1988) is the better one. Given the very different experimental conditions between the two studies, their results may not be directly comparable.

Derouane and Nagy (1987) propose an alternative theory. Its basis is the van der Waals model which “factorizes and scales the physical interaction of a sorbed atom or molecule with the curved surface environment of pores possessing atomic scale dimensions.” They scale the van der Waals interactions resulting from three dimensional confinement to the chemical shift of the trapped atom. The van der Waals interaction is factorized into two terms: polarizability of adsorbate, and surface curvature of adsorbent. The xenon atom’s polarizability is linked to surface curvature effects, imagining the trap as a sphere.

Using zeolites of known crystal structure, from which radius and thus W (van der Waals energy) are obtained, they find that the chemical shift of ^{129}Xe is a linear function of W . In a specific response to Demarquay and Fraissard’s mean free path model, these authors assert that theoretically at $kT < W$, spherical molecules or atoms stick to the pore wall, oscillate, and hop over corrugation barriers, but do not collide with the wall and reflect through the pore. They do not obtain pore center as an equilibrium position.

It can be helpful in assessing models for the source of xenon chemical shift to consider the energy landscape imposed by the proximity of micropore walls. This is important for estimating how xenon behaves in a micropore environment.

Cheung(1995) calculated the potential energy felt by a xenon atom in a micropore,

Figure 2.3. The potential energy function used was the sum of Lennard-Jones potentials (consisting of a van der Waals attraction term and a repulsive term) between the xenon atom and the adsorbent surface. The shape of the potential energy pattern through the pore depends on the size of the pore. The energy minimum site is in the pore center for pores the size of the xenon atom, but for much larger pores, the center develops a hump and the minimum is a doughnut-shaped ring closer to the pore walls.

Figure 2.3. Potential energy for xenon in the cross section of a long cylindrical pore. (a) pore comparable to the size of a xenon atom; (b) pore much larger than the xenon atom. From Cheung (1995).

It is apparent from this picture that unless the energy of the atom is high relative to the local minima and maxima, xenon is not likely to move *randomly* in the pore as assumed in the mean free path model. Cheung discusses the effect on chemical shift of the energetically favored position in the pore. By his calculations the reciprocal of the chemical shift is a linear function of pore size if the pore is 'much' larger than the xenon atom.

The application of the mean free path model to a variety of materials shows that the results of pore diameter calculations are inconsistent. This discussion will be limited to materials with pore sizes that are independently determined. The application of this method to coal is discussed in Chapter 3. Earl et al. (1994) report results of pore diameter calculations that are in keeping with known structure for several zeolites and for synthetic imogolite, which has similar chemical makeup but different physical

structure than zeolites. However, in sol-gel prepared silicas with 45 and 300 Å pores, the xenon chemical shift was significantly different from what would be expected according to the mean free path model, and the pressure dependence of chemical shift was nonlinear. An important point noted by these authors is that in transferring the mean free path/void space correlation to very different materials, it may no longer be valid due to significantly different pore wall chemistry and physics. This is very likely, as the calculations rely heavily on empirical evidence from one type of porous material.

As noted earlier in this section, a careful examination of the pore diameter calculation shows that it contains constants that are clearly related to zeolite structure, but which could conceivably be determined for different classes of materials. This means that in order to improve its applicability to materials of different pore wall chemistry, significant additional research would be required. At a more practical level, if the caveats of the theory are kept in mind, some instances in which it does not work could be avoided. For example, it is defined as specific to mean free paths for xenon from 1 Å to about 6 Å, a pore size range up to approximately 16 Å. In the study of Earl et al. (1994), it was applied - unsuccessfully - to materials with pore sizes that are very much greater. While this data is instructive, it does not provide evidence that the theory itself is flawed.

Annen et al. (1990) tested Demarquay and Fraissard's mean free path theory on a series of molecular sieves. For molecular sieves with FAU topology, chemical shift depends on framework composition, but with AFI topology (compositional region from AlPO_4 to silica), they do not. They conclude that chemical shift does not correlate with the size of framework void spaces because xenon in the 8 Å AFI channels has similar chemical shift to that in 13 Å SAPO-37. In this case, the pore sizes are in the appropriate range. However, some pertinent information is not addressed, such as the effect of divalent or higher-valent cations introduced in some molecular sieves as composition is changed; whether they acquire significantly different pore shape as composition is changed, and whether xenon is immobilized in the structure. All of these are important for the calculation of pore diameter.

For example, Demarquay and Fraissard's model accounts for electric effects from cations and magnetic effects of paramagnetics. Nevertheless, in the experiments from which the pore diameter calculation method was developed, electric and magnetic field effects were *eliminated* through careful selection of the zeolites used.

When applying this theory to new materials, if these contributors to chemical shift are present, the experimenter would have to account for their chemical shift contributions in order to use the model appropriately. This can be a valuable model, and is conveniently applied to a limited range of materials. However, it is not intended to be broadly applicable as it stands. While Annen et al. (1990) may turn out to have a valid point, their case is not well made in this study because a close examination of what is actually said by Demarquay and Fraissard was apparently not made.

2.5.2. The slope of chemical shift vs. density or pressure

The gas density (or pressure) dependence of the chemical shift for xenon adsorbed on a solid may be linear or nonlinear. It has been noted (Liu et al., 1993) that for materials with strong attractive sites such as divalent or higher-valent cations in zeolites, the pressure dependence is nonlinear. Xenon-xenon interactions can also affect the slope of the chemical shift vs. uptake line. Chen and Fraissard (1992a) note that the changes in slope, giving a nonlinear pressure dependence, may occur because different xenon interactions come into play in different circumstances. For example, 3- body collisions may become important after a certain pore filling limit. Cheung et al. (1988) suggested two types of adsorbed xenon, one on the wall and one more gas-like in cage center, which are exchanging. Because free gas has a linear chemical shift/pressure slope, these authors explained linearity or nonlinearity based on the relative predominance of one of these two types of adsorbed xenon.

Because a linear chemical shift vs. xenon pressure dependence was found for the samples used in this thesis, the influences on the magnitude of the slope are of greater interest than the shape of this dependence. According to Johnson and Griffiths (1987), the slope is dependent on the mobility of xenon in the zeolite. At one extreme, xenon can move rapidly and the chemical shift/pressure dependence is the same as for xenon in free space, with pressure in turn being dependent on the quantity adsorbed and the pore volume. In this case the slope should depend on the micropore volume. At the other extreme, for xenon constrained to one cavity at one atom per cavity, chemical shift should be independent of pressure. Intermediate situations can be conceived, such as several atoms in one cavity with essentially no diffusion between

cavities (series of microscopic systems), and this situation should give rise to a different chemical shift/pressure slope than an open pore system.

2.5.3. NMR indications of the physical state of xenon adsorbed in micropores

The state of xenon gas adsorbed in microporous materials is of interest when working at low temperatures where phase transitions to liquid and solid xenon could occur. While such low temperatures are not used in this thesis, phase transition behavior in micropores remains of interest as an illustration of how significantly different the micropore environment is from macroscopic ones. It assists in providing a context for making judgements about the behavior of xenon atoms in micropores postulated in several chemical shift - space size theories.

Earl et al. (1994) observed altered freezing behavior of xenon in microporous imogolite tubes by ^{129}Xe NMR. Bulk xenon outside the tubes froze at 161K, its normal freezing point, but at temperatures as low as 82K xenon in the pores did not, although increasing linewidth indicated decreasing molecular motion. They noted that cooperative effects, which are possible for bulk liquid, are necessary for the thermodynamic concept of freezing. In microporous spaces, only approximately one to eight xenon atoms could be close neighbors. Cheung et al. (1988) used Monte Carlo calculations to show that for a group of under 13 xenon atoms, the gas-liquid transition occurs below 86K compared to 166K for bulk xenon, and the liquid-solid transition occurs below 66K compared to 161K in bulk xenon.

Chen and Fraissard (1992a) investigated the state of xenon adsorbed in several zeolites under different conditions. At temperatures of $\sim 80^\circ\text{C}$, they concluded that xenon is relatively fixed in the potential well imposed by the zeolite structure, but especially in open structures (Y zeolites) fast exchange was found to occur at room temperature. This verifies Demarquay and Fraissard's model in which chemical shift is taken to be a weighted average due to rapid exchange between sites. They suggest that Derouane and Nagy's model (1987) is not valid until low temperature, about -100°C , when the xenon is more fixed in the pore wall; and in that case cation effects are not negligible.

In addition to the experimental data, there have been opinions expressed about the behavior of adsorbed gas that address whether the behavior assumed by Demarquay and Fraissard (1987) is likely. Ripmeester and Ratcliffe (1995) note that in the small-diameter channels of the molecular sieve ALPO-11, the xenon atom dwells most of the time enclosed in small cells, much as in a clathrate cage, but is occasionally able to jump from one cell to a neighboring vacant one, behavior that is quite different from that of a gas. According to Annen et al. (1990), it is "hard to believe" that molecules residing in microporous environments act as rigid spheres with mean free paths and elastic collisions; they would more likely behave as if they are in a liquid solvent.

2.5.4. Linewidth and anisotropy

Suh et al. (1991) presented evidence that the broad line for xenon adsorbed on amorphous carbons of high surface area (**Figure 2.4**) was due to sample inhomogeneity. They also found that the presence of acidic functional groups significantly increased the value of the xenon chemical shift extrapolated to zero pressure. They stated that this shift is a reflection of surface functionality, having separated this effect from concurrent pore diameter effect through N₂ t-plot estimation of micropore diameter before and after oxidation. The pore-size-predicted shifts were not as substantially different as the observed chemical shifts. Since this is one of the few studies dealing specifically with carbons and not zeolites, it is especially relevant to the studies on coal. It illustrates the importance of recalling that surface chemistry, as well as adsorbent porosity, can influence the xenon chemical shift.

Johnson and Griffiths (1987) reported variations in ¹²⁹Xe NMR linewidth and line symmetry for different zeolites, and for individual samples, a lesser variation of width with xenon loading. They argued that the most likely linewidth contributors are inhomogeneity/susceptibility effects, dipolar couplings, and spin-spin relaxation (T₂), all of which could be reasonably ruled out; the remaining possibility was exchange broadening. They also considered the peak profile as a xenon density distribution: a distribution of chemical shifts would result from a distribution of xenon density in cavities with restricted xenon motion (variation of shift through variation of the Xe-Xe

Figure 2.4. ^{129}Xe NMR spectra of xenon adsorbed on various amorphous carbons (a; b; d) and zeolites (c; e). From Suh et al. (1991).

term which is linear with xenon density). Because of the relative sizes of the xenon atom and the cavity, this distribution is likely to be quantized. This could result in discrete peaks. If mobility is less restricted, the peaks are broadened; fast exchange gives a narrower single peak. An intermediate situation is consistent with their data, showing anisotropic broadening.

Chemical shift anisotropy (CSA) is not expected for nuclei in rapid motion. It could conceivably be observed for xenon under conditions in which it is immobilized. There is disagreement as to whether CSA is observed in the adsorbed xenon NMR signal. The anisotropic environment of micropores may contribute to chemical shift anisotropy, according to Ripmeester and Ratcliffe (1995). They argue that the more

attractive the xenon-pore wall interaction is, (i.e., the more the xenon sticks to the pore wall), the more likely it is that there will be anisotropic effects. They reported a marked change in line shape with xenon loading in molecular sieve ALPO-11, both experimentally observed (**Figure 2.5**) and simulated.

Part of the line shape does not change with xenon loading. The continuous variation of the isotropic component with xenon loading is treated as a problem involving three chemical shift tensors characteristic of different site types. Ripmeester and Ratcliffe (1995) contrast this "dynamic" model of xenon CSA to the "simplistic" explanation of Springuel-Huet and Fraissard (1989) who depict the xenon electron cloud as first being molded by the pore channel and then influenced by additional xenon atoms as they pack along the channel.

Seidel et al.(1996) respond to Ripmeester and coworkers (1995, 1988) and Springuel-Huet and Fraissard (1989), with the assertion that linewidths and line shapes cannot be ascribed to static anisotropy. Their study is on ZnY zeolites with an inhomogeneity of Zn cation concentrations, for which a distribution of *isotropic* chemical shifts can be calculated. Their model also accounts for multi-site adsorption with differing adsorption constants, that is, different concentrations. The experimental linewidths fit the model. This means that they were found to be sensitive to the distribution of adsorption site concentrations (especially at higher pressure) and sample inhomogeneities giving a distribution of averaged isotropic shifts. They note that they eliminated the problem of insufficient equilibration time as a contributor to the linewidth.

Figure 2.5. Change in line shape with xenon loading for xenon adsorbed in molecular sieve ALPO-11. From Ripmeester and Ratcliffe (1995).

2.5.5. ^{129}Xe NMR applied to diffusion and exchange processes

Diffusion and exchange have a significant effect on NMR spectra of ^{129}Xe adsorbed on porous solids. Even in studies whose goals are unrelated to diffusion or exchange, their effects must be taken into account when evaluating ^{129}Xe NMR spectra. The extent of the possible influence of exchange on NMR spectra is made clear in a study by Ripmeester and Ratcliffe (1993) which showed powder packing effects on the chemical shift in a zeolite as well as quite severe particle size effects due to exchange averaging of ^{129}Xe signals in a mesoporous controlled-pore glass (**Figure 2.6**).

Figure 2.6. ^{129}Xe NMR spectra of xenon adsorbed on 40Å Vycor glass, from large (a, diameter $> 250\ \mu\text{m}$) to small (e, diameter $< 38\ \mu\text{m}$) particle sizes. Intra/extraparticle diffusion becomes more marked as the particle size decreases. From Ripmeester and Ratcliffe (1993).

Ryoo et al. (1994) report the effect of blocking the intercrystalline diffusion in zeolite mixtures. Fast xenon exchange averages xenon signals in NaY, CaY, and/or Pt/NaY mixtures. After coating the crystallites with a polymer in to block diffusion, the ^{129}Xe resonances from two mixed zeolites were distinguishable, as were resonances from xenon interacting with internal vs. externally deposited metal clusters. Chen and Fraissard (1992b) showed that different compositions in NaY/ CaY zeolite mixtures can be distinguished on the basis of relative intensities of xenon signals. The signals coalesce in mechanically mixed samples. Ripmeester and Ratcliffe (1993) emphasized the importance of accounting for the influence of exchange on the chemical shift before using it in applications such as pore size determination.

There are several ^{129}Xe NMR methods that have been used to observe and obtain quantitative information about diffusion or exchange. These are two-dimensional exchange spectroscopy (2D-EXSY), saturation transfer, pulsed field gradient (PFG), estimation by frequency difference between signals, and monitoring the effect on a xenon signal of a second diffusing species. In its application to diffusion and exchange, ^{129}Xe NMR has considerable strengths, because demonstrable physical principles underly its interpretation. This is in contrast to the numerous ways to analyze chemical shift that are based on conflicting sets of empirical evidence. The diffusion and exchange methods will be described with some examples of the kinds of information that can be obtained. The diffusion coefficient (D) and Einstein's relation of root-mean-square distance $(r^2)^{1/2}$ to D will be used frequently and are thus defined here:

$$D = D_0 \exp(-E/RT)$$

$$(r^2)^{1/2} = (6Dt)^{1/2}$$

where E is the activation energy, R is the gas constant, and T is the temperature (K).

In 2D-EXSY, magnetization transport during a time t_{mix} is measured, and the two-dimensional spectra are a direct measure of mass transport. Jeener et al. (1979) developed the theoretical scheme of 2D-EXSY. 2D-EXSY has been used with good results in ^{129}Xe NMR (Tomaselli et al., 1993; Larsen et al., 1993; Simpson et al., 1995). An example is its application by Moudrakovski et al. (1995) to the measurement of exchange rates between NaX and NaY particles in a mixture. Cross peaks that develop during the time t_{mix} illustrate the time frame of exchange of xenon between sites in NaX and NaY crystallites, **Figure 2.7**. The effective diffusion constant of xenon in the mixture was calculated as a weighted average of the inter- and intra-particle diffusion constants.

Saturation transfer, and the similar magnetization transfer, are one-dimensional methods to follow diffusion based on the saturation or inversion of one resonance, after which the recovery of that signal and others originating from other possible exchange sites are monitored. Jameson et al. (1994) used magnetization transfer to measure rate constants for cage-to-cage transfer of xenon atoms in zeolite NaA. Selective inversion of one resonance was accomplished with a DANTE sequence.

Pulsed field gradient (PFG) NMR has been applied to ^{129}Xe diffusion in zeolites (Heink et al., 1990; Karger et al., 1993). In this NMR technique, spin-echo

Figure 2.7. 2D-EXSY ^{129}Xe NMR spectra of xenon adsorbed in a mixture of NaX and NaY zeolites showing development of cross peaks with increasing t_{mix} . The appearance of cross peaks indicates the time scale in which the two xenon populations contact each other through diffusion. From Moudrakovski et al. (1995).

intensity is affected by an inhomogeneous magnetic field (magnetic field gradient) superimposed on the constant magnetic field for two time intervals. The relationship of spin-echo intensity to features of the gradient pulses is related to, and can be used to calculate, the mean-square displacement of the observed nuclei during the observation time. The mean square displacement of adsorbed xenon can be measured as a function of time, and from this Einstein's relation gives the diffusion coefficient D .

One of several techniques used on polymer blends by Mansfield et al. (1995) was based on the separation of two xenon signals in a polypropylene matrix with small domains of ethylene-polypropylene copolymer. The frequency separation of two signals for xenon in the polymer blend was used to obtain an upper limit for the

diffusion constant D for xenon in the rubbery phase. The time obtained from the frequency separation and the rubbery domain size taken as the diffusion distance, were plugged into Einstein's relation to yield an estimated diffusion coefficient.

Xenon also has potential as an indicator of diffusion of a co-adsorbate. Bansal and Dybowski (1990) tried looking at the effect of diffusing water on coadsorbed xenon in a zeolite. It was possible to measure time-dependent changes in the water concentration profile by following changes in the ^{129}Xe NMR signal.

2.5.6. Information about porosity in solids from non-xenon NMR

Gallegos et al. (1987) utilized the T_1 of water adsorbed in mesoporous controlled-pore glasses and silica to determine pore size distributions. In their two-fraction fast-exchange model, there are two environments for water in the pore, on the wall and in the pore central area, and the water molecules exchange between them. These positions should affect the T_1 of water differently. The T_1 is directly related to the pore surface area-to-volume ratio. From this model, the change in T_1 with pore size can be predicted. The NMR results were found to agree with mercury porosimetry measurements on the silicas.

Liaw et al. (1996) also used T_1 relaxation time of fluid in porous media (such as sandstone or chalk) to estimate pore volume-to surface-area, and develop a method to characterize fluid phase distribution when two immiscible fluid phases are present. The model was verified using samples of known surface-area-to-volume ratios.

The use of T_1 of adsorbed fluid is a valuable method, in that its results are accurate when tested on pore systems of known characteristics, it is nondestructive to the solid, it can be used with the three dimensionality of the pore system intact, and it gives more information than mercury porosimetry. It is useful for examining pore spaces that are large enough for the adsorbate atoms to exchange between walls and pore centers. This means that the applicability of such a model is to mesopores and above, spaces that can accommodate at least several adsorbate molecular diameters. In micropore spaces, which can be small enough for only one adsorbate molecule to fit, the assumptions central to these models are not met. While it may be possible to extend

this approach to microporous materials by further development of theory, it is not applicable in its current state.

Deuterium (^2H) NMR is a technique applicable to the investigation of diffusion in porous networks. Deuterated molecules can produce a variety of line shapes depending on molecular motion, and from this, information about the pore structure itself could be derived. Interpretation requires an ordered pore network, and the random nature of many porous networks are a drawback for this technique. D-NMR of benzene in microporous boehmite was investigated by Fukasawa et al. (1994).

Chapter 3

USE OF ^{129}Xe NMR FOR DETERMINING MICROPORE DIAMETERS IN COAL

3.1 Introduction

The experiments described in this chapter are used to determine the micropore sizes in coal by determining the pressure dependence of the chemical shift of ^{129}Xe adsorbed in powdered coal. They also introduce the general characteristics of straightforward ^{129}Xe spectra of coal and illustrate how their appearance varies among individual samples that encompass a range of coal ranks. To aid in this characterization, we have compared the calculated pore diameters and other features of the NMR spectra to the coal surface areas determined by volumetric adsorption of nitrogen and carbon dioxide. The following chapters will describe the investigation of other ways in which ^{129}Xe NMR may be used to describe the pore structure in coal, with emphasis on determining whether micropores in coal are connected or isolated.

3.1.1. Determination of micropore diameter using ^{129}Xe NMR

Demarquay and Fraissard (1987) showed empirically that the pressure dependence of the ^{129}Xe NMR chemical shift is related to the pore sizes in several zeolites. While their mean free path model apparently does derive an accurate pore diameter in selected zeolites, and in a microporous carbon (Wernett et al., 1990), the use of this theory remains controversial. Theoretical objections have been raised about the assumption that random collisions occur among xenon atoms in the adsorbed state,

(Annen et al., 1990; Ripmeester and Ratcliffe, 1990), as well as objections to some experimental results obtained using the mean free path model (Annen et al., 1990).

In Demarquay and Fraissard's study (1987), the chemical shift of ^{129}Xe extrapolated to zero pressure in zeolites of known pore dimensions was found to be a function of the mean free path of the gas. The method is applicable for xenon at low pressure (< 1 atm), adsorbed in pores that are sufficiently small to give a mean free path for xenon of 1-6 Å. The spectra were taken at a series of xenon pressures, and the chemical shift was plotted vs. the pressure; the mean free path of the adsorbed xenon can then be calculated from the intercept. Pore diameter can be calculated based on the known or assumed pore geometry.

This model has been applied to a microporous carbon of reasonably well defined pore structure by Wernett et al. (1990), and the calculated pore diameter was within the expected range. The model may be applicable to coal, although it must be borne in mind that coal is much more heterogeneous both physically and chemically than either zeolites or microporous carbons, and that paramagnetic species and/or impurities in coal can affect the NMR data. In a study by Tsiao and Botto (1991), analysis of the ^{129}Xe NMR spectra of three Argonne Premium coals gave micropore diameters in the 6-9 Å range. For an Illinois #6 coal sample, two distinct resonances were observed, suggesting that pore regions of different physical or chemical makeup are distinguishable by ^{129}Xe NMR.

There are unresolved issues related to the application of this pore diameter calculation to coal that are apparent in Tsiao and Botto's study (1991). Chief among them are related to the assignment of chemical shift values to the broad, sometimes asymmetrical resonance signals of xenon adsorbed in coal. Tsiao and Botto treat them as overlapped peaks and they deconvolute the spectra in order to make the chemical shift assignments. However, overlapping of peaks was clear on visual inspection for only one of their samples. In general, more uncertainty is brought into the chemical shift measurement for broad signals from xenon in coal compared to the much narrower signals in zeolites, from which the pore diameter calculation was developed.

There were indications in Tsiao and Botto's study (1991) that Demarquay and Fraissard's model (1987) may not be directly applicable to coals. The chemical shift vs. pressure relationship was not linear in the entire pressure range used; the intercepts

were obtained using nonlinear fits, and whether the intercepts from these fits give valid information on pore diameter is not clear. A general difficulty, not only with Tsiao and Botto's study, but with any study of this kind on coal, is that there exists no independent test of the micropore diameters in coal, and thus the results of this method aren't absolutely verifiable. Nor is there a test of what type of chemical shift-pressure relationship (e.g., linear, nonlinear), if any, gives a correct pore diameter.

Given the drawbacks inherent in testing a controversial theory to obtain information on essentially unknown pore structures in coal, the approach used in this study is to apply Demarquay and Fraissard's (1987) model as a starting point only. Other ways to derive meaningful information from NMR data will be explored by correlating features of the NMR spectra such as chemical shift and linewidth (which contain useful information regardless of the model) with independently verifiable data such as the surface area and coal rank.

3.1.2. Effect of powder density

The effect of increasing the powder density was investigated as a test of whether the outcome of the pore diameter calculations would be significantly affected by variation in routine sample handling procedures. The packing density, and particle size as well, could significantly alter ^{129}Xe spectra when moderate to fast intra/extraparticle xenon exchange exists. This was brought up in a study by Ripmeester and Ratcliffe (1993). Powder density changes in a zeolite were found to change the ^{129}Xe chemical shift at a given pressure. Particle size variation in a 40 Å controlled pore glass demonstrated a significant intra/extraparticle gas exchange effect. It is necessary to establish the sensitivity of the coal spectra to particle size and packing variations in order to estimate the reliability of chemical shift assignments used to calculate pore diameter. Particle size is examined in detail in Chapter 4, and powder density is considered in this chapter.

In order to explain the potential effect of increased density, physical exchange and its effect on NMR spectra of the exchanging species need to be described briefly. In an open, interconnected pore system, the gas may exchange in and out of the pores.

The adsorbed, intraparticle xenon has a significantly higher frequency signal than the extraparticle gas; thus, xenon in these two environments are readily distinguishable by ^{129}Xe NMR. If exchange occurs rapidly on the NMR timescale, the result is one signal which is a weighted average of the two environments sampled by the gas. The relevant NMR timescale is the time equivalent of the frequency difference between the two signals (Kaplan and Fraenkel, 1980). As an example, for two xenon signals at 0 and 160 ppm in an 8.4 T magnetic field, originating from ^{129}Xe located outside and inside the particles in a powdered coal sample, the frequency difference is 16,000 Hz. Diffusion of xenon gas into and out of a coal particle in about 6×10^{-5} s (60 μs) or less would average the two NMR signals. In general, at exchange rates that are slow on the relevant timescale, the signals are distinct and representative of the two environments, but at intermediate rates, the signals are displaced from these positions towards the average of their chemical shifts.

Increasing powder density by compression is a test, but not a proof, of whether physical exchange of adsorbed xenon is significant for the material studied. The NMR signal should not be affected if exchange is slow or is not occurring (all other things being equal). It should be displaced to greater chemical shift values for a given xenon pressure if exchange is intermediate. This is because there will necessarily be less exchanging gas in interparticle space if the volume of this space has been decreased, and the gas will experience more contact with the solid, thus increasing the chemical shift.

A possible drawback of pressing the powder is that the micropores may be deformed in the process, although this is unlikely. Experiments that do not require compression of the sample are available to approach the problem of demonstrating that an exchange process occurs. These include variation of particle size, discussed in Chapter 4, and saturation transfer, discussed in Chapter 5.

3.2. Experimental

Six coals from the Penn State/DOE coal sample bank were examined: lignite (ligA), subbituminous coal (subB), two high volatile bituminous coals (hvCb, hvAb),

low volatile bituminous coal (lvb) and anthracite (an). All samples used for the experiments in this chapter are -60 Tyler mesh. Pertinent data for the sample set are shown in **Table 3.1**. Samples were prepared on a two-arm vacuum/gas manifold. A 10-mm NMR tube fitted with a Rototite J. Young-type valve (Wilmad) was filled to a height of approximately 4 cm. The NMR tube attaches directly to the vacuum line, and may be opened to vacuum or gas without removal of the tube. Loose powder samples were loaded directly into the NMR tubes. Pressed pellets of coal were prepared using a die press at 3000 psi for approximately one minute. Pellets were broken into pieces about 4 mm in diameter and loaded into the tube. Smaller pieces and dust were discarded.

Samples were outgassed at 100 °C under vacuum for a minimum of 18 hours to a pressure of 5 μ m Hg. Each sample was cooled to room temperature under vacuum and natural abundance xenon gas (99.97% purity) was then introduced by closing the vacuum side and opening the gas side valves. The pressure in the xenon side of the manifold was monitored with a Barocel dual capacitance manometer and Televac MM200 digital gauge controller. No drop in xenon pressure in two minutes was taken as a reasonable equilibrium criterion. Samples were equilibrated for an average period of 40 minutes. The gas side valve and the Rototite valve on the NMR tube were each sealed and the NMR tube was removed from the manifold. The NMR tube was then inserted in the spectrometer. The probe was tuned after the insertion of each sample.

The ^{129}Xe NMR spectra were taken at a series of xenon pressures between 250 and 700 torr. Xenon pressure was changed for samples already exposed to xenon by returning the NMR tube to the manifold and applying vacuum to 10 μ m Hg or less, then opening the tube to xenon. For pressures over 500 torr, two or more aliquots (fillings of the gas arm of the manifold) were required.

The spectra were acquired on a Bruker AMX 360 NMR instrument operating at 99.61 MHz for xenon. A 90 degree pulse width was employed with 1.5 or 2 s delay. An echo pulse sequence of the form $(\pi/2)_x - \tau_1 - \pi_{xy} - \tau_2 - \text{AQ}_x$ was used to acquire the spectra for the Blind Canyon (DECS-6) coal. Between 1,500 and 5,000 scans were required for good signal-to-noise ratio for most coals. Spectra were referenced to the chemical shift of 1 atm xenon gas, set as 0 ppm.

Table 3.1. Origin, rank and elemental analysis of the coal sample set.

Sample #	Seam	State	Rank	Elemental Analysis (dmmf):			
				%C	%H	%O	mineral matter (dry)
DECS-11	Beulah	ND	lig A	74.4	4.4	19.9	11.0
DECS-26	Wyodak	WY	subB	76.3	6.1	16.2	8.6
DECS-7	Adaville#1	WY	hvCb	77.4	5.5	15.1	4.8
DECS-6	Blind Canyon	UT	hvAb	81.7	6.2	10.0	6.7
DECS-19	Pocahontas#3	VA	lvb	90.5	4.9	2.9	5.4
DECS-21	Lykens Valley #2	PA	an	91.9	3.9	2.9	12.6

dmmf: dry, mineral-matter-free basis

Surface areas for four of the coals were measured using a Quantachrome Autosorb-1 sorption system. Approximately 0.3-0.4 g of each sample was outgassed 12 to 24 hours at 110 °C. The nitrogen adsorption isotherms were measured at 77K. Seventeen adsorption points and nine desorption points were recorded, and standard multi-point BET plots (Gregg and Sing, 1982) were prepared. The carbon dioxide isotherms were measured at 273 K. Fifteen adsorption and nine desorption points were recorded, and standard Dubinin-Radushkevich plots (Gregg and Sing, 1982) were prepared.

3.3 Results and Discussion

The ^{129}Xe NMR spectra of six coals at varying xenon pressures are shown in **Figures 3.1 - 3.6**. In general appearance, these spectra usually consist of two signals. A broad signal, 2500 to 8000 Hz wide, at 100 to 200 ppm, originates from ^{129}Xe adsorbed in the internal surfaces of the coal particles. The signal profile is usually irregular rather than smooth. Some variation of the signal shape with increasing xenon pressure is observed, which may be due to the filling of different regions of the internal porosity as the pressure is increased. The shape variation may also be due to some extent to the difficult phasing of the spectra, which is discussed in Section 3.3.1.

The second signal at 0 to 5 ppm is sharper and narrower. There is considerable variation in its intensity, and it is out of phase with the adsorbed gas signal in some spectra. These variations in appearance will be discussed in Section 3.3.4. The 0 to 5 ppm signal is from ^{129}Xe that is comparable in chemical shift to free xenon (0 ppm at the pressures used in this thesis). Xenon atoms giving rise to this signal may be in the interparticle space, and have been referred to as such in the literature (Wernett et al., 1990; Ripmeester and Ratcliffe, 1993). It should be noted that this signal could also arise from xenon atoms in relatively large enclosures such as macropores. This signal will be referred to as the external gas signal.

Xenon giving rise to the external gas signal has enough contact with the solid surfaces to reduce its T_1 relaxation time considerably from that of true free xenon (ca. 12,000 seconds), such that it is detectable in the short-recycle timescale (2 s) used. The

T_1 relaxation time for xenon adsorbed in coal is on the order of 30 - 200 ms, and some shorter T_1 values, 15-20 ms, have been reported (Zhu, 1994). The extraparticle gas signal in ^{129}Xe spectra of many coals is detectable acquired with 2 s or more recycle delays. Both the intra- and extraparticle gas signals are distinguishable for all coals examined with the exception of the Lykens Valley anthracite, which exhibited only one signal, comparable to the intraparticle (or adsorbed) gas signals in the other coal spectra.

3.3.1. ^{129}Xe NMR spectra of coals

For most coals in the sample set the NMR spectra could be obtained satisfactorily using a standard Bloch decay with a 90 degree pulse. Acoustic ringing of the baseline was a common problem. It contributed to possible signal deformation and difficult phasing of some of the spectra. Baseline ringing could usually be modulated by a combination of appropriate delay between pulse and acquisition, and baseline correction. NMR spectra of the Blind Canyon hvA bituminous coal sample were not improved by these procedures. The signal was far weaker than for the other coals, and acoustic ringing was pronounced in the spectra. The weak signal indicates that adsorption of xenon by this coal is less than in the sample set as a group.

In an effort to eliminate the problem with acoustic ringing, an echo pulse sequence was used to acquire the Blind Canyon coal spectra. These are shown in **Figure 3.4**. Using this pulse sequence, acquisition of the ^{129}Xe signal is delayed while the ^{129}Xe magnetization is refocused. This allows the xenon signal to be acquired (as an echo) after the acoustic ringing of the probe has decayed to some extent. The resulting spectra were free of baseline deformation. The adsorbed xenon signal was readily detected and presented no phasing problems, as occurs often with Bloch decays. This result indicates that acquisition of ^{129}Xe spectra of coal using an echo pulse sequence certainly improves weak spectra, and may also be the preferable way to acquire all spectra in future work. The echo spectra in this chapter were acquired after the Bloch decay spectra for the coal sample set had been completed.

Figure 3.1. ^{129}Xe spectra of the lignite. (a) 540 torr; (b) 410 torr; (c) 340 torr.

Figure 3.2. ^{129}Xe spectra of the subbituminous coal. (a) 619 torr; (b) 565 torr; (c) 393 torr; (d) 303 torr.

Figure 3.3. ^{129}Xe spectra of the hvC bituminous coal. (a) 656 torr; (b) 514 torr; (c) 347 torr; (d) 280 torr.

Figure 3.4. ^{129}Xe spectra of the hvA bituminous coal. (a) 666 torr; (b) 520 torr; (c) 435 torr; (d) 379 torr.

Figure 3.5. ^{129}Xe spectra of the Iv bituminous coal. (a) 683 torr; (b) 538 torr; (c) 366 torr; (d) 322 torr.

Figure 3.6. ^{129}Xe spectra of the anthracite. (a) 620 torr; (b) 518 torr; (c) 395 torr; (d) 350 torr.

3.3.2. Chemical shift vs. pressure

Plots of the ^{129}Xe chemical shift vs. pressure are shown in **Figures 3.7 - 3.13**. The relationships are linear in all cases, with high values of the correlation coefficient (>0.97). The spectra do not appear to be composed of overlapped signals, with the exception of the hvC bituminous coal at higher pressures which has two distinguishable adsorbed xenon signals (see Figure 3.3). The chemical shift values are assigned by taking the highest point on the signals. Minor variations in phasing of the spectra produce an uncertainty of about ± 2 ppm in the assignment of chemical shifts of the lignite and subbituminous coal spectra, and ± 1 ppm in the remainder of the spectra.

Micropore diameters were calculated from the intercepts δ_s of the chemical shift vs. pressure plots, using the method of Demarquay and Fraissard (1987). The hvC bituminous coal was treated as two signals and separate calculations were made for each one. The uncertainty in the chemical shift values was assigned to the intercepts to calculate the uncertainty in the pore diameter. The results are summarized in **Table 3.2**.

mean free path **l** of Xe in the pore (in Å):
$$l = [(243)(2.054)]/\delta_s - 2.054$$

pore diameter **d**, assuming a cylindrical pore (in Å):
$$d = l + 4.4$$

The determining factor for obtaining the pore diameter by this technique is the value of the chemical shift vs. pressure intercept, which is inversely proportional to the pore diameter. The plot of intercept vs. rank (% C) for the entire sample set of six coals is shown in **Figure 3.14**. The trend in intercept with coal rank is bowl-shaped, with smaller intercepts at low rank, increasing through the bituminous range and then decreasing again with rank. This gives pore diameters with the opposite tendency, with relatively larger micropores at low rank becoming smaller in the bituminous range, and

Table 3.2. ^{129}Xe NMR chemical shift vs. pressure data and micropore diameter for six coals.

Coal	Seam	Rank	% C (dmmf)	Intercept δ_0 (ppm)	Correlation coefficient	Pore diameter (Å)
DECS-11	Beulah	lig A	74.2	102 $\pm$ 2	0.99	7.2 $\pm$ 0.1
DECS-26	Wyodak	subB	76.3	101 $\pm$ 2	0.98	7.3 $\pm$ 0.1
DECS-7	Adaville	hvCb	77.4	A 113 $\pm$ 1 B 114 $\pm$ 1	A 0.98 B 0.97	A 6.75 $\pm$ 0.05 B 6.70 $\pm$ 0.05
DECS-6	Blind Canyon	hvAb	81.7	155 $\pm$ 1	0.97	5.56 $\pm$ 0.05
DECS-19	Pocahontas	lvb	90.5	143 $\pm$ 1	0.99	5.83 $\pm$ 0.05
DECS-21	Lykens Valley	an	91.9	96 $\pm$ 1	0.98	7.50 $\pm$ 0.05

Figure 3.7. Chemical shift vs. pressure for the lignite.

Figure 3.8. Chemical shift vs. pressure for the subbituminous coal.

Figure 3.9. Chemical shift vs. pressure for the hvC bituminous coal, signal A (higher frequency).

Figure 3.10. Chemical shift vs. pressure for the hvC bituminous coal, signal B (lower frequency).

Figure 3.11. Chemical shift vs. pressure for the hvA bituminous coal.

Figure 3.12. Chemical shift vs. pressure for the lv bituminous coal.

Figure 3.13. Chemical shift vs. pressure for the anthracite.

larger again at high rank, **Figure 3.15**. This pattern is reminiscent of the trend in coal surface area vs. % C (Gan et al., 1972) and suggests that the micropore diameter may be directly related to coal surface area.

3.3.3. Comparison of the NMR and adsorption data

The nitrogen and carbon dioxide surface areas of five of the coals are shown in **Table 3.3**. The isotherms are provided in the appendix. Due to damage to the adsorption apparatus unrelated to these experiments, the nitrogen isotherm of the hvC bituminous coal was not obtained, and the anthracite was not examined. The NMR-derived micropore diameter calculated from the NMR data was compared to the CO₂ (Dubinin-Radushkevich) surface area, **Figure 3.16**. There is not a one to one correspondence overall. The pore diameter appears to increase sharply for coals of about 200 m²/g. The effect is apparently limited to a range of surface areas under 300 m²/g. There is an outlying point for the highest-surface-area coal (subbituminous). The slope of chemical shift vs. pressure as a function of coal surface area is shown in **Figure 3.17**. This plot has the same general shape as that of micropore diameter vs. surface area. The subbituminous coal is again an outlying point. Overall there are not enough coals in the group to give a good indication of the trends in ¹²⁹Xe NMR features with surface area. Surface areas of coals generally correlate with coal rank as shown by Gan et al. (1972), but they exhibit a very large scatter as well. If the relationship of pore diameter to coal surface area is studied in the future, ¹²⁹Xe NMR spectra of several coals at each rank would be desirable to allow for the surface area scatter.

The average pore diameters estimated from the D-R plots (CO₂, 273K) are compared to the NMR-derived pore diameters in **Table 3.4**. The micropore diameters from the D-R plots are in the same general size range as the NMR-derived pore diameters, 5.9 to 6.8 Å. The most dissimilar values are that of the lignite (5.9 Å from the D-R plot, 7.2 Å from NMR) and the hvA bituminous coal (6.5 Å vs. 5.6 Å).

Figure 3.14. Intercept (δ_s , ppm) of chemical shift vs. pressure plots for the six coals, plotted vs. rank (%C).

Figure 3.15. NMR-derived micropore diameters for the six coals, plotted vs. rank (%C).

Figure 3.16. NMR- derived micropore diameter vs. CO₂ (Dubinin-Radushkevich) surface area for five of the six coals studied.

Figure 3.17. Slopes (ppm/torr) of chemical shift vs. pressure plots for five coals, plotted vs. CO₂ (Dubinin-Radushkevich) surface area.

Table 3.3. Surface areas of five of the six coals studied.

Coal	N ₂ BET area, m ² /g	CO ₂ D-R area, m ² /g
ligA	0.9	221
subB	22.7	491
hvCb	nd	236
hvAb	0.7	121
lvb	0.6	177

nd = not determined

Table 3.4. Average micropore diameters estimated from D-R plots (CO₂, 273K) vs. pore diameter calculated from ¹²⁹Xe NMR spectra.

Coal	D-R plot, Å	¹²⁹ Xe NMR, Å
ligA	5.9	7.2
subB	6.8	7.3
hvCb	6.1	6.8
hvAb	6.5	5.6
lvb	6.4	5.8

3.3.4. Intensity of the external gas signal.

This signal appears at about 0-5 ppm for five of the six coals, as seen in **Figures 3.1 - 3.6**. The absolute intensity of the signal may vary with the number of scans collected for the spectrum and with the pressure of the gas; higher xenon pressure and/or more scans corresponding to stronger signals. The external gas signal intensity relative to the adsorbed gas signal intensity (at 100-200 ppm) may increase at higher pressures - an indication that at the higher pressure, more gas is outside the micropores. Analysis of relative intensity of the external gas signal with pressure changes may give useful information about the adsorption behavior of the coals. For example, once the external gas signal begins to increase in relative intensity, the micropore filling stage may be completed.

No external gas signal is observed for -60 mesh anthracite or for the microporous carbon discussed in Chapter 6. This may be due to exchange averaging of the signals, the signal may be saturated due to an excessively short delay, or the internal surfaces of the adsorbent may take up most of the available gas at the pressure used. If the external signal is not from extraparticle gas, but from xenon relatively restricted to large pores, its absence in some samples may indicate the absence of that structural feature in the samples.

In the case of the anthracite, the low frequency of the adsorbed gas signal (ca. 110 ppm, **Figure 3.6**) compared to that of the other coals (140-200 ppm, **Figures 3.1 - 3.5**) is consistent with the possibility of exchange averaging between adsorbed gas and external gas. Based on magnetization transfer experiments discussed in Chapter 5, however, intra/extraparticle exchange occurs in this anthracite but is not fast, ruling out exchange averaging. Saturation is unlikely to be the cause, since additional spectra were obtained with delays increased from 2 to 10 s without detecting an external gas signal. The remaining possibility is that the external signal is from large pores rather than external surface.

Interestingly, the external gas signal is detected for larger particle sizes of the anthracite, and this is unlikely to be due to an exchange effect in the small particles. This data is reported and discussed in detail in Chapter 4. The saturation transfer experiments in Chapter 5 indicate that the xenon populations that give rise to the two signals in larger particle size anthracite exchange on a time scale much shorter (~ 800 ms) than that characteristic of the diffusion of xenon from the particle exterior to its equilibrium locations (~ 15 hours). The explanation is advanced in the conclusion section that the external gas signal at 0 - 5 ppm is actually from xenon in larger pores within the particle. The absent signal in small anthracite particles is most likely due to the presence of much less macroporosity in these particles. The large pores may be the regions that break during the grinding process, effectively reducing their numbers as the particle size is decreased.

3.3.5. Signal shape and symmetry

There exists a qualitative relationship between ^{129}Xe signal symmetry and rank. ^{129}Xe NMR spectra for six coals of increasing rank are shown in **Figure 3.18**. The trend in signal shape is toward a narrower, more symmetrical signal as rank increases. The effect is most pronounced in the 90 and 92 %C samples. The linewidths plotted vs. coal rank (carbon content) are shown in **Figure 3.19**. The linewidth decreases linearly with increasing rank. Possible origins of the change in signal shape are increasing chemical homogeneity within the pores and narrowing pore size distribution. Increase in chemical homogeneity as coalification progresses is well established (Van Krevelen, 1993). Further investigation into the source of the linewidth is described in Chapter 5; it supports a narrowing of the adsorption spaces (pore geometrical or chemical characteristics may define the adsorption space) as rank progresses.

Figure 3.18. ^{129}Xe signals for the six coals at comparable pressures, 500 to 600 torr.

Figure 3.19. Linewidths of the ^{129}Xe NMR signals for xenon adsorbed in coal plotted vs. coal rank (carbon content).

3.3.6. Slope of chemical shift vs. pressure

The location of the chemical shift is influenced by both the chemical makeup of the pore surfaces and the frequency of collisions of Xe with the pore walls. In samples such as coal, in which neither the pore size nor the chemical composition can be controlled, the influence of each cannot be separated in order to treat chemical shift as a direct measure of pore diameter. Given these considerations, measurements of pore diameters in coals using the method of Demarquay and Fraissard (1987) cannot be assumed *a priori* to be reliable.

In this study the slope is investigated as an alternative or supplement to the chemical shift as a source of information on the pore structure. The slope varies considerably for the samples studied. While the slope of chemical shift vs. pressure has not been previously used in the measurement of pore sizes, it is thought to be an indicator of some aspect of pore structure. For example, Johnson and Griffiths (1987) postulated that it may be related to micropore volume. It is logical to consider larger pores as more accessible to xenon, in that gas diffusion is less restricted in larger than in smaller pores; more xenon may enter a larger pore for a given pressure increase, resulting in a steeper variation of chemical shift with pressure (i.e., a greater slope).

The slopes (ppm/torr) for six coals are plotted vs. rank (%C) in **Figure 3.20**. There is a general decreasing trend with rank (%C) for this group. Slopes are the highest and the data have the most scatter in coals under 80%C. Comparison with the rank dependence of the intercept (**Figure 3.14**) shows that the relationships of slope and intercept to rank are clearly not similar. The relationship of the slope to surface area (**Figure 3.17**) shows a steep rise at about 200 m²/g.

The examination of slopes for this group of coals provides clues, but not a final answer, on their relationship to properties of the coal surface. This study indicates that the determinants of slope and intercept of the chemical shift vs. pressure plots are probably different properties of the adsorbent, and that within a limited range, slope increases with surface area, and decreases with coal rank. Since coal rank and surface area are related in a general way, both observations are probably due to surface area changes.

Figure 3.20. Slopes (ppm/torr) of chemical shift vs. pressure plots for the six coals, plotted vs. rank.

3.3.7. Spectra of pressed pellets vs. loose powder

Investigation of the ^{129}Xe NMR signals of both pressed pellets of coal and loose powder was performed. Coal samples examined previously have been loose powders. If the chemical shift of pellets increases with respect to the loose powder, at a given equilibrium pressure of xenon, it would be an indication that intra- and extraparticle gas is exchanging on the NMR timescale. The pressed pellets of hvC bituminous coal were examined at a series of xenon pressures. Sample spectra are shown in **Figure 3.21**. There was a significant effect on both the chemical shift and the signal shape as a result of increasing powder density. The consequences for the chemical shift-pressure dependence and pore diameter calculations are summarized in **Table 3.5**.

The chemical shift extrapolated to zero pressure (δ_s) increased from by 10%. The decrease in the calculated pore diameter was relatively small, from 6.7 to 6.3 Å. The increase in chemical shift may be interpreted as due to greater gas-solid interaction and/or less exchange averaging with gas adsorbed on the external surface. If so, the difference in pore size calculated after pressing the pellet would be due to a more accurate intercept, and would not indicate an actual change in pore size. An alternative interpretation is that the change in chemical shift, and thus calculated pore size, is somehow due to an actual physical change in the microporous structure of the coal caused by compression. Changes in the appearance of the NMR signals before and after pressing the pellet may give some indication of whether sample compression can change the porous structure.

The signal shape was fairly symmetrical for the loose powder, with two overlapped signals apparent. This signal had approximately the same width but had fewer irregular features after pressing the powder. The second signal at higher frequency is apparently still present, but is not well resolved. It is closer to the main signal than in the powder.

A strong, sharp external-surface adsorbed gas peak is visible at about 0 ppm in the pressed pellet, which is much stronger relative to the barely visible external gas signal in the powder. The increased relative intensity indicates that in this preparation,

Figure 3.21. ^{129}Xe NMR spectra of the hvC bituminous coal. (a) loose powder (-60 mesh); (b) pressed pellet.

Table 3.5. Summary of NMR data for the hvC bituminous coal: pellets vs. powders.

	Powders	Pellets	Effect of increased density
Calculated pore diameter	6.7 Å	6.3 Å	decrease, 7 %
Chemical shift vs. pressure intercept	114 ppm	125 ppm	increase, 10%
chemical shift vs. pressure slope	0.05 ppm/torr	0.09 ppm/torr	increase, 73%

less of the gas dose was taken up in the internal surface of the coal particles compared to the powdered sample. These samples were brought to comparable pressures (the powder was the higher pressure). The shape change to a narrower external gas signal in the pressed pellet sample could indicate that there is less contact with the internal coal surface. The signal appears more free-gas-like, an indication of a more free-gas-like environment. This could occur through lessening of an exchange process or removal of the influence of the closeness of -60 mesh coal particles to each other.

The results of this experiment alone do not allow one to differentiate absolutely between exchange phenomena and pore compression interpretations of the powder density effect on the NMR spectra. However, the results of a magnetization transfer experiment described in Chapter 5 indicate that exchange between intra- and extraparticle gas in the hvC bituminous coal does occur, and does so fast relative to coals of higher rank. This finding supports the exchange-effect interpretation of the observed increase in chemical shift vs. pressure intercept with increased powder density. This exchange is not fast enough to make the spectra especially sensitive to sample packing, however. The changes produced by pressing the pellet were not severe; for example, the pore diameter calculation was affected by only 0.4 Å.

3.4. Summary

^{129}Xe NMR spectra as a function of pressure have been obtained for a sample set of six coals ranging in rank from lignite to anthracite. An echo pulse sequence was tested and found to produce good quality spectra with less deformation than observed in Bloch decays. The pressure dependence of the ^{129}Xe chemical shift was used to calculate micropore diameters (Demarquay and Fraissard, 1987). These ranged from 5.6 to 7.5 Å. Surface areas were measured using CO_2 and N_2 adsorption, and compared to features of the NMR spectra. The calculated pore diameter increases with surface area within a limited range. The strongest correlations found in this study were a decrease in linewidth with coal rank and a bowl-shaped dependence of calculated pore diameter on rank. This represents the first ^{129}Xe NMR results that illustrate the effect of coal rank.

The influence on the xenon signal of packing the powdered coal was tested and found to be a small decrease in calculated pore diameter, an increase in the chemical shift vs. pressure slope, and a significant change in the appearance of the NMR spectra. The fact that the chemical shift pressure dependence, (and less so, the calculated pore diameter) can be changed upon increasing the powder density is an indication that physical exchange between intra- and extraparticle gas may occur on the timescale of the NMR experiment for xenon adsorbed in the hvC bituminous coal. This is also an indication that the use of ^{129}Xe chemical shift to calculate the micropore sizes in coal should be viewed with caution. If intra/extraparticle gas exchange occurs fast enough to affect the NMR signals, these signals are no longer interpretable at face value by the Demarquay and Fraissard (1987) model.

It was also observed that the external gas signal does not appear in -60 mesh anthracite spectra, but does appear for larger particle sizes. Evidence is presented in Chapters 4 and 5 which indicates that this signal originates from xenon located in large pores and not the particle exterior.

Chapter 4

^{129}Xe NMR OBSERVATIONS OF THE ADSORPTION PROCESS: PARTICLE SIZE EFFECTS IN EQUILIBRIUM AND NONEQUILIBRIUM XENON ADSORPTION

4.1 Introduction

In his critique of the use of gas adsorption isotherms to characterize coal microporosity, Marsh (1987) noted that "the process of gas adsorption is one that can never be observed". An intriguing aspect of ^{129}Xe NMR is that, as this study will show, it *can* be used to observe the adsorption process as it occurs. This is of great potential utility in the exploration of the nature of the porous network in coals and carbons, because the features of interest - pore connectivity, open or closed porosity, extent of constriction of pore apertures - all affect the progress of adsorption of a gas into the pore system.

The majority of the evidence on the porosity of coal is taken from traditional volumetric or gravimetric adsorption experiments. In these measurements, all the information is derived from gas pressure or weight data (to determine, for example, gas uptake over time, or gas uptake at a particular temperature and pressure). The basic experimental evidence is quite straightforward. Its interpretation for microporous materials can be very complex, however; and it includes attempts to acquire crucial pieces of information that are something of a mystery based on the experimental data - such as when and if the gas forms a monolayer, when it is a multilayer, and whether the physical state of the adsorbed gas is known. In the ^{129}Xe NMR experiment, there is more detailed experimental evidence to draw from: the ^{129}Xe chemical shift is sensitive

to pressure, to the state of adsorbed xenon, and to the physical environment. This alone can indicate much more than how much xenon is adsorbed on the surface. This does not translate into answering questions about adsorption of gases other than xenon; thus it is not a method that will shed light on all adsorption processes per se. What it could do is give more information on those surfaces that cannot be characterized easily by gas adsorption and are not amenable to good alternative methods such as x-ray diffraction.

The number and relative intensities of xenon signals observed are indications of the number of different environments the gas is sampling in the solid, and the relative xenon population (above the threshold of detectability) in these environments. Here, these characteristics of the technique are exploited to describe a system where the xenon atoms are changing environments as diffusion progresses.

In particular, this study illustrates the utility of using ^{129}Xe NMR to track the xenon adsorption process for powder samples in a NMR tube. As these experiments are designed, diffusion occurs with a concentration gradient through a cylindrical bed of microporous particles. The gas diffuses through the interparticle space in the sample as well as through the porosity of the individual particles; this is termed transport diffusion. The time scale for transport diffusion, which is seconds to hours, is significantly affected by the configuration of the bed of particles, and thus is not solely characteristic of the porosity of the particles (Karger and Ruthven, 1992). The analysis will focus on what may be revealed by ^{129}Xe NMR about the rate of approach to equilibrium, the determination of achievement of equilibrium, and the meaning of changes in the external gas signal. The effect of particle size on the ^{129}Xe spectra for both equilibrium and nonequilibrium xenon adsorption is investigated in order to aid in the characterization of the micropore network.

4.2.Experimental

For the experiments to track the xenon adsorption process by NMR, three samples were prepared using a two armed, vacuum/gas manifold. Sphero carb 60-80 mesh (Phase Separations), a microporous carbon, was dried under vacuum for 2 hours at 110°C followed by at least 1 hour at room temperature. Two particle size fractions,

40-60 and -100 Tyler mesh, of Lykens Valley anthracite (Penn State/DOE coal sample bank) were dried for 6 hours at 100 °C and 24 hours at room temperature. All samples were prepared in 10 mm NMR tubes fitted with Rototite valves (Wilmad), which attach directly to the vacuum line. Samples were charged with xenon gas to a pressure of ~650 torr and were not allowed to equilibrate. The tubes were sealed and removed from the manifold within one minute. NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz.

The Spherocarb sample spectra were acquired over a three-hour period at 3- to 15-minute intervals; the -100 mesh anthracite spectra were acquired over a 6-hour period at 15-minute to 1-hour intervals; and the 40-60 mesh anthracite sample over a 24-hour period, at 7-minute to 2-hour intervals for 15 hours. An additional spectrum taken at 24 hours. A 90° pulse width was employed with 1.5 - 2 s delay. In order for changes that may occur quickly due to rapid adsorption to be detected, and to have the least possible averaging of spectral data on a system that is changing as the spectrum is acquired, each spectrum should represent a short window of time. Only the minimum number of scans necessary to distinguish the signal was used, which did not always give adequate signal-to-noise ratio. Sixteen scans per spectrum were used for Spherocarb, 88 scans per spectrum for the -100 mesh anthracite, and 160 scans for the 40-60 mesh anthracite. Xenon gas at 700 torr was used as an external chemical shift reference.

For the experiments designed to examine the particle size effect on the ^{129}Xe NMR spectra, four size-graded samples of an Upper Freeport mvb vitrinite were obtained, +60, 60-100, 100-200, and -400 U. S. mesh. Samples were dried, charged with xenon gas, and allowed to equilibrate for 40 minutes to a final pressure range of 630-650 torr xenon. A 90° pulse width was employed with 1.5 s delay. Between 3,000 and 5,000 scans were acquired. Xenon gas at 700 torr was used as an external chemical shift reference. The adsorption of xenon by the -400 mesh particle size sample was followed over time by NMR using the same procedure previously described, with 360 scan spectra acquired at 1 to 10-minute intervals over a 2-hr period, followed by acquisition of spectra at 16 and 24 hours.

4.3. Results and discussion

4.3.1. ^{129}Xe NMR under nonequilibrium xenon adsorption conditions: observation of the approach to equilibrium

The initial investigation of ^{129}Xe NMR spectra as a function of adsorption time was carried out on Spherocharb. Spherocharb is a high-surface-area ($\sim 900 \text{ m}^2/\text{g}$) carbon with significant micro- and macroporosity (Waters et al., 1988). Used as a gas chromatography column packing, Spherocharb separates light hydrocarbons (Robillard et al., 1979). ^{129}Xe spectra of Spherocharb are shown in **Figure 4.1**. (Chemical shift of the xenon signal for Spherocharb plotted vs. time is shown in **Figure 4.4**.) The adsorbed gas signal at 70-80 ppm grows in intensity with time, and the chemical shift decreases exponentially. Equilibrium as indicated by an unchanging chemical shift and is reached in 30 minutes. An external gas signal is not observed.

The anthracite sample, in two particle sizes, was used to compare changes in ^{129}Xe chemical shift, linewidth, and xenon uptake. Anthracites are lower-surface-area materials than Spherocharb, (about $400 \text{ m}^2/\text{g}$), although they have high surface area for coals. They are generally highly microporous and do not have a significant portion of meso- and macroporosity (Gan et al., 1972). There are indications that the larger porosity that they do have is in the form of cracks. These cut through regions of naturally developed porosity (Cody and Davis, 1991), as opposed to being part of a continuum, dendritic pore structure.

The anthracite -100 mesh spectra are shown in **Figure 4.2**, and the 40-60 mesh spectra in **Figure 4.3**. The chemical shift and the linewidth are plotted as functions of time for both particle sizes, **Figures 4.5 - 4.8**. Xenon uptake was measured separately on the manifold, plotted as pressure vs. time and used for comparison, **Figures 4.9 - 4.10**. The percent change in chemical shift vs. time is also plotted for the three samples, **Figure 4.11**. **Table 4.1** lists the time elapsed to 85% of total change in the chemical shift and gas uptake.

Figure 4.1. Time-dependent ^{129}Xe spectra of Sphero carb microporous carbon, 60-80 mesh, 4 minutes to 180 minutes from the time the sample was dosed with xenon.

Figure 4.2. Time-dependent ^{129}Xe spectra for the -100 mesh anthracite, 4 minutes to 3 hours from the time the sample was dosed with xenon.

Figure 4.3. Time-dependent ^{129}Xe spectra for the 40-60 mesh anthracite, 3 minutes to 24 hours from the time the sample was dosed with xenon. The signal at about 0 ppm disappears after about 5 hours.

Figure 4.4. Chemical shift vs. time for Sphero carb.

Figure 4.5. Chemical shift vs. time for the -100 mesh anthracite.

Figure 4.6. Chemical shift vs. time for the 40-60 mesh anthracite.

Figure 4.7. Linewidth vs. time for the -100 mesh anthracite.

Figure 4.8. Linewidth vs. time for the 40-60 mesh anthracite.

Figure 4.9. Xenon pressure drop vs. time for the -100 mesh anthracite.

Figure 4.10. Xenon pressure drop vs. time for the 40-60 mesh anthracite.

Figure 4.11. Percent of total change in chemical shift as a function of time for (A) Sphercarb; (B) anthracite, -100 mesh; and (C) anthracite, 40-60 mesh.

Table 4.1. Time at 85% of total change in chemical shift and gas uptake for Sphero carb and anthracite.

85% of total change	Sphero carb	anthracite -100 mesh	anthracite 40-60 mesh
chemical shift	30 min	2 hrs	12 hrs
linewidth	n/a	1 hr	6 hrs
xenon uptake	n/a	2 hrs	12 hrs

In the -100 mesh sample, chemical shift decays exponentially with time, which is the pattern also seen for the Spherocharb. For the 40-60 mesh sample, the chemical shift decreases with time, but fits neither an exponential nor a linear equation. This may be due to noisier signal outlines affecting the consistency of the identification of the signal maximum for chemical shift assignment; however, the chemical shift values do not scatter as the linewidth measurements do, and it thus may be that the pattern of change in chemical shift is in fact different than the exponential decays seen for Spherocharb and the -100 mesh anthracite. The chemical shift for the 40-60 mesh anthracite approaches a steady state much more slowly than the smaller particle size sample, with 85% of total change achieved in 12 hours, versus 2 hours for the -100 mesh sample.

Linewidths were compared to chemical shifts to see if they follow the same pattern. In both anthracite samples, the linewidth can only be considered an estimate, due to the small number of scans acquired, giving poor signal-to-noise ratio in the spectra. The signal-to-noise ratio is acceptable in the interest of the overall goal of the experiment, which is to have the spectra act as snapshots of the adsorption process. As a result, there is considerable scatter in linewidth for both particle sizes, and the data do not fit an exponential curve with a good correlation coefficient.

Nevertheless, closer inspection of **Figures 4.7** and **4.8** shows that there is a decreasing trend in linewidth over time for both particle sizes which for a majority of the data points resembles an exponential decay. The linewidth for the -100 mesh sample reaches equilibrium faster than the chemical shift. This is illustrated by the 85% of total change calculation, 1 hour for the linewidth vs. two hours for the chemical shift. In the 40-60 mesh sample, linewidth also approaches a steady state faster than the chemical shift in the 40-60 mesh sample, 6 hrs vs. 12 hrs. Compared to the -100 mesh, the 40-60 mesh linewidth reaches a steady state much more slowly, 1hr vs. 6 hrs, the implications of which will be discussed in the Section 4.4.

The uptake vs. time data for the two particle sizes (**Figures 4.9 - 4.10**) were measured on the gas manifold, and are used for comparison of the pressure-drop pattern to the NMR data. (They do not represent the actual pressures at the time of the NMR experiment.) Both are excellent fits to exponential decays. The rate of achievement of steady state xenon uptake over time, from the 85% of total change calculation, shows that, relative to each other, chemical shift and gas uptake are

approaching equilibrium at approximately the same rate for both particle sizes. The linewidth is reaching a steady state faster than either other indicator for both particle sizes. This could be tied to the change in chemical shift in that it reaches the (arbitrary) 85% completion mark in half the time in both cases. The existence of such a relationship would have to be corroborated with more experimental evidence.

The correspondence of the timing of chemical shift change and uptake change during xenon adsorption by the anthracites is in keeping with the established xenon density/chemical shift dependence (Dybowski et al., 1991). The measured pressure drop is indicating decreasing xenon density in the NMR tube, and increasing uptake by the coals. Note that the chemical shift does not increase with increasing amount of xenon taken up by the coal. The chemical shift follows the same pattern as the pressure in the tube, indicating that for the -100 mesh sample it is likely that the ambient pressure is 'felt' at the internal surfaces where the xenon is located. This is an indication that there is an open path from the outside of the particle to those parts of the internal surface that the xenon gas has reached during the experiment. For the 40-60 mesh sample, the chemical shift follows the pressure drop in a general way but is not an exponential decay overall. This may be related to the greater particle diameter; with proportionally less external surface area and, conceivably, less openings to the external surface in the larger particles, the gas adsorbed on the internal surfaces may be considered more sequestered from the outside.

The meaning of the change in linewidth is more a matter for speculation, since the linewidth measurements are not very precise. The NMR signal is wider earlier in the adsorption process, and reaches a steady state before chemical shift or uptake does. Consider the probable physical situation at the time the linewidth is broader. The diffusing xenon atoms early in the experiment are most likely located outside and around the particle perimeter, where those that are adsorbed may be more crowded than later after the adsorbed atoms have had opportunity to even out their concentration gradient. There may be a slight heating of the sample, since physisorption is almost always exothermic. In addition, if there are chemical structures on the pore walls that for any reason are more energetic adsorption sites for xenon, they will be covered first. The width at this stage, before xenon in the remaining environments contributes the majority of the signal, could be specific to this different type of Xe-solid interaction.

The possible causes of the change in linewidth during adsorption that can be ruled out are magnetic field inhomogeneity and exchange broadening. The solid sample itself would be the chief cause of magnetic field inhomogeneity across the tube diameter, which would contribute to linewidth; this can be ruled out because it does not change during the experiment. Intra/extraparticle exchange broadening presupposes that equilibrium adsorption has occurred, and is not favored for early xenon doses when there is a concentration gradient from the outside in. Signal broadening due to shorter spin-spin (T_2) relaxation time or to overlap of isotropic or anisotropic signals cannot be confirmed or eliminated based on the available information. The early coverage of more active adsorption sites is considered the most likely explanation.

4.3.2. Observation of the external gas signal

The NMR signal at 0-5 ppm arising from xenon in large spaces or outside the external surface - usually termed the external gas signal - is considered here in terms of its appearance during adsorption and the possible reasons it is not seen in the spectra of the smaller particle-size anthracite. The spectra of the 40-60 mesh anthracite illustrate the progress of the external gas signal from its maximum intensity when the sample is first dosed with xenon, to its reduction as the adsorbed gas signal grows, to its disappearance after about 5 hours. The spectra bracketing the time of the disappearance of the external gas signal are shown in **Figure 4.3**. The 40-60 mesh particles apparently have a slow enough uptake that this observation is possible. For the -100 mesh particles, the external gas signal was not observed, in general.

The most important feature illustrated in **Figure 4.3** is the *exchange of signal intensity* between the external and internal gas locations. The majority of the gas is in the external environment early in the adsorption process, as would be expected. This is indicated by the relatively strong external gas signal at about 0 ppm. It should be noted that the external gas signal does not represent all xenon that may be present outside the coal particles in the NMR tube. Completely free xenon has a very long T_1 relaxation time, which is reduced when the gas is in contact with a solid. For xenon in microporous spaces, the T_1 is reduced to the order of milliseconds; in larger spaces the

T_1 is typically longer. For example, Simpson et al (1995) report that the T_1 of xenon at a pressure of 10 atm outside 18 μm diameter polystyrene beads is 26 s. The spectra reported in this chapter show signals from xenon with a sufficiently short T_1 to give a NMR signal using a 1.5-2s delay.

The adsorbed gas signal at about 150-120 ppm grows with time as the external signal diminishes (thus the exchange of intensity). The spectra demonstrate the progression of xenon gas from the outside to the internal porosity of the coal particles. If xenon passed through the solid coal matrix as an intermediate environment before reaching the porosity, a third NMR signal would be expected. Dissolved xenon would be in a smaller space than that in a pore; in addition, the restriction of motion in such an environment would mean that it would not rapidly exchange with xenon in porous spaces. Thus, a signal from dissolved xenon should be resolved from that in a pore space. However, there is no evidence for dissolution of xenon at any point in the adsorption process. This means that passage of xenon into the internal porosity of coal does not entail passage through the solid matrix as an intermediate step. It remains possible that a small amount of xenon could dissolve in the coal matrix and not be detected in these experiments. Nevertheless, the solid matrix cannot be the major route of access to the porosity, because roughly the same amount of gas that gives a detectable signal when in the pores would have had to pass through the solid before reaching them.

The peculiarity of the anthracite compared to the other coals used in this study is that it is the only one for which the external gas signal is usually not detected in the NMR spectra of the powders at 300 to 700 torr. This signal is also absent in the spectra of Sphero carb, which is a high surface area (900 m^2/g) microporous carbon. The surface areas of Pennsylvania anthracites from the same region as the Lykens Valley sample used here are approximately 400 m^2/g , fairly high for coal. Given the surface areas of these materials, the lack of a ~ 0 ppm signal in the NMR spectra could be due to xenon uptake by the samples that is so large that what remains free in the NMR tube is too little to be detected. However, spectra of -60 mesh anthracite brought to equilibrium on the manifold (**Figure 3.6**), where the pressure is monitored, show no 0 ppm gas signal even for pressure in the NMR tube up to 650 torr.

Exchange averaging was carefully considered as a cause of the absence of an external gas signal in the anthracite spectra discussed in this chapter and in Chapter 3.

The spectra for the small particle size (**Figure 4.2**) show the adsorbed gas signal at 140-120 ppm. The external gas signal is not visible. In spectra taken in less than three hours adsorption time, equilibrium has not been established. The concentration gradient and direction of diffusion is from the external to the internal particle surfaces. Under these conditions, physical exchange should not occur, and thus the spectra show that in the *absence* of exchange, the external gas signal is not visible for the small-particle-size anthracite. This rules out intra/extraparticle exchange as the reason this signal is absent.

It is possible that the external signal is not from xenon at the open surface (or interparticle space), but from xenon in macropores or mesopores. To produce the signal near 0 ppm, the pore wall separation should be large enough that the xenon signal there is primarily free-gas-like, but small enough to cause a decrease in T_1 sufficient to detect the signal with 2 or 3s delays. Macropores and mesopores actually fit these criteria better than the external surface does, because they are smaller than the interparticle space, and thus are more likely to produce the necessary reduction in the T_1 . If the T_1 of xenon in the interparticle space is over approximately 500 ms (an estimation based on 1/4 of a 2 s recycle delay), its signal may not be detected in the spectra shown in this thesis, due to saturation. It is reasonable to expect that the interparticle xenon T_1 is longer (for example, see Simpson et al., 1995).

Based on these considerations, it is reasonable to suggest that the source of the external gas signal is xenon in macropores and possibly mesopores; these locations are external to the microporous regions but are not outside the particle. The experiments reported in Chapter 5 provide support for this interpretation, and it will be discussed further in Section 5.4. This interpretation is significant to the experiments reported in this Chapter. The exchange of intensity between the external and adsorbed xenon signals, which has been observed during adsorption by large particle-size anthracite, may be best described as the loss of a signal from larger pores while the signal from smaller pores increases. This could in turn indicate that the larger pores are the route of access to the smaller pores. (It should be understood that the extraparticle xenon in the NMR tube, although it is not shown as an NMR signal because it is saturated, does contribute to the diffusion process.) In addition, the existence of an external gas signal in large but not small particle-size anthracite could be due to the absence of large pores or large fractures in the small particles. Their absence in small particles may be due to the breakage of these large pores or fractures in the process of grinding the anthracite to reduce the particle size.

4.3.3. Usefulness of ^{129}Xe NMR as a method to track xenon adsorption

The strength of the ^{129}Xe NMR tracking technique, and the sense in which it is a unique tool, is that it can distinguish between different locations of xenon populations during the adsorption process. It can also identify intermediate environments occupied only when xenon is en route to its final, equilibrium location. In structural studies of porous materials in which xenon diffusion is sufficiently slow, this could provide important information on the pore network connectivity. This is shown for two anthracite particle size fractions reported here. These experiments can detect the achievement of equilibrium by monitoring the changes in chemical shift with time. For the samples tested, this agrees with uptake vs. time measurement. Further testing using more samples should be done, and if this relationship holds, it can be concluded that equilibrium information may be just as well determined without the use of spectroscopy, if identification of equilibrium adsorption is the only aim. However, in this study it proved significant for the investigation of pore connectivity in anthracite to show that uptake and chemical shift correspond to each other throughout the adsorption process, and not only at equilibrium.

4.3.4. Particle size effects on chemical shift under equilibrium adsorption conditions

The influence of diffusion or exchange of xenon into and out of porous solids on the ^{129}Xe NMR signal can be significant depending on the rate of exchange (Ripmeester and Ratcliffe, 1993). For example, the fast interparticle diffusion of xenon in zeolites results in averaging of the environment experienced by xenon over many crystallites on the NMR timescale. When xenon is confined to one crystallite, the NMR signal is significantly different (Ryoo et al., 1994). In order to properly interpret ^{129}Xe NMR spectra of coal, it is necessary to establish whether significant intra/extraparticle exchange of xenon gas can occur in coals. This question is approached here by

comparing ^{129}Xe NMR spectra at adsorption equilibrium as a function of the particle size.

The intra- and extraparticle xenon populations have distinct chemical shifts; the first at about 100-200 ppm, and the second at 0-5 ppm. Exchange between the xenon populations that give rise to these two signals would be caused by diffusion of a significant portion of the adsorbed xenon population to that region of the coal particles corresponding to the external gas signal. Due to two possible ways to interpret the external signal, there are two ways to describe the exchange process: 1) through a particle and to the extraparticle gas; or, 2) through a microporous region within the particle and to the gas in the large pores (as was discussed in Section 4.3.2.). The experiments reported in this section address the question of whether particle size affects exchange between the populations represented by the two signals, without *a priori* preference for interpretation 1) or 2). The particle size could affect the degree to which intraparticle diffusion results in exchange with the external gas on the time scale of the NMR experiment. If the diffusion path length is on the order of the particle size within the time period of interest, reducing the particle size will result in mixing of the two gas populations in the given time period. In this case, the NMR signals will show evidence of exchange.

The spectra of four particle size fractions of microporous Upper Freeport mvb vitrinite are shown in **Figure 4.12**. There are no significant differences in the spectra for the 60, 60-100, or 100-200 mesh size fractions. The adsorbed xenon signal is at 180 ppm, and the external-surface adsorbed gas signal is at 0 ppm. In the -400-mesh size sample, the external gas signal is at 5 ppm, an increase with respect to that of the larger particle sizes. The adsorbed gas signal is at ~170 ppm, a decrease with respect to that of the the larger sizes. The displacement of the adsorbed and external gas signals toward each other in the -400 mesh sample, as well as the broader appearance of the gas signal, is preliminary evidence that intra/extraparticle exchange intermediate between fast (complete averaging of the signals) and slow (no effect on the non-exchanging positions of the signals) may be occurring in this sample on the time scale of the experiment (Radovic et al., 1997).

This experiment suggests that exchange on the time scale of ~130 ms (the acquisition time) may be detectable in the very small particles, and shows clearly that this is not the case for the larger particles. The particle size effect evidence was not

conclusive as to the cause of the altered appearance of the -400 mesh sample spectrum. In order to explore this issue further, adsorption of xenon by the -400 mesh vitrinite was tracked by acquiring NMR spectra during the adsorption process, **Figure 4.13**. The gas signal is wide from the first spectrum, and this cannot be caused by exchange broadening. The time tracking technique shows the signal when there *is no exchange* for those spectra that are acquired prior to equilibrium, when the direction of diffusion is inward. This is apparent in **Figure 4.12** from the loss of gas signal intensity as the adsorbed gas signal gains intensity, indicating the movement of xenon from the outer to the inner surface environment. Exchange in and out would occur after equilibrium was reached. It can be concluded that the wider external gas signal at ~5 ppm in -400 mesh vitrinite is due to causes other than exchange. A strong possibility is that it is due to smaller spaces between the particles, which would cause greater interaction of the free gas with the solid surface.

For all particle size fractions, the signals were not dramatically affected by changes in particle size, and it may be concluded that for this vitrinite, the intraparticle diffusion rate is sufficiently slow that particle size itself will not significantly alter the chemical shift. The effect on ^{129}Xe chemical shift for solids with a higher intraparticle diffusion rate could be more marked than in this sample. This is potentially a significant consideration that should be investigated before the application of pore size measurement techniques, (such as that of Demarquay and Fraissard, 1987) which rely on proper definition of all contributors to the chemical shift.

Figure 4.12. ^{129}Xe spectra at 500 to 600 torr xenon of size graded Upper Freeport mvb vitrinite: -400, 100-200, 60-100, and +60 mesh.

Figure 4.13. Time-dependent ^{129}Xe spectra of Upper Freeport mvb vitrinite, -400 mesh, 6 minutes to 24 hours from the time the sample was dosed with xenon.

4.4. Conclusions

For two particle sizes of an anthracite, the particle size effect on the adsorption rate and the correlation of uptake to chemical shift throughout the adsorption process are significant findings with important implications for the structure of the micropore network. There is a marked (ten-hour) difference in the time it takes for the 40-60 and -100 mesh anthracite samples to approach adsorption equilibrium. If diffusion of xenon occurred by dissolution into the solid matrix, an effect suggested by Larsen and coworkers (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992), such severe particle size effects would not be observed; in support of this, the chemical shift/ xenon pressure correspondence as the uptake is occurring indicates the existence of porosity *open to the surface* in this coal. Xenon dissolved in liquids, for example, where they are not in direct contact with the free gas, do not show a pressure-dependent chemical shift (Stengle et al., 1981).

If, on the other hand, the anthracite had an unconstricted network of micropores, diffusion of xenon through the network would be easier and would not be expected to have a large dependence on particle size. In addition, it would not require as much time as is typically required by coals to reach adsorption equilibrium. Sphero carb is a microporous carbon with open porosity. It apparently has large micropores relative to the size of the xenon atom ($\sim 15\text{\AA}$ vs. $4.4\text{\AA}$, Wernett et al., 1990). The equilibrium xenon adsorption for Sphero carb is reached in 30 minutes, as determined by following the change in ^{129}Xe chemical shift. Overall the results are consistent with the concept of a porous network in anthracite that is both open and constricted; considerably more constricted than that of a microporous carbon (Sphero carb). This model has extensive support (Mahajan, 1991; Walker and Mahajan, 1993; Menon et al., 1993; Radovic et al., 1997), and is in contrast to the conclusions reached by Larsen and coworkers (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992).

In addition, the significantly faster uptake of xenon by small anthracite particles compared to the large particles suggests that the surface density of pore constrictions decreases as the particle size decreases in the anthracite. This is in keeping with the observation of particle-size-dependent surface area in anthracite reported by Nandi and Walker (1970); who noted that the smaller particles had increased surface area which

was greater than would be expected based on increased external surface in the smaller particle size. This could be due to the opening, upon breakage of the larger particles, of previously closed or effectively closed porosity. Nandi and Walker (1970) suggested that cracks due to fracture are formed in the smaller particles. The results of the examination of the external gas signal reported in this Chapter indicate the opposite. The external (0-5 ppm) signal most likely originates from xenon in large pores, and is detected in the spectra of large, but not small, anthracite particles. According to the interpretation suggested here, large pores, of which cracks would be one example, are evident in the larger, and not the smaller anthracite particles.

The implications for the microporous structure of Upper Freeport mv bituminous vitrinite are, first and foremost, that the porosity is open, as xenon is shown in the time-dependent spectra to move from the outside of the particle inward within 15 minutes of dosing the sample. There is no third signal evident that would indicate xenon passage from the outside through some intermediate structure such as a solid matrix, before reaching its equilibrium locations on the internal surface. Second, the variation of particle size from 60 down to -400 mesh does not result in detectable intra/extraparticle diffusion effects on the ^{129}Xe NMR spectra. This is an indication that xenon diffusion in this coal is slow, which could be caused by a highly constricted path. It could also be interpreted as a consequence of the fact that, in this range of particle sizes, the diffusion path length through the particle is so much longer than the particle diameter that diameter changes in the range tested do not shorten the path enough to cause a noticeable effect. This, in turn, is evidence for a highly interconnected, tortuous path through the particle.

Chapter 5

INVESTIGATION OF THE POROUS STRUCTURE OF COAL USING ^{129}Xe NMR WITH SELECTIVE SATURATION AND SATURATION TRANSFER

5.1 Introduction

This chapter will explore adsorption site distribution and pore network connectivity in coal using ^{129}Xe saturation and saturation transfer. These techniques have widely varied utility in NMR spectroscopy, as reviewed by Freeman (1988). ^{129}Xe NMR studies that, while not the same as the one to be described here, use some similar basic concepts, have been performed. Selective inversion has been used in ^{129}Xe NMR studies to study intercage exchange in a zeolite (Larsen et al., 1993; Jameson et al., 1994), to demonstrate that two xenon populations are coupled (Ripmeester and Ratcliffe, 1993), and to measure diffusion coefficients in polystyrene (Simpson et al., 1995). 2D-EXSY has been used by Moudrakovski et al. (1995) to monitor xenon intra/extraparticle diffusion in zeolites, and by Zhu et al. (1997) to examine intraparticle xenon diffusion in coal.

As shown previously, typical ^{129}Xe NMR spectra of coal consist of a broad signal due to xenon adsorbed in the internal porosity of the coal, and a sharper signal at about 0 ppm. This second signal, termed the external gas signal, is from xenon in a more free-gas-like environment than that in the internal microporosity. It has been suggested in Chapter 4 that this signal originates from xenon in large (meso or macro) pores; alternatively, it may be from xenon in the interparticle space. The adsorbed and external gas signals are well separated.

In the presaturation experiment only a portion of the frequency range covered by the adsorbed xenon signal was irradiated, through the use of a low power presaturation pulse followed by a high power 90° pulse. The features of interest are then whether and to what extent presaturation produces saturation of the signal it is focused on, and how the other signal(s) in the spectrum is affected. The key ideas used in conceptualizing this experiment are as follows: NMR signals from ^{129}Xe adsorbed inside the coal particles are distinguishable from those outside; xenon atoms are to some degree mobile in their adsorbed state; and if a xenon atom is saturated in one environment, it can carry the saturation with it if it moves to a new environment in less than its spin-lattice (T_1) relaxation time. The possible outcomes of the presaturation experiment are as follows:

(1) The xenon atoms are in distinct internal adsorption sites and are effectively immobile during the time the pulse is applied. In this case we would expect to see a well defined break or a dip in the outline of the adsorbed gas signal in the area where the low power pulse was applied.

(2) The xenon atoms do have distinct internal adsorption sites, but diffuse among them during the presaturation time. Here we would expect to see saturation of the adsorbed gas signal, or overall loss of signal intensity, which may be accompanied by a change in the signal shape.

Note that outcomes (1) and (2) are related in that they are only distinguished by the time frame of site to site diffusion. For example, if the xenon atoms sample all the sites in 100 ms, then in a 10 ms period they are effectively immobile in their adsorption sites. A 10 ms presaturation pulse, assuming it is sufficiently narrow and delivers enough power to cause saturation, would be able to selectively saturate a portion of the overall adsorbed gas signal. A 100 ms pulse, however, should saturate the entire signal. Variation of the time frame of the experiment can identify the transition from one effect of presaturation to another.

(3) Xenon atoms are diffusing both into and out of the particle during the time the sample is presaturated. In this case, we would expect the intensity of both adsorbed and external-surface signals to decrease or completely saturate.

(4) The linewidth is not due to a distribution of sites, but to a short T_2 and/or magnetic field inhomogeneity. The signal intensity could be decreased by presaturating

the peak maximum, but the shape should remain the same, and presaturating the signal off center should have much less or no effect.

5.2. Experimental

Powdered samples of Wyodak subbituminous coal (76.3% C), Adaville high volatile C bituminous coal (77.4%C), Sewell medium volatile bituminous coal (88.9% C) and Lykens Valley anthracite (91.9 %C) were obtained from the Penn State/DOE coal sample bank and sieved to 60-100 Tyler mesh particle size. They were dried overnight in 10 mm NMR tubes with rototite valves (Wilmad), heated to 90° C for 2 to 4 hours, then kept under vacuum at room temperature for 24 hours or more. Once dry, the samples were charged with xenon to ~1 atm pressure (730-760 torr). Equilibration time was 19-21 hours.

NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A low power presaturation pulse was applied with the carrier frequency centered on the signal of interest followed by a 90° high power pulse and 3 s delay. The low power pulse length was varied as described in the next section. Spectra were obtained from 300 to 1000 scans depending on the individual sample. All sets of spectra for a particular sample were acquired with the same number of scans. Xenon gas at 700 torr was used as an external chemical shift reference.

5.3 Results and discussion

5.3.1. Presaturation of the ^{129}Xe NMR spectrum of coal.

The ^{129}Xe NMR spectrum of xenon gas adsorbed on the subbituminous coal, with the presaturation pulse well separated from the xenon signals for reference, is shown in **Figure 5.1**. The signal centered at 160 ppm is from xenon adsorbed on the internal surfaces of the coal, and that at 0 ppm is the external gas signal.

Figure 5.1. ^{129}Xe NMR spectrum of the subbituminous coal with a 2ms, 40 dB presaturation pulse centered at -1000 Hz (approx. -60 ppm).

Figure 5.2. ^{129}Xe NMR spectra of the subbituminous coal. A 2ms 40 dB presaturation pulse is centered at (a) 22,594 Hz (~ 176 ppm), (b) 21,234 Hz (~ 163 ppm), (c) 20,618 Hz (~ 156 ppm) (d) 17,654 Hz (~ 126 ppm).

Four different regions of the adsorbed gas signal were presaturated, and the results are shown in **Figure 5.2**. The four spectra have a 2 ms presaturation pulse centered at four different sections of the broad adsorbed gas signal. The spectra clearly show a trough, or hole burned, located at the center of the presaturation pulse. A change in the location of the pulse changes the location of the hole. The greatest effect is at 156 and 162 ppm, near the center of the signal. Presaturation at the outer edges leaves more residual signal, particularly in the spectrum presaturated at 126 ppm. Comparison with the reference spectrum shows that there is overall signal intensity loss accompanying the change in signal shape.

A spectral hole, or the loss of a portion of the adsorbed xenon signal, is evidence that some of the xenon atoms contributing to a broad signal have a resonant frequency close to the applied pulse; some do not, however, hence the residual portions of the signal. The sensitivity of the ^{129}Xe chemical shift to the dimensions and chemical composition of the space in which it is adsorbed is well known. A signal that is broad due to an overlap of chemical shifts indicates that there exist slightly different adsorption sites, or environments, for xenon in the adsorbent.

5.3.2. Variation of power level

There is a range of possible low power levels that can be used in this experiment. In addition to a narrow excitation bandwidth, the power level should be able to induce saturation in the desired range of pulse lengths. The pulse length required has to be shorter than the intraparticle diffusion time in order to observe removal of part of the signal. Workable time/power combinations vary with the sample used and so should be tested for each.

The power level used significantly affects the appearance of the spectral hole as well as the length of time the signals survive presaturation. The different lengths of time required to saturate the entire signal at two different power levels can have two sources. On one hand, the higher power level has a wider excitation bandwidth, leaving less residual intensity which would appear to survive a shorter time as the pulse is

lengthened. On the other hand, some lower power levels are insufficient to cause saturation at all. These signals have reduced intensity but survive long periods of presaturation. At the least, an optimum power level would have to be defined for this technique to be meaningful for *quantitative* measurement of the diffusion time of xenon through porous particles. As a means to compare different porous solids, however, relative changes in the saturation transfer results are clearly useful.

The effect of presaturation pulse power level on the appearance of the 'hole' was tested for the mv bituminous coal from 33 to 43 dB, **Figure 5.3**. For the higher power levels used (40, 37, and 33 dB), a hole with signal remaining on either side could be produced in 0.3 to 0.5 ms; the best defined hole, with the most remaining signal, was the 0.4 ms/40 dB combination. There was least residual signal at 0.2 ms/33 dB which had only one shoulder. At the lowest power levels examined, 43 and 46 dB (not shown), pulse lengths in the range 0.3 to 100 ms at 46 dB, and 0.6 to 1 ms at 43 dB, did not produce a hole. There was overall intensity loss and signal shape change in the form of a small shoulder, and saturation of the adsorbed xenon signal was complete in 100 ms at 46 dB, compared to 5 ms at 40 dB.

5.3.3. Saturation transfer to the external gas

The low power pulse length was increased to observe the effect of presaturating the adsorbed xenon long enough for diffusion to occur. Four coals were presaturated on the principal adsorbed xenon signal for increasing lengths of time. The low power pulse length was varied in order to map out the time frames of hole burning, if any, saturation of the adsorbed gas signal, and saturation of the extraparticle gas signal.

The reference spectra are presaturated on the center of the adsorbed gas signal at very low power (80 dB power for 0.1 ms). All subsequent spectra for a given sample were phased relative to the reference. The subbituminous coal was presaturated at 40 dB power on the 150 ppm adsorbed xenon signal for increasing times from 1 ms to 40 ms. The results are shown in **Figure 5.4**. The spectra show a clear 'hole' at 1 and 2 ms which is almost saturated at 5 ms. From 1 to 5 ms, the interparticle gas signal at 0

Figure 5.3. ^{129}Xe NMR spectra of the mv bituminous coal presaturated on the principal signal (~170 ppm) using four different power levels; from highest to lowest: (a) 33 dB, 0.2 ms; (b) 37 dB, 0.3 ms; (c) 40 dB, 0.4 ms; (d) 43 dB, 0.6 ms.

Figure 5.4. Effect of increasing presaturation pulse length on ^{129}Xe spectra of the subbituminous coal. Reference: 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power, 20,000 Hz).

Figure 5.5. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of the mv bituminous coal. Reference: 0.1 ms, 80 dB. (All subsequent spectra are at 37 dB power, 21,870 Hz).

ppm is unchanged. At 10 ms, the adsorbed signal is completely saturated and the interparticle gas signal has some insensitivity loss. At 30 ms the gas signal is reduced to a little over the noise level, and at 40 ms it is saturated. As a test, spectra were run for this sample under the same conditions but with the presaturation pulse at the equivalent of -150 ppm for 10 to 40 ms; this caused no saturation or other changes in the spectra.

The mv bituminous coal was presaturated at 37 dB on the 177 ppm adsorbed xenon signal for increasing times from 0.1 ms to 800 ms. The results are shown in **Figure 5.5**. There is a 'hole' in the signal at 0.3 ms accompanied by overall intensity loss. At 1 ms the signal is almost saturated. There was no effect on the interparticle gas signal. At 200 ms the adsorbed signal was completely saturated while the interparticle gas signal was less intense. At 400 ms the gas signal intensity decreased noticeably, and at 800 ms it was nearly saturated.

The anthracite was presaturated at 40 dB on the 157 ppm signal for increasing times from 1 to 300 ms. The results are shown in **Figure 5.6**. There is a 'hole' at 1, 2, and 5 ms that persists through 10 ms as the signal loses intensity. The external gas signal is reduced in intensity at 100 ms, and is almost saturated at 300 ms.

The hvC bituminous coal reference spectrum (**Figure 5.7**) shows that there are two overlapped adsorbed xenon signals. When this coal was examined as a -60 mesh powder, the spectra appeared to have a shoulder at the higher frequency side of the main signal (**Figure 3.3**). In Chapter 3, pore size calculations were made based on the pressure dependence of the ^{129}Xe chemical shift for both the shoulder and the main signal. The result was 6.7 and 6.8 Å pores. While the main signal and the shoulder were ~10 ppm apart, the apparent slopes of the chemical shift vs. pressure were different and both had nearly the same intercept, from which the pore diameter was calculated. Possibly due to the different particle size used in this experiment, 60-100 mesh, two signals are clearly distinguishable at 130 and 176 ppm, and the major signal is that at higher frequency, unlike the spectra in Chapter 3. The 60-100 mesh spectra in **Figure 5.7** appear to have an additional signal (that at lower frequency), and are not a better resolved version of the -60 mesh spectra (**Figure 3.3**).

The lower frequency signal (130 ppm) was presaturated for increasing times from 0.4 to 40 ms, **Figure 5.7**. The effect at 0.4 ms appears to be the removal of the

Figure 5.6. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of the anthracite. Reference: 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power, 20,296 Hz).

Figure 5.7. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of the hvC bituminous coal. Pulse centered on signal at ~ 130 ppm. Reference: 0.1 ms, 80 dB. (All subsequent spectra are at 40 dB power, 17,629 Hz.)

Figure 5.8. Effect of presaturation on the higher frequency ^{129}Xe signal in the hvC bituminous coal. Pulse is centered on signal at ~ 176 ppm. Reference: 0.1 ms, 80 dB; 19,057 Hz. (subsequent spectra are at 40 dB power; 21,968 Hz.).

130 ppm signal, with the 176 ppm signal surviving with slight intensity loss. From 1 to 5 ms, the 176 ppm signal continues to lose intensity, saturating at 10 ms. The external gas signal begins to lose intensity at about 5 ms, saturating at 40 ms.

Next, for the hvC bituminous coal, the presaturation pulse was centered on the higher frequency (176 ppm) signal for 1 and 5 ms, **Figure 5.8**. At 1 ms, the 176 ppm signal is nearly saturated. There is significant intensity loss to the signal at 130 ppm, whereas when the pulse is on the 130 ppm signal (**Figure 5.7**), the signal that was not presaturated had lost little intensity. For the pulse on the 176 ppm signal for 5 ms, both signals are saturated. By contrast, with the pulse on the 130 ppm signal, complete saturation occurs at 10 ms presaturation time. The extension of saturation from the 130 to the 176 ppm region is slower than that from 176 to 130 ppm. The reasons for this could be, in part, related to the relative speed of diffusion of xenon through the two pore regions that are indicated by the two signals, but is likely to also be an effect of the experimental conditions. This issue is addressed next.

The relative lengths of time that the two hvC bituminous coal signals survive are not necessarily direct indications of the rate of motion of xenon atoms through the corresponding porous regions if the way the pulse is applied also affects the relative intensity of the signals. An example is if the pulse is applied off center for one of the signals. The location of the presaturation pulse can affect how long a signal survives it, and if the pulse is off center, there is more residual intensity. This is shown in **Figure 5.1**. An important consideration related to the location of the presaturation pulse is whether the overlap region between the signals is more affected in one experiment than in the other. This could occur in a situation where the peak center for one signal overlaps a portion of the other signal, which does appear to be the case for the spectra shown in **Figures 5.7 and 5.8**. The 130 ppm signal is more asymmetrical, tailing to the high frequency end. This means some of the 130 ppm signal area is under the maximum of the 176 ppm signal, meaning presaturating that area affects the 130 ppm signal directly, due to the pulse, as well as indirectly, through diffusion of saturated xenon atoms into the second pore region.

The time frames of diffusion of saturated xenon through the solid and out into the interparticle space can be clearly illustrated by increasing the pulse length until the saturation extends to the remainder of the signal it is focused on, and to the external gas

signal. The relative changes in time or sequence of these events can be used to compare materials with different pore structures. Caution must be exercised, however, in using this technique as a definite measure of diffusion time, because the times can be affected by the presaturation pulse power level and carrier frequency. The technique has been applied in a standardized way to each coal sample before making time comparisons. Each was run at similar power level, and it was established that this power was sufficient to produce saturation in a time shorter than the T_1 or the inter-extraparticle diffusion rate - that is, each run was performed under conditions where a spectral hole could be produced. The saturation transfer times are thus expected to provide reliable information for comparison of the coals to each other.

5.4. Conclusions: Implications for the porous structure of coals

From the hole-burning effect. A spectral hole can be produced in the ^{129}Xe spectra of all four coals examined. The fact that a spectral hole can be produced in the adsorbed xenon signal indicates that the signal source is the overlap of multiple chemical shifts. Wernett (1991) and Johnson and Griffiths (1987) have speculated that the ^{129}Xe NMR signal profile describes the pore size distribution. This interesting hypothesis is supported by these results and has not been verified previously.

Given, however, that coal not only has a distribution of pore sizes, but a distribution of chemically distinct areas due to its heterogeneity, it should be borne in mind that the ^{129}Xe chemical shift is sensitive to both the dimension and the chemistry of the space in which xenon resides. Because of this, the more accurate term to reflect the environment contributing to the ^{129}Xe chemical shift is adsorption site distribution, rather than pore size distribution. The results of the presaturation experiment demonstrate that the signal profile is an indication of the distribution of adsorption sites having different physical characteristics. This is most likely to be a distribution of pore size, and possibly a distribution of pore wall chemistry as well.

From saturation of the adsorbed xenon signal. The different saturation transfer rates arise from differences in diffusion of xenon through the void spaces in coals. First, the saturation of only the adsorbed xenon signal will be considered. The pulse length at

which saturation transfer from the 'hole' effect to the entire adsorbed xenon signal is accomplished indicates the time frame in which xenon atoms exchange among all the sites in the particle, and ranges from about 3 ms for the mv bituminous coal to over 10 ms for the anthracite. The study of this phenomenon was approached by Zhu et al. (1997) using 2D-EXSY to detect coupling between partially resolved signals in a hv bituminous coal. Their study shows intraparticle diffusion between two distinct pore regions, with contact between xenon in these two regions in 15 ms. This is broadly consistent with, but somewhat longer than, the times to saturate the adsorbed signals reported in this thesis. The fact that there is partial resolution of the two signals monitored by Zhu et al. (1997) indicates that the pore regions corresponding to those signals are more distinct from each other physically, and may thus have slower exchange of xenon between the sites, than those which contribute to broad *single* signals. This is not necessarily always the case, however; the anthracite examined in this thesis, which has one adsorbed gas signal, requires well over 10 ms to saturate. Multiple, resolved NMR signals from adsorbed xenon were not observed for most coals examined in this thesis, with the exception of the hvC bituminous coal. The hole-burning technique can estimate the time frame of intraparticle diffusion for single signals that are composed of an overlap of chemical shifts and does not require that the signals be separated.

For the subbituminous coal, the adsorbed signal takes somewhat longer to completely saturate than for the mv bituminous coal. This could be interpreted as an indication of longer time for saturated xenon atoms to diffuse among the internal sites in the former coal. Since the porosity of the subbituminous coal is relatively open compared to that of the higher-rank coal, diffusion between the sites is not expected to be slower in the subbituminous coal. Rather, the longer time required to diffuse among the internal sites could be due to wider distribution of these sites in the subbituminous coal compared to the mv bituminous coal. The width of the adsorption site distribution is most clearly demonstrated by the wider linewidth. The mv bituminous coal has a narrower linewidth, an indication of greater adsorption site homogeneity. The anthracite was somewhat different in that its narrow signal took the longest to completely saturate. This is most likely an indicator of constricted pore network connections - a wide distribution of sites does not exist, as indicated by the narrow linewidth, but apparently the xenon atoms do not move among them as readily as in the other coals. For the hvC bituminous coal, two broad signals are partly resolved. Due to their overlap, the time

frame in which they can both be saturated is not necessarily due to different rates of xenon diffusion between the two sites, but is also influenced by the application of the presaturation pulse to the overlap region.

From saturation transfer to the external gas. The external gas signal can be saturated as a result of presaturating the adsorbed gas signal for a suitable duration. This presaturation experiment clearly shows that exchange of xenon occurs between the two gas populations that give these signals, which has not been shown elsewhere for coal. There are two possible interpretations of the source of the (~ 0 ppm) external gas signal: 1) that it is extraparticle gas, and 2) that it is gas in macropores and possibly mesopores. In either case, it is from gas outside the microporous regions. This signal will be referred to in this discussion simply as the external gas signal. The time scale on which these gas populations exchange at equilibrium xenon adsorption (ms to s), reported in this Chapter, is in contrast to the time scale on which xenon diffuses into the coal particles (hrs), reported in Chapter 4. This is due to the two different types of diffusion that are being measured. Physical exchange as reported in this Chapter is a self-diffusion process, and these processes typically occur on the order of seconds, whereas transport diffusion through a bed of microporous particles occurs on a time scale on the order of hours (Karger and Ruthven, 1992). In addition, the interpretation has been offered here that the external signal is from xenon in large pores. If so, then in an exchange process, adsorbed gas must pass through microporous domains to reach large pores, but does not have to pass through the entire particle to do so as would be necessary in the case of exchange with external-surface gas.

Experiments on two coals using 2D-EXSY (Zhu et al., 1997) have not shown exchange between the adsorbed and external gas signals. However, the relevant mixing times used were short, 15 ms or less. Based on the indications from the work in this thesis, exchange between the two xenon populations (which can be considered intra/extraparticle exchange if the external signal is, in fact, originating from gas outside the particle) occurs in 30 ms or more and varies considerably with coal rank.

The short times (30–40 ms) to produce saturation transfer to the external gas signal in the subbituminous and hvC bituminous coals are interpreted as due to relatively easy motion of xenon atoms which were saturated while in the internal microporosity, to the external region. The relatively fast saturation transfer is consistent with larger pore connectivity to the microporous regions. The activation energy for

diffusion of argon increases for coals with narrower porosity (Nandi and Walker, 1966), meaning that in small pores the rate of diffusion is slower than in larger pores. The low-rank coals examined here, at 76.3 and 77.4 %C, have meso- as well as microporosity, as determined by N₂ and CO₂ adsorption. This is typical (Gan et al., 1972). The NMR data in this study is in keeping with the presence of larger pores, in which diffusion of xenon would be faster, acting as feeder pores to the microporosity in the subbituminous and hvC bituminous coals.

The comparatively slow rate of saturation transfer to the external signal (>800 ms) in the mv bituminous coal points to fewer openings to the external region compared to low-rank coals; an equivalent effect on diffusion rate would come from smaller (constricted, microporous) connections to the external region. Both are consistent with the notion of a highly interconnected microporous system lacking a significant amount of larger porosity. Gan et al. (1972) determined such pore size distribution variations with coal rank or carbon content; the presence of meso- and macroporosity decreases as coalification progresses. The mv bituminous coal, at 88.9% C, is in the range where coal becomes predominantly microporous. Although micropores are typically too small to observe directly, such a network has been suggested from TEM studies by Harris and Yust (1981) which showed a microporous region that was exclusively microporous and also highly interconnected.

The anthracite spectra also required a long presaturation time to affect the external gas signal (300 ms), but not as long as for the mv bituminous coal (>800 ms). This allows further details of the dependence of pore structure on rank to be brought out. Based on the current interpretation of the saturation transfer time, the anthracite possesses a constricted pore network, but has either more or larger openings to the external surface than does the mv bituminous coal. Interestingly, this fits with evidence for fracture in anthracite particles (Cody and Davis, 1991; Nandi and Walker, 1970). These fractures, thought to be secondary structural features, intersect the primary (microporous) structure, and may open up more constricted microporous regions compared to particles without fracture. The evidence in this study supports such a model.

The features of the pore structure emerging from the ¹²⁹Xe NMR results are in keeping with what can be derived from other studies on the relationship between pore structure and rank. Surface area and porosity as functions of rank (Gan et al., 1972)

exhibit a broad minimum at about 81% C and rise sharply after about 88% C. X-ray diffraction studies (Hirsch, 1954) indicate that low-rank coals, up to 85% C, are amorphous; higher-rank coals develop randomly oriented aromatic layers in the 85-90% carbon range, while the highest-rank coals develop ordered aromatic lamellar regions at >90% carbon.

The low-rank coals, which have high surface area as measured by CO₂ adsorption, are amorphous; minimum surface area is exhibited by the coals that are starting to show evidence of structural order, and the subsequent rise in surface area at high rank corresponds to developing microporosity that is related to the development of graphitic crystallites. The narrow spaces between these crystallites form the microporosity. This porosity is of a very different nature from that present in low-rank coals, which reside predominantly in the spaces between poorly packed macromolecular chains. The presaturation and saturation transfer results provide important additional insights into the pore structure of coals. The microporosity in high-rank coal is relatively isolated from the external region, while in low-rank coal it is more openly connected. In addition, the ¹²⁹Xe linewidths indicate a narrower adsorption site type distribution (pore size distribution; pore wall chemistry distribution) as coal rank increases.

The information on pore network connectivity is thought to be useful in resolving the continuing controversy on whether coal micropores are primarily open or closed (Larsen et al., 1995; Walker and Mahajan, 1993). The complete saturation of the adsorbed xenon signal, with no portion resistant to saturation after allowing up to 20 ms diffusion time, demonstrates *interconnection* of porosity. There was no isolated adsorbed xenon signal for any of the four coals, including the hvC bituminous coal which most clearly had separate pore regions contributing to the adsorbed xenon signal. This is an indication that the xenon atoms are diffusing through an open, connected porous network. If a significant portion of the porosity existed as isolated pockets, diffusion through the coal would require passing through regions of both solid matrix and pores. If xenon were dissolved in the solid, its NMR signal would be expected to be resolved from the xenon in the pores; this was not observed. A signal from dissolved xenon could also be overlapped with the signal from xenon in micropores. If it were overlapped, it would be detectable due to a longer lifetime of one portion of the adsorbed xenon signal in the saturation transfer experiment, since it is very unlikely that

xenon can diffuse through the solid matrix at a rate comparable to its passage through pores. In fact, the adsorbed signal is saturated uniformly and there is no resistant portion of the signal. It remains possible, although it is unlikely, that a dissolved xenon signal could be directly under the presaturation pulse, in which case it would not be detected. Overall, this experiment suggests that the detectable proportion of the adsorbed xenon is in an open pore network and is not dissolved in solid coal.

Chapter 6

PORE STRUCTURE CHANGES IN A MICROPOROUS CARBON FOLLOWING OXYGEN CHEMISORPTION AND DESORPTION

6.1. Introduction

The changes in the ^{129}Xe NMR signal for xenon adsorbed on a microporous carbon after successive oxidation and oxygen desorption steps were observed in an effort to describe the effect of controlled variations of the pore size and/or pore structure of the carbon. The intent of this study is to determine, first, whether ^{129}Xe NMR can detect minor alterations of pore size, and second, what pattern of pore size alteration occurs with successive treatments. This will be used to confirm or disprove the intuitively obvious decrease in micropore diameter when oxygen functional groups are attached to the pore walls following oxidation, and the increase in micropore diameter due to carbon loss as CO and CO₂ upon desorption, with concomitant removal of pore constrictions. Quantitative information on pore widening and narrowing is important in the development of carbons with tailored pore size. The results are also potentially useful in studies of the effect of weathering (oxidation due to exposure to ambient atmosphere) on the porous structure of coal.

Spherocarb microporous carbon was chosen to study the effects of pore size alteration because it has been physically well characterized. It is a high-surface-area carbon material designed for use as a gas chromatography column packing. It is reported to separate light hydrocarbons in GC analysis (C₁-C₄, Robillard et al., 1979) as well as air, CO, and CH₄ (reported by Phase Separations). The physical properties of Spherocarb have been extensively investigated in a study by Waters et al. (1988). Density and surface area data on Spherocarb are summarized in **Table 6.1**. The BET surface area (N₂, 77K) is virtually equal to the D-R surface area (CO₂, 298K). Thus,

Spherocarb does not act as a molecular sieve toward these gases, which would result in a significantly smaller N_2 surface area. This indicates that the micropores are not especially narrow; nor are they large enough for capillary condensation of N_2 to occur, which would result in larger N_2 surface area.

^{129}Xe NMR has been used to determine the pore diameter of Spherocarb by Wernett et al. (1991), who reported $15\text{\AA}$ pores. Waters et al. (1988) provided scanning electron microscope images which suggested that Spherocarb has significant macroporosity ($> 200\text{\AA}$) in addition to its predominant microporosity ($< 20\text{\AA}$). The ^{129}Xe NMR experiments reported in this thesis will detect an NMR signal from xenon in the micropores of the carbon, but not from the macropores. Adsorbed xenon that is restricted to the macropores is in a free-gas-like environment and is unlikely to contribute to a ^{129}Xe NMR signal with different chemical shift from that of the free gas; in addition, the T_1 of xenon is expected to be long enough in the macropores that the signal may not be evident at all, and this is the case in the spectra reported here. The macropores could indirectly influence the spectra if xenon rapidly exchanged between them and the micropores, however, which would have the effect of averaging the chemical shift values.

6.2. Experimental

Spherocarb 60-80 mesh (Phase Separations, Norwalk CT) was treated by oxygen chemisorption or desorption in the following steps: as-received Spherocarb was pretreated, oxidized, desorbed, oxidized a second time, and desorbed a second time. Oxidation and desorption were carried out in a Thermolyne 21100 tube furnace. As-received Spherocarb was pretreated at 250°C under nitrogen gas for two hours, then examined by NMR as described later in this section. Pretreatment removes any functional groups adsorbed on the as-received carbon that are labile at 250°C . Desorbing these first eliminates any ambiguity as to the cause of weight change in the subsequent oxidation step. Sample oxidation was performed by heating in a shallow tray at 250°C for 4-5 hours under an air flow of 170 mL/min . The sample was then cooled under air, weighed, and examined by NMR. Oxygen desorption from the sample was performed by heating to 850°C under a nitrogen flow of 200 mL/min .

Once the temperature reached 850 °C, which usually required 20 to 30 minutes, the sample was allowed to cool under nitrogen gas, removed, weighed, and examined by NMR. Subsequent oxidation and desorption steps were carried out on the same sample, so that the changes produced in the sample are cumulative.

^{129}Xe NMR spectra were acquired after each successive treatment. The sample was placed in a tared 10 mm NMR tube with a Rototite valve (Wilmad) and a glass rod. The rod served to decrease the total amount of Sphero carb necessary to fill the tube to sufficient height. Due to the large capacity of Sphero carb for xenon, this allowed the experiment to consume less gas overall while still providing very good signal-to-noise ratio; using less sample also helped to ensure that sample loss after desorption treatments would not result in insufficient sample for NMR. The sample was evacuated on the vacuum line to 10-15 $\mu\text{m Hg}$, at which point the tube was closed, removed from the line, weighed, and returned to the line. The tube was then re-evacuated and then dosed with xenon. The initial pressures ranged from about 600 to 900 torr and were selected based on the desired end pressure. Due to the large capacity of Sphero carb for xenon and the 900 torr limit of the gas line, second xenon doses were necessary for the higher-end pressures. Second doses were applied within a minute of the first. After exactly thirty minutes of adsorption time, the tube was sealed and weighed. The sample was then immediately inserted in the NMR instrument. The weight data was taken so that xenon uptake, by weight, could be compared to the pressure and to the ^{129}Xe chemical shift.

^{129}Xe NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A 90° pulse was applied with 2 s delay. Spectra in this group were run for 40 to 80 scans. Four spectra at a series of xenon pressures under 700 torr were acquired for each sample treatment. Xenon gas at 700 torr was used as an external chemical shift reference.

Table 6.1. Physical properties of Spherocarb, from Waters et al. (1988).

Average particle diameter, μm	140 $\pm$ 9
Apparent bulk density (Hg porosimetry), g/cc	0.56
Skeletal density (Hg porosimetry), g/cc	1.25
Helium density, g/cc	2.15
BET surface area (N_2 , 77 K), m^2/g	864
Dubinin-Radushkevich surface area (CO_2 , 298 K), m^2/g	869

6.3. Results and discussion

Xenon adsorbed in Spherocharb gives one signal, which is symmetrical and significantly narrower than that of coal, averaging 2000 Hz. ^{129}Xe NMR spectra acquired at a series of xenon pressures for pretreated regular Spherocharb are shown in **Figure 6.1**. No external gas signal at 0 ppm is observed. The oxidation/desorption treatments do not affect the appearance of the signal, and the spectra of the treated samples have the same appearance as that of the starting material.

^{129}Xe chemical shift vs. xenon uptake (grams xenon/ grams sample) are plotted for each treatment of the sample, **Figure 6.2 to 6.6**. Chemical shift vs. pressure for each sample is shown in **Figures 6.9 to 6.13**. The correlation of xenon uptake to the chemical shift was very good for all samples in this experiment, with correlation coefficients of 0.99 or better. The xenon chemical shift vs. pressure was not as good, however, with correlation coefficients in the range 0.90 to 0.99 with one sample exhibiting nonlinear behavior (desorption #1, **Figure 6.11**). Interestingly, the chemical shift remains linear with the weight uptake throughout; even for the sample in which chemical shift is a nonlinear function of xenon pressure, chemical shift is still a *linear* function of xenon uptake. The xenon uptake by weight is more closely related to the chemical shift than is the xenon pressure, and thus it may provide more accurate pore diameters when used according to the model of Demarquay and Fraissard (1987).

The intercept of ^{129}Xe chemical shift vs. xenon uptake (which is expected to be interchangeable with pressure when the isotherm is linear), is inversely related to the pore size according to the model of Demarquay and Fraissard (1987). Wernett et al. (1990) calculated the average pore diameter making the assumption that the pores are spherical. This choice could have been made based on the name of the material, which suggests some spherical quality, but there is no indication of pore shape from the manufacturer. It is evident on inspection of Spherocharb that it is the particles that are spherical. This is the more obvious reason that Spherocharb is so named. The pore shape must be assumed to apply the pore diameter model; thus, calculations in this chapter will be based on the perhaps more plausible cylindrical pores. The chemical shift vs. uptake (g/g) intercept changes upon sample treatment (**Table 6.2**) appear to be as expected: Oxidation increases the intercept relative to that for the preceding

Figure 6.1. ^{129}Xe spectra of regular Sphero carb, pretreated at 250 °C under N_2 . (a) 272 torr Xe; (b) 353 torr; (c) 418 torr; (d) 548 torr.

Figure 6.2. ^{129}Xe chemical shift vs. xenon uptake (g/g) for pretreated regular Sphero carb.

Figure 6.3. ^{129}Xe chemical shift vs. xenon uptake (g/g) for Spherocarb after oxidation #1.

Figure 6.4. ^{129}Xe chemical shift vs. xenon uptake (g/g) for Spherocarb after desorption #1.

Figure 6.5. ^{129}Xe chemical shift vs. xenon uptake (g/g) for Spherocarb after oxidation #2.

Figure 6.6. ^{129}Xe chemical shift vs. xenon uptake (g/g) for Spherocarb after desorption #2.

Table 6.2. Pore diameter calculations for Sphero carb subjected to two oxygen chemisorption and desorption cycles.

	as received*	oxidation 1	desorption 1	oxidation 2	desorption 2
Weight change, %	n/a	-0.8	-17	+7.6	-15.3
intercept, ppm	46.96	55.60	44.07	53.43	51.55
Diameter, Å	13.0	11.3	13.7	11.7	12.0

* pretreated in N₂ at 250 °C

step. According to the model of Demarquay and Fraissard (1987), this is consistent with the existence of relatively smaller pores after oxidation. Smaller pores are indeed expected after addition of oxygen functional groups to the pore walls. However, this is not the only explanation of the increase in xenon chemical shifts. The polarity of the oxygen functional groups on the pore walls could also cause an increase in chemical shifts overall. Suh et al. (1991) found that acidic functional groups on amorphous carbon increased the ^{129}Xe chemical shift to a greater extent than would be caused (estimating from Demarquay and Fraissard, 1987) by the degree of pore narrowing (measured using nitrogen adsorption).

The results in **Table 6.2.** also show that oxygen desorption decreases the intercept relative to the previous oxidation, indicating relatively larger pores, in agreement with the expected trend after the removal of oxygen functional groups from pore walls. This pattern held throughout the series, but the pore widening upon desorption was not cumulative. The calculated average pore diameter was greatest after the first desorption cycle; after the second desorption step it was actually smaller than that of the starting material.

The magnitude of the pore diameter changes calculated from the intercept was about ± 1 to 2 angstroms, which is about the length of a carbonyl group. If carbon-oxygen functional groups line the pore walls evenly, the diameter would decrease by about twice this amount. The magnitude of the pore size change suggests that oxygen functional groups are not covering the pore walls uniformly. This is quite reasonable since some sites on the wall may be more reactive than others; in addition, a prohibitive degree of crowding would be necessary to cover most of the pore walls. Since adsorbed xenon moves through the porosity during the NMR experiment, the diameter determined by ^{129}Xe NMR is probably an average value. It is not unreasonable that its value should decrease as some of the widened pores do not contribute to the adsorbed gas signal.

The slope of ^{129}Xe chemical shift vs. pressure for the series was also examined. It changed for each sample treatment. However, while the intercept changes can be related to pore size changes, the cause of the slope changes is not known for certain. Thus, the purpose of comparing slopes to sample treatments is to search for clues to whether the slope is directly related to structure. The relationship between slope and pore diameter is shown in **Figure 6.7.** It is apparent that there is not a direct

relationship. The slope as it changes with time order of treatment is shown in **Figure 6.8**. A lower slope is characteristic of the oxidized samples. These samples, with pore walls lined with oxygen functional groups, have slightly narrower pores on average than the desorbed samples. For these, the chemical shift vs. uptake slope is also smaller. The desorbed samples, with pore walls lined primarily with carbon atoms, have inconsistent values of the chemical shift vs. uptake slope.

A possible explanation for such behavior is that Spherocharb may not be homogeneous, and that one component may be removed or altered in the process of sample treatment. Spherocharb is marketed as a carbon molecular sieve, although its micropores are apparently too large for it to be a molecular sieve in a strict sense. Some carbon molecular sieves are made with an "eggshell" design, which means that they are two-component materials with an external layer, possessing narrow micropores, surrounding the bulk of the adsorbent material. The possibility that Spherocharb is manufactured with two layers could not be verified through the U. S. distributor. Spherocharb was developed, and is patented, in Japan. The trademark could not be linked to a U. S. patent. Others that have studied Spherocharb, such as Waters et al. (1988), have also reported that the method of manufacture could not be ascertained.

Since it is significant to the interpretation of the results of this study, what information is available on Spherocharb particle morphology will be considered, with emphasis on whether there is any indication that Spherocharb is not a homogeneous material. Scanning electron micrographs of the external surface of Spherocharb particles and reflected-light photomicrographs of particle cross sections were taken by Waters et al. (1988) at various degrees of carbon loss upon combustion. Combustion oxidizes the carbon, removing it as CO and CO₂, which is also the effect of oxygen chemisorption/desorption used in this study, but combustion is a more severe, less controlled method.

The cross sectional photomicrographs indicate that the porosity in the particle centers, after varying degrees of mass loss, is unchanged for most particles. The resolution limit is 1 μm . The unchanged internal porosity, at this level of magnification, is an indication that the internal region was not penetrated by oxygen during combustion. About 5% of the particles had very large internal cavities of half or more of the particle diameter before combustion. After combustion, these showed evidence that oxygen had freely penetrated the cavities.

Figure 6.7. Slope (ppm)(g)/gXe of chemical shift vs. uptake plots as a function of the calculated pore diameter for the series of treatments of Spherocharb.

Figure 6.8. Evolution of the slope of the chemical shift vs. uptake plots $[(\text{ppm})(\text{g})/\text{gXe}]$ with oxygen adsorption/desorption treatment.

The SEM photomicrographs of the external particle surface showed that Spherocarb particles are spherical and retain this overall shape after mass loss. The external surface of the particles develop an increasing number and size of macropores ($> 200\text{\AA}$) with increasing carbon burnoff, appearing pitted and spongy. The cross sections indicate that *these pores extend very little distance into the particle*. The authors interpret the extent of the development of external surface macropores in terms of the extent of oxygen diffusion under the combustion conditions, and this is certainly important, but the observed preferential mass loss from a thin outer layer could also conceivably indicate that the outer layer is a different, more labile material than the inner core. This is supported by the fact that Saran char, a homogeneous microporous carbon which was examined in the same study, did not develop a layer of distinctly different morphology at the external surface upon combustion.

Based on these considerations, the possibility is suggested that Spherocarb may be composed of a layer of one carbon material surrounding a core of a second carbon material. In the course of the sample treatments reported in this Chapter, at the time of the second desorption, the pore diameter decreased and the chemical shift slope pattern changed, yet the desorption process cannot result in the creation of a smaller pore region from a larger one. It is, however, reasonable to assume that the desorption process destroys a portion of the carbon solid material, leaving behind a portion that may be of a different composition.

Figure 6.9. Chemical shift vs. xenon pressure for pretreated regular Spherocharb.

Figure 6.10. Chemical shift vs. xenon pressure for Sphero carb after oxidation #1.

Figure 6.11. Chemical shift vs. xenon pressure for Sphero carb after desorption #1.

Figure 6.12. Chemical shift vs. xenon pressure for Sphero carb after oxidation #2.

Figure 6.13. Chemical shift vs. xenon pressure for Sphero carb after desorption #2.

6.4. Conclusions

A preliminary comparison was made of ^{129}Xe chemical shift vs. pressure to chemical shift vs. xenon uptake by weight. The results show that the chemical shift vs. uptake is strongly linear, while chemical shift vs. pressure is not always linear in the pressure range studied. The uptake by weight is a more reliable measure of xenon density in the sample than equilibrium pressure, and is preferable to measuring the pressure unless the sample isotherm at the experimental temperature is known to be linear.

The intercept of chemical shift vs. weight uptake (g/g) following adsorption of xenon indicates pore diameter changes in Spherocharb that are consistent with slight narrowing, opening, and re-narrowing of porosity following the series of treatments oxidation, desorption, re-oxidation. The magnitude of the pore diameter change is approximately $\pm 1\text{\AA}$. The slope of chemical shift vs. weight uptake appears more closely related to sample chemistry (oxidized vs. not oxidized) than to pore diameter.

A final oxygen desorption results in a pore diameter within the established pattern, in that it is larger than in the directly preceeding oxidation step. However, the calculated pore diameter is smaller than that of the the starting material, which is not consistent with significant carbon loss from the same pore walls that have gone through the oxidation and desorption steps. The last desorption step also has a smaller slope of chemical shift vs. xenon uptake than occurs for the remainder of the sample set. These results are inconsistent with the widening of existing porosity due to loss of carbon-oxygen compounds from the pore walls in the last desorption step. It is more suggestive of access by xenon to a different porous region in the solid that has been previously closed. The existence of two distinct pore regions in Spherocharb is indicated, but not proven, by the cumulative pore size changes determined with ^{129}Xe NMR.

Chapter 7

SUMMARY, CONCLUSIONS, AND DIRECTIONS FOR FUTURE RESEARCH

7.1. Summary and conclusions

Three different ^{129}Xe NMR techniques have been used in this report for the investigation of coal micropore structure: selective presaturation with saturation transfer, the time tracking of the xenon adsorption process by NMR, and the use of an established chemical shift-pore diameter model. Presaturation/saturation transfer and time tracking of the adsorption process were developed as part of this work to determine the connectivity of the micropore structure. These methods were used together to formulate the following model of coal structure. The micropore structure of coal is open to the external surface, it is constricted, and its connectivity changes with coal rank. The results support the concept that in low-rank coals, microporosity is part of a dendritic system incorporating larger porosity; in contrast, in higher-rank coals, coal microporosity is part of an interconnected, honeycomb-type network with both fewer large pore regions, and more constricted openings to them. This is illustrated in **Figure 7.1**. This concept is consistent with the work of Gan et al. (1972) on the pore size distribution in coals as a function of rank, and further establishes the recently challenged fact that the pores are indeed interconnected.

The technique of selective presaturation applied to xenon adsorbed in a porous material is a unique adaptation of some well established NMR principles, as described in Chapter 5. This method is potentially very versatile. It relies on the balance of power level and pulse length to follow patterns of xenon motion in and out of a particle. The diffusion or exchange rate in the system studied must have longer characteristic times than the time it takes to saturate the signal of choice at an appropriate power level. The higher the power level used, the wider the excitation bandwidth and the less selective

the presaturation pulse can be. This method clearly demonstrates the existence of a distribution of environments for adsorbed xenon in solids where the signals from xenon adsorption sites are not resolved as individual xenon signals. The hole-burning effect on the adsorbed xenon signal can be extended, using longer presaturation time, to the entire adsorbed xenon signal. This is an effect of xenon diffusion among the internal-surface adsorption sites. Saturation transfer to the external gas signal is observed with increasing presaturation time, and is an effect of xenon exchange out of the microporous domains into large pore spaces. These experiments have been used to show again that coals have an open microporous network, that the porosity is constricted (especially for high-rank coals), and that the connectivity to the external surface changes markedly with rank.

The time tracking technique can distinguish different locations of xenon populations during the adsorption process, which is very useful for the description of unknown pore structures. It has had some use, with a different perspective from its use in this thesis, in other studies. Ryoo et al. (1994) used it to see if a polymer coating intruded into zeolite pores, and Springuel-Huet et al. (1996) used it to follow benzene adsorption in a zeolite. From the perspective of investigating unknown pore structures, it can identify intermediate environments occupied only when xenon is en route to its final, equilibrium location in the solid. Tracking xenon adsorption can also potentially distinguish the transition in chemical shift of adsorbed xenon from its value during a diffusion-dominated experiment (in which chemical shift is free of exchange effects), to its value when - and if - exchange takes place once equilibrium is established.

The results of all these ^{129}Xe NMR experiments consistently highlight several key aspects of coal pore structure. One is that the pore network is open to the external surface. The internal porosity is not accessed by dissolution of xenon gas in the solid coal matrix. The absence of a pressure-invariant chemical shift in the ^{129}Xe NMR spectra, and the absence of any part of the adsorbed signal that was resistant to saturation transfer, are thought to be convincing evidence for this. It was further shown in the time-dependent spectra that early in, and throughout, the adsorption process, there is no indication of dissolution of xenon in solid coal. Dissolution of a small amount of xenon below the detectability limits of the experiment was not ruled out.

Low-rank coal showing dendritic-type pore structure incorporating large pores.

High-rank coal showing primarily microporous regions with microporous connections to large pores or fractures.

Figure 7.1. Conceptual illustration of pore networks in low-rank and high-rank coal consistent with the results of ^{129}Xe NMR presaturation, saturation transfer, and adsorption tracking experiments. Microporous regions are dark.

While open, the pore network is also highly constricted in coals of higher rank. (Indeed, for many applications this may make it effectively closed.) The degree of constriction of the pore network is shown by the effect of particle size variation on the ^{129}Xe NMR signal for xenon in a mv bituminous vitrinite. Particle size variation from +60 to -400 mesh has little effect on the spectra, which means exchange between xenon in the micropores and that in larger pores or the external surface is not significant in the vitrinite. Xenon diffusion is also quite slow in this vitrinite compared to most coals studied. Time-dependent spectra of the vitrinite during adsorption indicate that there is a direct path to the microporosity. This again supports the idea that the means by which xenon diffuses into the vitrinite is through a highly constricted and/or highly convoluted path through the pore structure. There is no indication from the NMR spectra that xenon is dissolved in the solid.

The particle size effect on adsorption rate in an anthracite indicates that the porosity in the smaller particles is less constricted, or that they possess more openings to the external surface. The pattern of xenon uptake over time during adsorption on the anthracite was the same as the pattern of chemical shift over time; this further supports an open pore network in the anthracite. An external gas signal was observed for large anthracite particles but not for small particles. It is suggested that this may indicate that there is more larger porosity or fracture in the large anthracite particles.

Two general types of connectivity of coal pore networks were found using the selective presaturation/saturation transfer experiments. These show that differences in the physical exchange rate of xenon between the micropores and large pores in four coals are significant, and the effect is related to the rank of the coal. The saturation transfer rates indicate much faster exchange of xenon between internal microporosity and large pores external to the microporosity, in low-rank than in high-rank coals. This supports the idea that in low-rank coals, micropores are connected to larger, feeder pores. The higher-rank coals show evidence of a highly interconnected micropore network with limited access to larger pores. In an anthracite the access of xenon to larger pore regions, while much more limited than in low-rank coal, is faster than in a mv bituminous coal, which may be due to a lower degree of tortuosity of its micropores, or to the presence of cracks in the particle which would increase the

number of openings to the micropores without providing a route connected to them as a system, as a dendritic pore structure would.

This study has shown that the width of the adsorbed xenon signal for coals is due to overlap of multiple chemical shifts; thus, the signal width is a reflection of the width of the adsorption site distribution that is available to xenon in the coals. The adsorbed signal linewidth decreases with increasing coal rank. This illustrates that the adsorption site distribution - taken to mean pore size distribution with possible influence from a pore-wall chemistry distribution - becomes more homogeneous as coal rank increases.

The interpretation of ^{129}Xe chemical shift pressure dependence has been explored. There are difficult issues concerning whether the pore diameter calculation method from the mean free path model is sound (Chapters 2 and 3). These cannot be resolved by the study conducted here on coal, because the micropore diameters cannot be definitively evaluated any other way. The pore diameter range found here, 6 to 8 Å, is in the same size scale as that found by Tsiao and Botto (1991); it is also of the same scale as the CO_2 D-R plot estimation of pore size. The average pore diameters determined by NMR in Chapter 3 show a rank dependence which has not been reported in other xenon NMR studies on coal. The chemical shift vs. pressure intercepts reveal a pattern in relation to coal rank that is similar to surface area vs. rank (Gan et al., 1972). The smallest pore diameters in the sample set are 5.6 - 5.8 Å, found in the Blind Canyon hvAb coal and the Pocahontas lvb coal. Average pore diameters calculated by this method are larger at the low and high rank ends. However, the CO_2 D-R plot estimates of average pore size for the same coals do not show this pattern. Since both this method and the NMR method for determination of average pore size are experimental, the exact values of the pore sizes should be treated with caution.

Nevertheless, the average pore diameters obtained may fit the picture emerging from the dynamic NMR methods. The coals with the greatest evidence for constricted porosity are in the same rank range as those for which the smallest porosity was calculated, a mv bituminous vitrinite and a mv bituminous coal. The anthracite appeared by saturation transfer to have more open porosity than the mv bituminous coal. This also agrees in a general way with the larger pore diameter calculated for the anthracite, and tends to support the validity of the average pore diameters calculated.

The slope of chemical shift vs. pressure in the six coals examined tends to decrease with increasing coal rank; however, the slope did not have a definite relationship to coal surface area. The evidence from the Spherocarb study in Chapter 6 indicates that the slope of chemical shift vs. uptake was smaller in oxidized than in non-oxidized samples. This could mean that smaller slope is related to smaller pore size or to the presence of more electronegative pore wall substituents (oxygen vs. carbon). The data from the six coals support this in that the oxygen content decreases with rank throughout the series. The pore size decreases through ~90% carbon and then shows an increase. Overall, however, this investigation did not yield a definite relationship of chemical shift vs. pressure slope to *structural* features of the samples studied.

Another issue of concern is whether the chemical shifts, and not just the shift vs. pressure slope, could be influenced in part by interaction with more electronegative pore wall substituents such as oxygen. If so, the interpretation of chemical shift in terms of pore diameter is not reliable, at least in groups of samples with a variety of pore wall chemistries. This is addressed in the Spherocarb study. The smallest pore diameters were found in the oxidized samples; however, since these were also projected to have oxygen atoms occupying some of the pore space, these effects could not be separated. Interestingly, the pore sizes in the coals may give an answer to this question. The oxygen content of coals decreases monotonically with rank (Van Krevelen, 1993). If the presence of oxygen determined the pore diameter calculated by NMR, then it would also steadily decrease. Since it reaches a minimum and rises again, and since other experiments verify this, it remains possible that the pore diameter is the primary influence on the values of the xenon chemical shifts in these coals, and that the average pore diameters calculated by NMR are broadly accurate.

7.2. Directions for future research

The connectivity of a pore network is most clearly identifiable if it can be imaged. The most promising future direction for research in this area is that ^{129}Xe can be developed for use in magnetic resonance imaging (MRI) of pore structures. Pore sizes could possibly be differentiated based on different xenon mobility, T_1 , or chemical shift, all of which are sensitive to the size of the structure enclosing the xenon

atoms. While the chemical shift for xenon in enclosures up to approximately 20Å differs significantly from that of the free gas, the differences in T_1 values between adsorbed and free xenon - which can range from ms to hours - are likely to remain significant over a much larger size scale. Based on the very broad range of T_1 values as well as the sensitivity of chemical shift to size in microporous spaces, ^{129}Xe MRI could potentially provide better resolution than is currently available. The general utility of imaging coal is that the pore structure in three dimensions would be available on intact samples; regions of different connectivity in different coal macerals may be separately identifiable in a single sample; and the effect of oxidation, weathering, or solvent extraction on the pore structure could be determined.

Another useful study would address the accurate determination of ^{129}Xe T_1 relaxation time in coal. Xenon T_1 relaxation time varies with the environment in which xenon is adsorbed and is longer for extraparticle xenon. The T_1 relaxation times of xenon in those coals where intra/extra particle exchange is fast cannot be measured by standard inversion-recovery experiments alone. This is because xenon atoms sample environments which cause the relaxation time to change during the course of the experiment. The T_1 could be determined by data analysis that separates the relaxation rate from the exchange rate (Jackman et al., 1991), if the rate of intra/extraparticle exchange is known. Saturation transfer may be used to estimate the exchange rate; alternatively, 2D-EXSY experiments could be performed to determine a quantitative intra/extraparticle exchange rate.

Lastly, it would be interesting to test the assertion made in this report that the external xenon NMR signal at 0-5 ppm in fact originates from xenon in large pores rather than at the external surface. Spectra acquired with very long delays (over approximately 4 min) may reveal an external-surface gas signal in addition to the signal in this location that is usually detected using shorter delays. The determination of saturation transfer time from adsorbed gas to this true external-surface gas would be a useful extension of the work reported in Chapter 5, which characterizes exchange times between xenon in micropores and that in large pores.

REFERENCES

- Anderson, R.B., Hall, W.K., Lecky, J.A. and Stein, K.C. Sorption studies on American coals. *J. Phys. Chem* **60**, 1548 (1956).
- Annen, M.J., Davis, M. E., and Hanson, B. E. ^{129}Xe NMR spectroscopy on molecular sieves SAPO-37, $\text{AlPO}_4\text{-5}$, SAPO-5 and SSZ-24. *Cat. Lett.* **6**, 331 (1990).
- Bale, H. D., Carlson, M. L., Kalliat, M., Kwak, C. Y., and Schmidt, P. W. Small-angle X-ray scattering of the submicroscopic porosity of some low-rank coals. In The Chemistry of Low-Rank Coals (Schobert, H. H., Ed.), American Chemical Society, Washington, D.C. 1984, p. 79.
- Bansal, N. and Dybowski, C. Using xenon-129 NMR spectroscopy to measure diffusivity of water in microporous Y zeolites. *J. Magn. Reson.* **89**, 21 (1990).
- Bonardet, J., Fraissard, J., Unger, K., Kumar, D., Ferrero, M., Ragle, J., and Conner, W. C. The use of ^{15}N NMR for the understanding of nitrogen physisorption. In Characterization of Porous Solids III, Studies in Surface Science and Catalysis, (Roquerol, J., Rodriguez-Reinoso, F. Sing, K. S. W., and Unger, K. K., Eds.), Vol. 87, Elsevier Science, 1994, p. 319.
- Bottani, E. J., Bakaev, V., and Steele, W. A. A simulation/experimental study of the thermodynamic properties of carbon dioxide on graphite. *Chem. Eng. Sci.* **49** (1994), 2931.
- Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309 (1938).
- Chen, Q. J. and Fraissard, J. Application of the ^{129}Xe NMR technique. 1. Variable-temperature ^{129}Xe NMR study of xenon adsorbed in zeolites. *J. Phys. Chem.* **96**, 1809 (1992a).

- Chen, Q. J. and Fraissard, J. Application of the ^{129}Xe NMR technique. 2. ^{129}Xe NMR study of xenon diffusion between zeolite crystallites. *J. Phys. Chem.* **96**, 1814 (1992b).
- Cheung, T. T. P. Temperature dependence of ^{129}Xe NMR of xenon in microporous solids. *J. Phys. Chem.* **99**, 7089 (1995).
- Cheung, T. T. P., Fu, C. M., and Wharry, S. ^{129}Xe NMR of xenon adsorbed in Y zeolites at 144K. *J. Phys. Chem.* **92**, 5170 (1988).
- Cody, G. D., and Davis, A. Direct imaging of coal pore space accessible to liquid metal. *Energy Fuels* **5**, 776 (1991).
- DeDios, A. C. and Jameson, C. J. The NMR chemical shift: Insights into structure and environment. *Annual Reports on NMR Spectroscopy* **29**, 1 (1994).
- Demarquay, J. and Fraissard, J. ^{129}Xe NMR of xenon adsorbed on zeolites. Relationship between chemical shift and the void space. *Chem. Phys. Lett.* **136**, 314 (1987).
- Derouane, E. G., and Nagy, J. B. Surface curvature effects on the NMR chemical shift for molecules trapped in microporous solids. *Chem. Phys. Lett.* **137**, 341 (1987).
- Dubinin, M.M., Zaverina, E.D., and Radushkevich, L.V. *Zh. Fiz. Khimii* **21**, 1351 (1947).
- Dubinin, M. M. Microporus structures and adsorption properties of carbonaceous adsorbents. *Carbon* **21**, 359 (1983).
- Dubinin, M. M. Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures. *Pure Appl. Chem.* **61**, 1841 (1989).
- Dybowski, C., Bansal, N., and Duncan, T. M. NMR spectroscopy of xenon in confined spaces: Clathrates, intercalates, and zeolites. *Annu. Rev. Phys. Chem.* **42**, 433 (1991).

Earl, W. L., Kim, Y-W., and Smith, D. M. NMR measurement of pore structure. In Characterization of Porous Solids III, Studies in Surface Science and Catalysis, (Roquerol, J., Rodriguez-Reinoso, F. Sing, K. S. W., and Unger, K. K., Eds.), Vol. 87, Elsevier Science, 1994, p. 301.

Emmett, P. H. and Brunauer, S. The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts. *J. Am. Chem. Soc.* **59**, 1553 (1937).

Freisen, W. I., and Mikula, R. J. Mercury porosimetry of coals - pore volume and compressibility. *Fuel* **67**, 151 (1988).

Fukasawa, J., Kaneko, K., Poon, C.-D., and Samulski, E. T. Molecular motion in micropore space. In Characterization of Porous Solids III, Studies in Surface Science and Catalysis, (Roquerol, J., Rodriguez-Reinoso, F. Sing, K. S. W., and Unger, K. K., Eds.), Vol. 87, Elsevier Science, 1994, p. 311

Freeman, R. A Handbook of Nuclear Magnetic Resonance. Longman Scientific and Technical, Essex, U.K. 1988.

Gallegos, D. P., Munn, K., Smith, D. M., and Stermer, D. L. A NMR technique for the analysis of pore structure: Application to materials with well defined pore structure. *J. Colloid Interf.Sci.* **119**, 127 (1987).

Gan, H., Nandi, S. P., and Walker, P. L. Jr. Nature of the porosity in American coals. *Fuel* **51**, 272 (1972).

Gregg, S. J., and Sing, K.S.W., Surface Area, Adsorption, and Porosity 2nd edition. Academic Press, London (1982).

Harris, L. A. and Yust, C. S. Transmission electron microscope observations of porosity in coal. *Fuel* **55**, 233 (1976).

Harris, L. A. and Yust, C. S. The ultrafine structure of coal determined by electron microscopy. in Coal Structure, A.C.S. Washington, D. C. pp.321-336 (1981).

- Heink, W., Karger, J., Pfeifer, H., and Stallmach, F. Measurement of the intracrystalline self-diffusion of xenon in zeolites by the NMR pulsed field gradient technique. *J. Am. Chem. Soc.* **112**, 2175 (1990).
- Hirsch, P. B. X-ray scattering from coals. *Proc. Royal Soc., (London)* **A226**, 143 (1954).
- Ito, T., De Menorval, L. C., Guerrier, E. and Fraissard, J. P. NMR study of ^{129}Xe adsorbed on L, Z, and ZSM zeolites. *Chem. Phys. Lett.* **111**, 271 (1984).
- Jackman, L. M., Rakiewicz, E. F., and Benesi, A. J. Solution structure and dynamics of a mixed tetramer of lithium 3,5-dimethyl phenolate and lithium perchlorate in diethyl ether and some related systems. *J. Am. Chem. Soc.* **113**, 4101 (1991).
- Jameson, C. J., Jameson, K. A., and Cohen, S. M. Temperature and density dependence of the ^{129}Xe chemical shift in xenon gas. *J. Chem. Phys.* **59**, 4540 (1973).
- Jameson, C. J., Jameson, K. A., Gerald, R. E. and DeDios, A. C. Nuclear magnetic resonance studies of xenon clusters in zeolite NaA. *J. Chem. Phys.* **96**, 1676 (1992).
- Jameson, K. A., Jameson, C. J., and Gerald, R. E. Cage-to-cage migration rates of Xe atoms in zeolite NaA from magnetization transfer experiments and simulations. *J. Chem. Phys.* **10**, 1775 (1994).
- Jeener, J., Meier, B. H., Bachmann, P., and Ernst, R. R. Investigation of exchange processes by two-dimensional NMR spectroscopy. *J. Chem. Phys.* **71**, 4546 (1979).
- Johnson, D. W. and Griffiths, L. Application of xenon-129 NMR to the characterization of zeolites. *Zeolites* **7**, 484 (1987).
- Kaplan, J. I., and Fraenkel, G. NMR of Chemically Exchanging Systems. Academic Press, New York (1980).
- Karger, J., Pfeifer, H., Stallmach, F., Feoktistova, N. N., and Zhdanov, S. P. ^{129}Xe and ^{13}C PFG n.m.r. study of the intracrystalline self-diffusion of Xe, CO_2 , and CO. *Zeolites* **13**, 50 (1993).

Karger, J. and Ruthven, D. M. Diffusion in Zeolites and Other Microporous Solids. J. Wiley, New York (1992).

Lamond, T. G. and Marsh, H. *Carbon* **1**, 281 (1964).

Larsen, J. W., Hall, P., and Wernett, P. C. Pore structure of the Argonne Premium coals. *Energy Fuels* **9**, 324 (1995).

Larsen, J. W., and Wernett, P. C. Pore structure of Illinois No. 6 coal. *Energy Fuels* **2**, 719 (1988).

Larsen, J. W., and Wernett, P. C. The Argonne coals do not have an extended interconnected pore network. in *American Chemical Society preprints (Division of Fuel Chemistry)*, pp 849-855, San Francisco, 1992.

Larsen, R. G., Shore, J., Schmidt-Rohr, K., Emsley, L., Long, H., Pines, A., Janicke, M., and Chmelka, B. F., NMR study of xenon dynamics and energetics in Na-A zeolite. *Chem. Phys. Lett.* **214**, 220 (1993).

Leon y Leon, C. A. Importance of the Surface Properties of Carbons for Their Use as Catalyst Supports. Ph.D. Thesis, The Pennsylvania State University, 1993.

Liaw, H.-K., Kulkarni, R., Chen, S., and Watson, T. Characterization of fluid distributions in porous media by NMR techniques. *AIChE J.* **42**, 538 (1996).

Lin, J. S., Hendricks, R. W., Harris, L. A., and Yust, C. S. Microporosity and micromineralogy of vitrinite in a bituminous coal. *J. Appl. Cryst.* **11**, 621 (1978).

Liu, S. B., Lee, C. S., Shiu, P. F., and Fung, B. M. Interpretation of xenon adsorption isotherms and Xe-129 NMR chemical shifts on ion-exchanged NaY zeolites. In Zeolites and Microporous Crystals, Studies in Surface Science and Catalysis, (Hattori, T. and Yashima, T., Eds.), Vol. 83, Elsevier, 1994, p. 233.

Maggs, F.A.P., *Res. Corresp.* **6**, 135 (1958).

Mahajan, O. P. CO₂ surface area of coals: The 25-year paradox. *Carbon* **29**, 735 (1991).

Mandelbrot, B. B. The Fractal Geometry of Nature. Freeman, San Francisco (1982).

Mansfield, M., Flohr, A., and Veeman, W. S. Application of ^{129}Xe NMR to polymer blends. *Appl. Magn. Reson.* **8**, 573 (1995).

Marsh, H. Adsorption methods to study microporosity in coals and carbons - a critique. *Carbon* **25**, 49 (1987).

Marsh, H. and Siemieniewska, T. The surface areas of coals as evaluated from the adsorption isotherms of carbon dioxide using the Dubinin-Polanyi equation. *Fuel* **44**, 355 (1965).

Menon, V. C., Kyotani, T., Danner, R. P., and Radovic, L. R. On the porous structure of coals: Evidence for the existence of interconnected pores from activated diffusion effects at room temperature. *Proc. 7th International Conference on Coal Science*, (K. H. Michaelian, Ed.), Vol. I, Banff, Alberta, Canada, 1993, p. 398.

Moudrakovski, I. L., Ratcliffe, C. I., and Ripmeester, J. A. Application of ^{129}Xe 2D-EXSY NMR to intra- and interparticle exchange in zeolites. *Appl. Magn. Reson.* **8**, 385 (1995).

Nandi, S. P., and Walker, P. L. Jr. Diffusion of argon from coals of different rank. In *Coal Science*, ACS, Washington, D.C. (1966), p. 379.

Nandi, S. P., and Walker, P. L. Jr. Activated diffusion of methane in coal. *Fuel* **49**, 309 (1970).

Proctor, W. G. and Yu, F. C. On the magnetic moments of Xe^{129} , Bi^{209} , Sc^{45} , Sb^{121} , and Sb^{123} *Phys. Rev.* **78**, 471 (1950).

Radovic, L. R., Menon, V. C., Leon y Leon, C. A., Kyotani, T., Danner, R. P., Anderson, S., and Hatcher, P. G. On the porous structure of coals: Evidence for an interconnected but constricted micropore system and implications for coalbed methane recovery. *Adsorption* **3**, 221 (1997).

Ripmeester, J. A., Ratcliffe, C. I., and Tse, J. S. The nuclear magnetic resonance of ^{129}Xe trapped in clathrates and some other solids. *J. Chem. Soc. Faraday Trans. 1* **84**, 3731 (1988).

Ripmeester, J.A. and Ratcliffe, C.I. On the application of ^{129}Xe NMR to the study of microporous solids. *J. Phys. Chem.* **94**, 7652 (1990).

Ripmeester, J.A. and Ratcliffe, C.I. ^{129}Xe NMR spectroscopy in microporous solids: the effect of bulk properties. *An. Chim. Acta* **283**, 1103 (1993).

Ripmeester, J.A. and Ratcliffe, C.I. The anisotropic chemical shift of ^{129}Xe in the molecular sieve ALPO-11: A dynamic averaging model. *J. Phys. Chem.* **99**, 619 (1995).

Robillard, M. V., Siggia, S., and Uden, P. C. Effect of oxygen on composition of light hydrocarbons evolved in oil shale pyrolysis. *Anal. Chem.* **51**, 435 (1979).

Ryoo, R., Kwak, J.H., and Demenorval, L.-C. A ^{129}Xe NMR spectroscopic technique to probe exclusively the internal surface of zeolite crystallites by coating of the external surface. *J. Phys. Chem.* **98**, 7101 (1994).

Sanders, J.K.M.; Hunter, B.K. Modern NMR Spectroscopy: A Guide for Chemists, Oxford University Press, New York, 1993.

Seidel, A., Rittner, F. and Boddenberg, B. ^{129}Xe NMR chemical shifts and linewidths of xenon in zeolites ZnY. *J. Chem. Soc., Faraday Trans.* **92**, 493 (1996).

Setek, M., Snook, I. K., and Wagenfeld, H. K. Determination of the microstructure of wet and dry brown coal by small-angle x-ray scattering. in The Chemistry of Low Rank Coals. American Chemical Society, Washington, D.C. p. 95 (1984).

Simpson, J. H., Wen, W.-Y., Jones, A. A., Inglefeld, P. T., and Bendler, J. T. Measurement of diffusion coefficients in polystyrene using xenon-129 NMR. *Appl. Magn. Reson.* **8**, 349 (1995).

Springuel-Huet, M.-A., and Fraissard, J. ^{129}Xe NMR of xenon adsorbed on the molecular sieves AlPO₄-11 and SAPO-11. Chemical shift anisotropy related to the assymetry of the adsorption zones. *Chem. Phys. Lett.* **154**, 299 (1989).

Springhuel-Huet, M.-A., Nosov, A., Karger, J., and Fraissard, J. ^{129}Xe NMR study of the bed resistance to molecular transport in assemblages of zeolite crystallites. *J. Phys. Chem.* **100**, 7200 (1996).

Stengle, T. R., Reo, N. V., and Williamson, K. L. Nuclear magnetic resonance solvent shifts of xenon. A test of the reaction field model. *J. Phys. Chem.* **85**, 3772 (1981).

Stoeckli, F., Huguenin, D., Greppi, A., Jakubov, T., Pribylov, A., Kalashinkov, S., Fomkin, A., Pulin, A., Regent, N., and Sherpinski, V. On the adsorption of CO₂ by active carbons. *Chimia* **47**, 213 (1993).

Suh, D. J., Park, T.-J., Ihm, S.-K., and Ryoo, R. ¹²⁹Xe NMR spectroscopy of xenon gas adsorbed on amorphous carbons. *J. Phys. Chem.* **95**, 3767 (1991).

Tomaselli, M., Meier, B. H., Robyr, P., Suter, U. W., and Ernst, R. R., Direct measurement of xenon exchange between gas and liquid phase by 2D NMR. *Chem. Phys. Lett.* **214**, 1 (1993).

Tsiao, C. and Botto, R. E. ¹²⁹Xe NMR investigation of coal micropores. *Energy Fuels* **5**, 87 (1991).

Van Krevelen, D. W., Coal, 3rd edition, Elsevier, Amsterdam (1993).

Walker, P. L. Jr. and Mahajan, O. P. Pore structure in coals. *Energy Fuels* **7**, 559 (1993).

Walker, P. L. Jr. and Kini, K. A. Measurement of the ultrafine surface area of coals. *Fuel* **44**, 453 (1965).

Walker, P. L. Jr. Microporosity in coals: Its characterization and implications for coal utilization. *Phil. Trans. Royal Soc. Lond.*, **300**, 65 (1981).

Walker, P. L. Jr. and Mahajan, O. P. Pore structure in coals. *Energy Fuels* **7**, 559 (1993).

Washburn, E. W. Note on a method of determining the distribution of pore sizes in a porous material. *Proc. Natl. Acad. Sci. USA* **7**, 115 (1921).

Waters, B. J., Squires, R. G., and Laurendeau, N. M. Morphological development and intrinsic reactivity for combustion of two microporous carbon chars. *Combust. Sci. Technol.* **62** 187 (1988).

Wernett, P. C., Larsen, J. W., Yamada, O., and Yue, H. J. Determination of the average micropore diameter of an Illinois no. 6 coal by ^{129}Xe NMR. *Energy Fuels* **4**, 412 (1990).

Wernett, P. C. Characterization of the Pore Structure of Coals. Ph. D. Thesis, Lehigh University (1991).

Zhu, X., Moudrakovski, I. L., and Ripmeester, J. A. ^{129}Xe NMR two-dimensional exchange spectroscopy of diffusion and transport in coal. *Energy Fuels* **11**, 245 (1997).

Zhu, X. ^{129}Xe NMR Spectroscopy in Coal Micropores. M.S. Thesis, Carleton University, 1994.

APPENDIX A:
ADSORPTION ISOTHERMS AND THEIR ANALYSES

Figure A1. N₂ adsorption isotherm (77K) for the Beulah lignite.

Figure A2. BET plot for the Beulah lignite.

Figure A3. CO₂ adsorption isotherm (273K) for the Beulah lignite.

Figure A4. D-R plot for the Beulah lignite.

Figure A5. N₂ adsorption isotherm (77K) for the Wyodak subbituminous coal.

Figure A6. BET plot for the Wyodak subbituminous coal.

Figure A7. CO₂ adsorption isotherm (273K) for the Wyodak subbituminous coal.

Figure A8. D-R plot for the Wyodak subbituminous coal.

Figure A9. CO₂ adsorption isotherm (273K) for the Adaville hvC bituminous coal.

Figure A10. D-R plot for the Adaville hvC bituminous coal.

Figure A11. N₂ adsorption isotherm (77K) for the Blind Canyon hvA bituminous coal.

Figure A12. BET plot for the Blind Canyon hvA bituminous coal.

Figure A13. CO₂ adsorption isotherm (273K) for the Blind Canyon hvA bituminous coal.

Figure A14. D-R plot for the Blind Canyon hvA bituminous coal.

Figure A15. N₂ adsorption isotherm (77K) for the Pocahontas IV bituminous coal.

Figure A16. BET plot for the Pocahontas lv bituminous coal.

Figure A17. CO₂ adsorption isotherm (273K) for the Pocahontas IV bituminous coal.

Figure A18. D-R plot for the Pocahontas lv bituminous coal.

Table A1. Summary of CO₂ adsorption data for five coals.

Coal	D-R slope	Average pore size, nm	D-R surface area, m ² /g
ligA	-0.1085	0.59	221
subB	-0.1578	0.68	491
hvCb	-0.1244	0.61	236
hvAb	-0.1286	0.65	121
lvb	-0.1438	0.64	177

APPENDIX B:

Chemical shift vs. pressure data for six coals

**Chemical shift, linewidth, and xenon uptake vs. time data
for anthracite and Spherocarb**

Table B1. Chemical shift vs. pressure data for the six coals examined in Chapter 3.

lig A		subB		hvCb		hvAb		lvb		an	
P, torr	ppm	P, torr	ppm	P, torr	ppm	P, torr	ppm	P, torr	ppm	P, torr	ppm
540	150	619	161	656	124	666	187	683	161	620	119
410	139	565	152	514	122	520	178	538	157	517	114
340	132	393	140	347	120	435	176	366	153	395	111
		306	129	280	118	379	173	322	151	350	109

Table B2. Chemical shift and linewidth vs. time data for 40-60 and -100 mesh anthracite; chemical shift vs. time data for Spherocarb.

Spherocarb		anthracite -100 mesh			anthracite 40-60 mesh		
time, min	chem. shift, ppm	time, hrs	chem. shift, ppm	linewidth Hz	time, hrs	chem. shift, ppm	linewidth Hz
4.0	91	0.10	139	3372	0.05	146	n.d.
5.5	90	0.14	137.1	3247	0.33	144	5206
7.5	89	0.17	134.6	3182	0.50	143	4422
10.5	88	0.30	134.0	3375	0.66	142	4330
14.5	85	0.50	132.0	3057	1.00	140	4165
23	82	0.70	128.2	2993	2.00	138	3454
33	80	1.00	125.8	3118	2.75	137	4000
55	79.5	1.50	125.6	2929	4.25	137	3561
76	78.0	1.66	125.8	3182	4.75	136	3558
96	78.4	3.25	121.2	2929	5.25	135.6	3870
120	78.4	4.25	120.6	2908	5.75	135	4708
		5.25	120.6	2926	7	132	3289
					8	131	3286
					9	130	3015
					11	129	3234
					13	127	3179
					15	124	3289
					24	123	

Table B3. Xenon pressure drop vs. time for the anthracite, 40-60 and -100 mesh.

anthracite, -100 mesh		anthracite, 40-60 mesh	
time, hrs	pressure, torr	time, hrs	pressure, torr
0.003	598	0.17	608
0.009	583	0.25	604
0.017	576	0.50	592
0.033	563	0.75	583
0.083	545	1.50	569
0.17	530	2.0	562
0.50	501	3.0	553
1.0	484	4.0	547
1.5	474	5.0	542
2.0	467	22	504
2.5	463	24	503
3.0	459		
3.5	455		