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**^{129}Xe NMR SPECTROSCOPY OF XENON IN COAL
MICROPORES**

by

XU ZHU, B.Sc.

**A thesis submitted in the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Chemistry**

**Carleton University
Ottawa, Ontario
December 1994**

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**^{129}Xe NMR SPECTROSCOPY OF XENON IN COAL
MICROPORES**

By

XU ZHU

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Abstract

The applicability of ^{129}Xe NMR spectroscopy to study coal microporosity in coal was investigated. The coal samples used were a subbituminous coal from Alberta, and a high volatile bituminous (HVB) coal obtained from the Argonne Premium Coal Samples Bank.

First of all, the experimental conditions required for obtaining reliable spectra were determined. Then a number of factors necessary for the correct interpretation of the spectral data were examined. Gas uptake and 2D EXSY experiments were used to show that interparticle exchange is not important, and that intraparticle diffusion of xenon is smallest at low loading levels. By application of magic angle spinning it was shown that chemical shift anisotropy and nuclear dipolar coupling do not contribute to the spectral width, and therefore the spectral shape reflects a distribution of chemical shifts.

The chemical shift contribution due to xenon-pore wall interactions was isolated by extrapolating the loading-dependent shifts to zero loading. The shifts were interpreted by using a correlation established for xenon trapped in well-defined sites. All three coal samples were shown to have submicropores with an average free radius of 0.30 to 1 nm. In addition, the HVB coal has a larger pore as well. 2D EXSY NMR was used to show that xenon atom exchange between large and small pores takes place on a time scale of msec.

Spectra obtained for coal samples dried in different ways showed that the average pore size decreased in proportion to the amount of residual water retained in the pores. Non-linearity in the chemical shift vs xenon loading curve was attributed to coal swelling. Examination of some oxidized coal samples showed that the chemical shift behavior could be used to monitor changes in swelling capacity which accompanies coal oxidation.

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List of Abbreviations

$\text{\AA}$	angstrom, 10^{-10} m
a/b	the ratio of short and long axes of the ellipses formed by the 2D contour line
BET	Brunauer-Emmett-Teller <i>isotherm</i>
B_0	applied magnetic field
δ	chemical shift in ppm
EPR	electron spin resonance
FT	Fourier transform
$\hbar$	$h/2\pi$
h	Plank's constant
I	nuclear spin
μ	nuclear magnetic moment
L	Xe loading
m_l	magnetic quantum number
MAS	magic angle spinning
NMR	nuclear magnetic resonance
σ	nuclear shielding tensor
σ_{ii}	principal component of nuclear shielding tensor
ω	angular frequency
P_i	fractional population

γ	magnetogyric ratio
RF	radio-frequency
τ_i	residence time
SAXS	small-angle x-ray scattering
SANS	small-angle neutron scattering
T_1	spin-lattice relaxation time
T_2	spin-spin relaxation time
t_l	life time of a xenon atom within a particle
t_e	criterion for fast and slow exchange [$2\pi(\delta_s - \delta_g)$]
t_m	mixing time
2D EXSY	two-dimensional exchange spectroscopy

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Chapter One:

Micropore Structure of Coal

1.1 Introduction

The element carbon plays such an overwhelmingly important role in life that its relative scarcity may come as a surprise. Carbon accounts for only 0.04% of the total mass of the earth, and a mere 0.02% of the carbon in the top 5 km of the earth's crust occurs in a form which can react with oxygen; the remaining carbon is in the form of carbonates, carbon dioxide, etc. Most of the reactive carbon occurs in concentrated forms of the fossil fuels (coal, oil and natural gas). The known reserves of coal represent by far the largest proportion.¹

Fossil fuels are today not only an important source of energy but also provide the raw material for a variety of manufactured products such as plastics, pharmaceuticals, iron and steel, and aluminium. Some of these products are manufactured by the use of carbon derived from oil and gas, but with the anticipated depletion of oil and gas reserves, the importance of coal as a source of energy and chemical feedstocks is increasing. Much effort has been expended on the development of coal as energy and feedstock sources including an intensive investigation of the physical and chemical aspects of coal structure.²

This chapter presents an overview of coal structural features, followed by details of coal microporosity pertinent to the research presented herein.

1.2 General Description of Coal

Coal is a sedimentary rock. It is composed of organic substances called *macerals* as the major fraction, minerals as the minor fraction, and various quantities of water, and gases in its submicroscopic pores.³

Coal results from the accumulation of plant debris that was subsequently covered, compacted, and gradually changed into an organic rock through the stages of peat, lignite (brown coal), bituminous coal and ultimately anthracite.³⁻⁵ The coalification process results in an increase of carbon content, a decrease in "volatile matter" and oxygen content. Figure 1.1 shows a simplified representation of coal genesis and the changes in elemental composition that occur with increasing coal rank. The rank of coal, which represents the extent of *macerals* metamorphosis, may be classified based on: the content of carbon, oxygen and hydrogen; the content of volatile matter; and the calorific value, etc.

The coal genesis process suggests that coal is a non-homogeneous material. Indeed, coal is not a uniform mixture of molecules made up of carbon, hydrogen, oxygen, sulphur, and other elements; nor is it an uniform "polymeric" substance. Rather it is an aggregate of microscopically distinguishable, physically distinctive, and chemically different heterogeneous substances.⁵

Although coal is visibly heterogeneous in composition, there are still many regular and repeating features which have definable physical and chemical structure. A thorough knowledge of these features is indispensable in the understanding of the behavior of coal in various physical and chemical processes such as mining, crushing, and conversion to liquid

	Coalification →				
	Plant	Peat	Lignite	Bituminous Coal	Anthracite → Graphite
C %		55	70	80-90	92
H %		10	8-5	6-4	3
O %		35	25	10-5	2
C_{ar}/C_{tot}			0.5	0.60	→ 0.95
H/C			1		→ 0.5

* ar-aromatic; tot-total.

Figure 1.1 Genesis of coal and elemental composition of coals.⁴

or gaseous fuels, combustion, and weathering.

1.3 Chemical and Physical Structure of Coal

Coal is a heterogeneous material with three domains: macroscopic, microscopic, and submicroscopic. On the macroscopic scale, a dominant feature of bituminous coal is its banded appearance. These bands consist of irregularly alternating layers of differing composition which are referred to as lithotypes.⁵ Lithotypes are 1-10 cm wide and differ in density, reflectivity, strength, and, to some degree, volatile content. At the microscopic level, the organic regions of the lithotypes are complex aggregates, and these ultimate microscopic organic constituents are coal *macerals* (10^{-6} - 10^{-4} m). *Macerals* consist of organic macromolecules along with smaller volatile or easily extractable molecules which contribute a small percentage to the total carbon content.⁶ The comprehensive macromolecular structure of coal (or more specifically coal *macerals*) remains unsolved, and so does the complete understanding of the coal molecular "architecture". Several attempts have been made to develop models of coal macromolecular structure.⁶⁻⁹ (vide infra)

It is generally accepted that the chief building blocks of coal macromolecules are small aromatic and hydro-aromatic systems or clusters.^{6,8} Two examples are given below.

Each cluster can be linked to one, two, three or more clusters by predominately methylene

(-CH₂-), and to a lesser extent, by ether (-O-) and thioether (-S-) cross-links.¹⁰

A two-component model has been accepted to account for the structure of coal *macerals*, which is based on both chemical and physical structure of coal *macerals*.¹¹

According to the model, the three-dimensional macromolecular network of coal *macerals* forms the immobile component, and a multitude of small molecules varying in size forms the mobile component. The mobile component is embedded in the structure of the immobile component. Figure 1.2 shows the sketch of this model. The three-dimensional

Figure 1.2 Conceptual coal model: two-component system.¹¹

macromolecular network of coal *macerals* resembles that of polymers.¹²⁻¹³

One important facet of coal structure is the pore system within the organic matrix. The extensive distribution of the pore size and shape arises from the irregular arrangement of the three-dimensional cross-linked macromolecular network.⁵ The pore structure of coal significantly affects the electrical, strength, density, and molecular transport properties of coal, and therefore, is of great importance. Some examples illustrating the importance of coal porosity in coal mining, preparation, and utilization are as follows:⁵ (i) In their natural state in seams, coals contain significant amounts of adsorbed methane which sometimes causes explosions during mining. The ease of the methane diffusing out of coal is determined by pore volume and pore size distribution. (ii) Coal preparation by the removal of mineral matter makes use of the difference in the specific gravities of the coal and minerals; the specific gravity of the organic phase of coal is a function of its porosity. (iii) Coal gasification and the use of metallurgical coke involve chemical reactions between gases and coal surfaces. Since most of the surface area of coals and cokes is associated with micropores, the overall rates of reaction are determined by the ease with which the reactant molecules can diffuse into the pores and the product molecules can diffuse out of the pore system. Additional examples can be found in the literature.⁵

1.4 Pore Structure of Coal

1.4.1 Classification of pore size. Coal exhibits a large distribution of pore size, from smaller than 5 Å to beyond 1000 Å. The IUPAC (1972) classifies pores of different size in

the following manner:⁵

Macropores	> 500 Å
Mesopores	20 - 500 Å
Micropores	8 - 20 Å
Submicropores	< 8 Å

1.4.2 Pore Structure Model. The currently accepted model for coal pore systems is that coal contains an interconnected network of slit-like pores involving numerous bottlenecks. In this model, a molecule diffuses through the pore system and will eventually travel the entire internal surface area of coals if it can squeeze past the bottlenecks.¹⁴⁻¹⁶

A recent study based on the Brunauer-Emmett-Teller (BET) adsorption model of small hydrocarbon gases, CO₂, and N₂ of coal suggests a totally different model of the coal pore system.¹⁷ In this model coal contains isolated rather than interconnected pores. The pores are like a discrete series of bubbles and independent cavities occurring within the solid coal which have a range of sizes, and their surface is fractal, with fractal dimensionality varying with rank. Accessibility to the pores involves diffusion through the solid, glassy coal.

It should be noted that the entire pore structure, and thus the porosity of coal, is still unsolved. Although the meso- and macroporosity of coal can be studied by standard adsorption methods, information on the microporosity is more difficult to obtain. All adsorption methods for the determination of coal porosity are based on application of certain models including Langmuir, BET, Dubinin-Radushkevich and Dubinin-Astakhov,

along with an assumption of availability of the pores to the probe molecules.¹⁸ In the case of coal microporosity, the limitations of standard adsorption methods become obvious.¹⁵ For instance, coals can swell to the extent permitted by distortion of the cross-linkages from their equilibrium configurations in the presence of certain adsorbates.¹⁹ As a result, the pores can not accommodate more than a monolayer of adsorbate without distortion, thus the results of coal microporosity can be appreciably altered by the adsorbates.^{13,19}

For the isolated pore model, the results of microporosity by adsorption measurements will depend on the ability of adsorbates to penetrate the solid coals.

Microporosity plays an important role in the behavior of coal. It makes up as much as 88% of the total pore volume of low rank coals and up to 12% of the total pore volume of anthracites. Also most of the surface area of coals is located in the micropores.²⁰

1.5 Methods for Studying Coal Pore Structure

1.5.1 Adsorption Method. (1) *Pore Volume.* The pore volume is determined conventionally from absolute density measurements by using helium and mercury as displacement fluids. Helium is a good probe, since it is chemically inert, and because it has a very small atomic diameter (1.2 Å), it penetrates the entire pore structure.⁵ Mercury at normal pressures does not penetrate pores < 10 µm. Thus the total available volume of pores having diameter < 10 µm is given by the difference between the specific volume of mercury and of helium. In other density measurements, using more convenient liquids

(water, methanol) as displacement fluids, the measured density depends on how completely the pore space is permeated and the extent of liquid-surface interaction.²¹

(2) *Internal Surface Area.* The standard method for measuring the internal surface area of a porous solid is by adsorption measurement of N₂ at its boiling point (-196 °C) and the value is calculated using the BET equation.³ When applied to coal samples, significantly lower values were found compared to the adsorption measurement of CO₂ at -78 °C.²² The difference was explained by the fact that diffusion of adsorbates in coal pores is an activated process and liquid nitrogen does not have sufficient thermal energy to overcome the activation barrier to pass the "bottlenecks" in the pore network.

Table 1.1 Surface area of coals as measured by different adsorbates and at different temperatures(in m²/g).²⁵

coal rank C %	N ₂ -196 °C	Kr -78 °C	CO ₂ -78 °C	Xe 0 °C	CO ₂ 25 °C
95.2	34	176	224	226	224
90.0	0	96	146	141	146
86.2	0	34	107	109	125
83.6	0	20	80	62	104
79.2	11	17	92	84	132
72.7	22	84	198	149	139

Adsorption of CO₂ at -78 °C is extensively used in coal surface area measurements, since the measurements are performed at higher temperature relative to the

adsorption of N_2 , and the small molecular diameter of CO_2 (3.3 Å).²³⁻²⁵ Walker and Kini²⁵ determined the surface area of coals by measuring the adsorption of N_2 (-196 °C), Kr (-78 °C), CO_2 (-78 °C), (25 °C), and Xe (0 °C). The surface area values are listed in Table 1.1, and show that the coal surface area obtained using CO_2 and Xe are close for high rank coals. The authors concluded that both CO_2 at -78 °C and Xe at 0 °C probably enter all pores in the coal.²⁵

(3) *Pore Size Distribution.* The pore size distribution of coal can be determined by mercury porosimetry⁵ and gas sorption isotherm analysis.²⁶ In mercury porosimetry, mercury is forced into coals at increasing pressures, and the volume of mercury intrusion is measured as a function of applied pressure. Pore radius (r) corresponding to pressure (p) is calculated from⁵

$$r = 106 / p \quad (1.1)$$

The pore volume distribution curve is obtained by plotting the incremental volume over the incremental radius (dv/dr) against the average diameter. This method is used only for macropores and larger mesopores possessing a radius > 100 Å. The gas sorption isotherm method estimates the pore size distribution by determination of the distribution of surface area. Again, the method is used only in the mesopore range and for the larger micropores (>10 Å).

1.5.2 Small-Angle X-Ray Scattering (SAXS) and Neutron Scattering (SANS).

Small-angle scattering (SAS) techniques are not limited by the size of the pore entrance, thus they are sensitive techniques to detect both open and closed coal pore structure.^{5,27}

SAS utilizes the phenomenon of diffraction by microscopic inhomogeneities present in most materials. The intensity of SAS depends upon the square of the contrast between the inhomogeneity and its surrounding matrix. For SAXS the contrast is the electron-density difference between the two components, while for SANS the contrast is the neutron scattering-length-density.^{5,27,28} The techniques are limited by their failure to resolve micropore diameters of coals less than 10 Å.^{27,28}

1.5.3 Electron Spin Resonance (ESR). By diffusing spin probes of different shapes and of varying diameter or length, such as pyridine, nitroxyl molecules, into the swellable pores of the coal samples, the relative spin probe concentration can be measured by electron spin resonance (EPR) methods for each spin probe. From the measurement of the relative number of spin probes, a size distribution can be estimated.²⁹ The information of coal pore structure obtained by EPR spin probes is dependent on the probes, which are usually larger than small molecules such as CO₂ and Xe.

1.5.4 ¹²⁹Xe Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹²⁹Xe NMR spectroscopy has been used to study void space of clathrate hydrates and zeolites.^{30,31,32} In the study of clathrate hydrates, which are closed-cage systems, a general correlation between the isotropic ¹²⁹Xe chemical shift and the free space of the Xe trapping site was recognized.³¹ In the study of zeolites, which are open channel systems, extrapolation of the function of the chemical shift versus Xe loading to zero loading gives the chemical shift which characterizes the Xe-micropore surface interaction. The extrapolated chemical

shift together with the linewidth of the ^{129}Xe NMR signal can provide information on the average pore size and pore size distribution of coal micropore structure. The Xe atom has a van der Waal's radius of 2.2 Å which permits its diffusion into micropores of coal. Therefore, this technique can be a very useful tool to extract important information on coal micropore structure.

A detailed discussion of the applicability of this technique to the study of coal micropores structure will be presented in Chapter Three.

1.6 Summary

As one of the important physical features of coal, the porosity of coal is of great significance because of its influence on coal behavior during mining, preparation, and utilization processes. Macro- and mesopores of coal can be studied by standard adsorption methods. The information on micropores, on the other hand, is much more difficult to obtain, as micropores have the dimensions of molecules and no satisfactory methods for studying them have been developed. Due to its small diameter (2.2 Å), Xe atom can diffuse through the small openings of micropores. Therefore, if a meaningful ^{129}Xe NMR spectrum can be obtained and properly interpreted, ^{129}Xe NMR spectroscopy should be a very useful technique to obtain the important information on coal microporosity.

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Chapter Two:

Nuclear Magnetic Resonance Spectroscopy

2.1 Basic Theoretical Concepts

General Introduction. The fundamental property of the atomic nucleus pertinent to nuclear magnetic resonance (NMR) spectroscopy is the nuclear spin (I), which has values of 0, 1/2, 1, etc., in units of $\hbar$ ($\hbar = h/2\pi$, h is Plank's constant). The actual value of the spin of any given nucleus depends on its isotope. The nuclear magnetic moment (μ) is directly proportional to I :

$$\mu = \gamma I \hbar \quad (2.1)$$

where γ is the magnetogyric ratio and is a constant for each particular nucleus. In an external magnetic field, a nucleus of spin I has $2I+1$ energy levels, which are given by the value of the magnetic quantum number m_I . The energy of the various spin states is simply proportional to the nuclear magnetic moment and the applied field:

$$E = -\gamma \hbar m_I B_0 \quad (2.2)$$

where B_0 is the applied field. The selection rule for NMR transitions is that m_I can only change by one unit, i.e. $\Delta m_I = \pm 1$. Thus the transition energy is given by

$$\Delta E = -\gamma \hbar B_0 \quad (2.3)$$

For the detection of this transition energy, radiation given by $\Delta E = h\nu$ must be applied and combining this with Eq. (2.3) gives the fundamental resonance condition for all NMR experiments:¹

$$\nu = \frac{\gamma}{2\pi} B_0 \quad (2.4)$$

Actually, NMR spectroscopy involves the absorption of radio-frequency energy by nuclear spins as they resonate and reorient in the presence of both the externally applied magnetic field and the internal magnetic field produced by internal electronic and magnetic interactions. The resonance frequency and reorientation time are sensitive to the local environment of the nucleus and to the mobility of the atoms and molecules. The sensitivity to the local environment, together with a natural isotopic selectivity, enables NMR spectroscopy to provide detailed information about structure and dynamics of many classes of materials.^{2,3}

Nuclear Spin Hamiltonian. A general Hamiltonian for the interactions experienced by a nuclear spin can be represented by the sum:⁴

$$\mathbf{H} = \mathbf{H}^Z + \mathbf{H}^Q + \mathbf{H}^{CS} + \mathbf{H}^D + \mathbf{H}^J + \mathbf{H}^{SR} \quad (2.5)$$

where $\mathbf{H}^Z$ is the Zeeman interaction of the nuclear magnetic moment with the applied magnetic field B_0 , which is responsible for the removal of the degeneracy of the spin energy levels of any non-zero spin nucleus; $\mathbf{H}^Q$ is the quadrupolar interactions (only for $I > 1/2$), which arises from the interaction of the nuclear electric quadrupole moment with the non-spherically symmetrical field gradient around the nucleus; $\mathbf{H}^{CS}$ is the chemical shift interaction, which is due to the shielding effect on the nucleus of the fields produced by the surrounding electrons; $\mathbf{H}^D$ is the direct dipole-dipole internuclear interaction; $\mathbf{H}^J$ is the electron-mediated (indirect) internuclear interaction; and $\mathbf{H}^{SR}$ is the coupling of spins with the magnetic moment produced by the angular momentum of the molecule. Since only the

chemical shift H^{CS} and dipolar H^D interactions are relevant to the ^{129}Xe NMR spectroscopic study in this Thesis, the description will be limited to the chemical shift interaction H^{CS} and the dipolar interaction H^D .

(1) *Chemical Shift Interaction.* The chemical shift interaction is caused by a secondary magnetic field, which is produced by the motional screening of electrons. The secondary magnetic field is proportional to the applied magnetic field B_0 , but opposite in direction. The Hamiltonian of the chemical shift interaction can be described as:

$$H^{CS} = \gamma \hbar \mathbf{I} \cdot \boldsymbol{\sigma} \cdot \mathbf{B}_0 \quad (2.6)$$

where $\boldsymbol{\sigma}$ is the nuclear shielding tensor. (vide infra)

Since both magnetic field and spin magnetization are vector properties, the interaction between them should be described by a tensor, which is called the nuclear shielding tensor. In a laboratory frame of reference, the z direction is the same as the applied magnetic field, and by choosing an appropriate molecule-fixed axis system, the nine components of the nuclear shielding tensor can be transformed into the *principal axis system* (PAS) with the three principal components:⁵

$$\begin{vmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{vmatrix} \longrightarrow \begin{vmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{vmatrix} \quad (2.7)$$

where the σ_{11} , σ_{22} , σ_{33} are three principal components of the tensor. Figure 2.1 shows the schematic presentation of the nuclear magnetic shielding tensor.

Figure 2.1 Schematic representation of magnetic shielding tensor ellipsoid.

x, y, z – laboratory system; 1, 2, 3 – sample system.

The experimentally measurable quantity of the shielding tensor is σ_{zz} in the laboratory frame, which is a linear combination of the three principal components, σ_{ii} :⁷

$$\sigma_{zz} = \sum_{i=1}^3 \sigma_{ii} \cos^2 \theta_{iz} \quad (2.8)$$

where the angles θ_{iz} are angles between σ_{ii} and $\mathbf{B}_0$. The further expression of Eq. (2.8) can be:⁷

$$\sigma_{zz} = \text{Tr}\sigma + 1/3 \sum_{i=1}^3 (3\cos^2\theta_{iz} - 1)\sigma_{ii} \quad (2.9)$$

The first part of Eq. (2.9) is the *trace* of the tensor given by:

$$\text{Tr}\sigma = \sigma_{11} + \sigma_{22} + \sigma_{33} \quad (2.10)$$

the *trace* is directionally invariant or isotropic, so the first part of Eq. (2.9) is referred to isotropic term. The second part of Eq. (2.9) is directionally dependent, or anisotropic. The anisotropic part gives rise to chemical shift anisotropy $\Delta\sigma$, which is given by:

$$\Delta\sigma = \sigma_{33} - 1/2 (\sigma_{11} + \sigma_{22}) \quad (2.11)$$

with the conventional adoption $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. If the tensor is axially symmetric because of local molecular symmetry, then σ_{33} is defined as $\sigma_{\parallel}$ and $\sigma_{11} = \sigma_{22}$ as $\sigma_{\perp}$. Thus:

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} \quad (2.12)$$

In solution, where rapid isotropic molecular motion occurs, the shielding tensor is averaged to the one-third of the trace: $\sigma_{\text{iso}} = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33})$, and a single line is observed with frequency:

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma_{\text{iso}}) \quad (2.13)$$

For a single crystal containing nuclei which are in translationally equivalent positions, a single line is also observed whose frequency varies with the orientation of the crystal in the magnetic field B_0 .

In a polycrystalline powder sample, on the other hand, the distribution of nuclear orientations results in absorption over a range of frequencies, giving a powder

pattern. A schematic powder pattern spectra for a powder sample with different site symmetries is shown in Figure 2.2.

Figure 2.2 Schematic powder patterns for different site symmetries. (a) cubic symmetry; (b) axial symmetry; (c) lower symmetry.⁷

(2) *Dipolar Interaction.* The dipolar interaction H^D arises from direct through-space dipole-dipole interactions between nuclei. The dipolar Hamiltonian for the coupling between two unlike nuclei i and j is

$$H^D = \mathbf{I}_i \cdot \mathbf{D} \cdot \mathbf{I}_j \quad (2.14)$$

the further expression of Eq. (2.14) is as follows.⁹

$$H^D = 1/2 \gamma_i \gamma_j \hbar^2 r_{ij}^{-3} (\mathbf{I}_i \mathbf{I}_j - 3 \mathbf{I}_{iz} \mathbf{I}_{jz}) (3 \cos^2 \theta_{ij} - 1) \quad (2.15)$$

where γ_i , γ_j are nuclear gyromagnetic ratios, r_{ij} the distance between internuclear vector, and θ_{ij} is the angle between r_{ij} and the magnetic field B_0 . Some important features of the dipolar interaction are:

(i) In solution state the molecular isotropic tumbling causes the angle dependent term $3\cos^2\theta_{ij} - 1$ in Eq. (2.15) to be zero, (since the isotropic average value of $\cos^2\theta_{ij} = 1/3$) and the dipolar interaction vanishes.

(ii) The dipolar interaction strongly depends on the internuclear distance (inverse cubic dependence) and is, therefore, important only for nuclei in close proximity.

(iii) If the sample is rapidly spun at the *magic angle* to the magnetic field, the time-averaged value of H^D will vanish (vide infra).

The magnitude of the dipolar interactions often is too large to be reduced to zero by spinning the sample at conventional speeds. The strong dipolar interactions are removed by either dipolar decoupling or multiple-pulse methods.¹⁰

2.2 Magic Angle Spinning

In solid-state NMR spectroscopy, the presence of many overlapping powder patterns 'wipes out' most of the structural details in the spectra of complex samples. In order to get a high resolution spectrum, the magic angle spinning (MAS) technique is used. MAS involves spinning the sample at the "magic angle" which is $54^\circ 44'$ relative to the applied magnetic field.¹¹ Figure 2.3 depicts the geometric arrangement for MAS. The principle of the MAS technique is given by the following description.

As shown in Figure 2.3, it can be deduced that if the rotation axis of sample is inclined by an angle ψ from B_0 , the time-averaged value of the angle-dependent term of Eq. (2.12) becomes:

$$(3\cos^2\theta_{iz} - 1) = 1/2 (3\cos^2\psi - 1)(3\cos^2\chi_i - 1) \quad (2.16)$$

with χ_i as the constant angle between the principal tensor axis i and the axis of rotation, within the range of

$$0 \leq \chi_i \leq 2\pi \quad (2.17)$$

when the spinning angle ψ is equal to the magic angle, the $(3\cos^2\psi - 1)$ term in Eq. (2.16) is equal to zero, giving the time-averaged value of $(3\cos^2\theta_{iz} - 1)$ term as zero. As a result, the anisotropic term in Eq. (2.12) vanishes and only the isotropic term stays.

Figure 2.3 Schematic representation of the geometric arrangement for MAS.⁸

2.3 Pulse Fourier Transform Technique.

The behaviour of spin magnetization in a magnetic field can be conveniently described by using vector diagrams. It is useful to describe NMR experiments in a rotating reference frame rather than a fixed laboratory reference frame. The rotating frame is one in which the z' axis is the same as the magnetic field direction but the x' and y' axes rotate about the z' axis at a frequency γB_0 . The basic Fourier Transform experiment (FT) and the behaviour of the spin magnetization in the rotating frame are described as follows:¹²

In a laboratory frame of reference, spins with a magnetic moment μ and gyromagnetic ratio γ precess about the magnetic field B_0 along the z -axis at the Larmor frequency $\omega_0 = \gamma B_0$. The excess spins aligned along the magnetic field B_0 give rise to a resultant spin magnetization vector M . The applied radio-frequency field B_1 is an oscillating field in the x - y plane at a similar frequency ω (Figure 2.4 a)

$$B_1 = B_1 (\cos \omega t + \sin \omega t) \quad (2.18)$$

If a reference frame is chosen which rotates at the frequency of the oscillating field B_1 , the effective field becomes:¹²

$$B_{\text{eff}} = B_0 + \omega/\gamma + B_1 \quad (2.19)$$

where the ω/γ is the "fictitious" field. When the radio-frequency is exactly at the resonance frequency ω_0 , the chosen frame becomes the rotating frame (vide supra), the "fictitious" field will cancel exactly the B_0 along the z axis, leaving only B_1 in the x - y plane to interact with the spin magnetization (Figure 2.4 b). If B_1 is turned on for a time t , the spin magnetization vector will be rotated by an angle $\theta = \gamma B_1 t$. A 90° pulse flips the

Figure 2.4 Behaviour of spin magnetization. (a) In the laboratory frame. (b) In the rotating frame and under the influence of RF field. (c) 1 in rotating frame; 2-3 after a 90° pulse; 4-5 flowing the RF pulse.

magnetization vector into the x-y plane, which generates a signal in the sample coil which is in the x-y plane (Figure 2.4 c. 2-3). Following the RF pulse, the transverse magnetization begins to dephase in the x-y plane due to spin-spin interactions (Figure 2.4 c. 4-5). As the components of the transverse magnetization fan out, the intensity of the signal reaching the receiver gradually decreases. This decay of signal intensity with time is known as the free induction decay (FID). The FID is a time domain function, and after phase-sensitive detection and digitization, the FID is Fourier transformed into a frequency domain function, which is the NMR spectrum.

Following an RF pulse, the spin magnetization returns to its equilibrium position along the z-axis with a characteristic time constant denoted by T_1 . T_1 characterizes the time needed to establish longitudinal thermodynamic equilibrium magnetization after the sample has initially been exposed to the magnetic field, or after manipulation of magnetization by an RF pulse. To attain equilibrium, energy must be exchanged between nuclear spin and the assembly of molecules which is commonly referred to as "lattice", so T_1 is called the spin-lattice relaxation time. After an RF pulse, the spin magnetization dephases in the x-y plane with characteristic time constant denoted as T_2 ; such a process is called spin-spin relaxation.

The relaxation parameters can provide important dynamic information such as (1) molecular rotational and angular-momentum correlation times; (2) translational diffusion constants, and (3) inter- and intramolecular exchange rates.

2.4 *Dynamic NMR (DNMR)*

Since Xe atoms may possess high mobility, rapid exchange may occur when Xe atoms are adsorbed in coal micropores. The exchange processes will affect ^{129}Xe NMR parameters; therefore, it is necessary to introduce some basic concepts of DNMR herein.

An important feature of NMR spectroscopy is its sensitivity to molecular dynamics in the presence of chemical exchange processes.¹³ In a chemical exchange system, molecules often exist in two (or more) states that are in rapid equilibrium with each other. In some cases, the rate of such a process falls within the range of the "NMR timescale" which generally refers to the lifetimes of the order of 1 second to 10^{-6} second for each state. This allows NMR spectroscopy to give exchange information in the system, which is often not achievable by other spectroscopic methods.

Several DNMR techniques have been developed for studying chemically exchanging systems, including line-shape analysis, magnetization transfer, and two-dimensional (2D) NMR.^{6,13,14} For simplicity, consider chemical exchange between two magnetically inequivalent sites. Two-site exchange processes can be analyzed simply by inspection of the NMR line-shape, since the exchange processes are evident from characteristic changes in the shape of the NMR signal: broadening, coalescence, and sharpening. Details are described as follow:⁶

It is convenient to introduce some notations before the description of two-site exchange.

1. *Residence times* in each site are designated as τ_A and τ_B . The rates of transfer from each site, which are given by first-order rate constants, are the reciprocals of the τ_A

1. *Slow Exchange*: If exchange of the observed nucleus between sites A and B is very slow, the spectrum will consist of two lines separated by a chemical shift difference of $2\pi(\nu_A - \nu_B)$ Hz. τ_A and τ_B must be large compared to $(\nu_A - \nu_B)^{-1}$. Under these circumstances, the frequency of the A site is

$$\nu_A = -M_0 \frac{\gamma_B T_{2A} P_A}{1 + T_{2A}^2 (\omega_A - \omega)} \quad (2.28)$$

and the width of the A signal will be (in Hz)

$$\pi\delta\nu_A = \frac{1}{T_{2A}} + \frac{1}{\tau_A} \quad (2.29)$$

Similar equations can be obtained for site B. Exchange thus results in an excess broadening, $(\pi\tau_i)^{-1}$, of the signal at each site over that observed in the absence of exchange.

2. *Fast Exchange*: with fast exchange between two sites, τ_A and τ_B are small compared to $(\nu_A - \nu_B)^{-1}$. If the rate is fast enough the two signals completely collapse to a single sharp resonance:

$$\nu_0 = P_A \nu_A + P_B \nu_B \quad (2.30)$$

characterized by an averaged spin-spin relaxation time:

$$\frac{1}{T_2} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} \quad (2.31)$$

The linewidth is given by

$$\delta\nu = \frac{1}{\pi T_2} \quad (2.32)$$

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Figure 2.5 Simulation of spectra for two-site exchange. $P_A = P_B = 0.5$; $\delta\nu = 20$ Hz; and $k = 0.1, 5.0, 10.0, 22.2, 44.4, 100, 500$, and 10000s^{-1} .¹³

3. *Near the exchange rate limits.* When the rate of two-site exchange increases from the slow-exchange regime so as to affect the NMR spectrum, but before the signal is completely collapsed, the spin-spin relaxation time becomes:

$$\frac{1}{T_2'} = \frac{1}{T_2} + P_A^2 P_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B)^2 \quad (2.33)$$

The second term on the right of Eq. (2.33) corresponds to the excess broadening due to slow exchange. For equal populations of sites A and B, ($P_A = P_B = 1/2$ and $\tau_A = \tau_B = 2\tau$) the excess broadening becomes (in Hz):

$$4\tau\pi(\nu_A - \nu_B)^2 \quad (2.34)$$

and is inversely proportional to the exchange rate. Figure 2.5 is the simulation spectra of two sites exchange with different rates.

2.5 ^{129}Xe NMR Spectroscopy

Xenon gas (from the Greek, "stranger") was discovered by Ramsay and Travers in 1898.¹⁵ The element is a monatomic inert gas having a van der Waals radius of 2.2 Å. It has atomic number 54, and nine stable isotopes have been identified: ^{136}Xe , ^{134}Xe , ^{132}Xe , ^{131}Xe , ^{130}Xe , ^{129}Xe , ^{128}Xe , ^{126}Xe , and ^{124}Xe .¹⁵ Of the stable isotopes, only two have magnetic moments: ^{129}Xe and ^{131}Xe .

^{129}Xe is a nucleus with spin $I = 1/2$ and a natural abundance of 26.4%. Its NMR receptivity relative to ^{13}C is 31.8.¹⁶ Detection of its resonant absorption in a sample of naturally abundant xenon is relatively straightforward. The most useful NMR parameter of ^{129}Xe is its chemical shift, which has a range of over 7500 ppm, enormous

compared to the chemical shift range of ^1H (20 ppm) or ^{13}C (250 ppm). The diamagnetic term for isolated atoms has been calculated for xenon, and is about 5600 ppm to lower frequency relative to the bare nucleus.¹⁵ The large range of the ^{129}Xe chemical shift is due to the large and extremely polarizable electron cloud of xenon. Small perturbations of this electron cloud are directly transmitted to the nuclear environment, and thus changes the chemical shielding of the electrons. Figure 2.6 shows ^{129}Xe chemical shifts for several xenon compounds, phases, and environments.¹⁶

Figure 2.6 ^{129}Xe NMR chemical shifts of several representative xenon compounds, phases, and environments¹⁶

well as density.¹⁸ The chemical shift of liquid xenon ranges between ~240 ppm at 160 K and ~160 ppm at 244 K. The chemical shift of the solid xenon covers a range from ~270 ppm to ~305 ppm, depending on the temperature.²¹

¹²⁹Xe chemical shift of Xe adsorbed in microporous solids.

(i) *Small closed pore system.* The dependence of the shift on density of the gas and on the presence of other collision partners shows that the interaction of a xenon atom with its environment profoundly affects the observed NMR properties. In macroscopic systems, the walls are sufficiently far apart that xenon interactions with them are rendered statistically insignificant relative to interactions with other xenon atoms or molecules. However, if a xenon atom is confined in a small closed pore system e.g., a Xe clathrate (from Latin, "enclosed or protected by crossbars or gratings"), the Xe atom is contained in a cavity of molecular dimensions formed by molecules of the host lattice. In such situations, the interaction between xenon and walls of cavity become significant. Ripmeester *et al.* first showed the applicability of ¹²⁹Xe NMR to study internal structures of clathrate and clathrasil cavities where Xe is located.²²⁻²⁴

As shown in Figure 2.7, the ¹²⁹Xe chemical shift and the lineshape sensitively reflect the sizes (the larger the cage size, the smaller the chemical shift), and symmetries of cages (isotropic lineshape for cubic symmetry sites and anisotropic lineshape for lower symmetry sites). The analysis shows a linear correlation between the mean free radius of the space available to a Xe atom and the isotropic chemical shift with a slope of $-5.147 \times 10^{-3} \text{ \AA/ppm}$ (Figure 2.8).²⁴

Figure 2.7 ^{129}Xe NMR spectrum of xenon occluded in the 0.57 nm and 0.75 nm diameter cavities of dodecasil-3C compound.²⁴

Figure 2.8 Correlation of ^{129}Xe isotropic NMR chemical shifts with the radius of the free-space volume available to the xenon atom for Xe-clathrate and clathrasil complexes.²⁴

(ii) *Open channel systems.* In an open channel system Xe can exchange between different trapping sites. A typical example of Xe in open channel systems is Xe adsorbed in zeolites. Zeolites are crystalline silicoaluminates, both naturally occurring and synthetic, with regular structural properties.²⁵ The regular crystalline structures formed by zeolite frameworks partition space into regions of molecular dimensions connected in regular arrays. Xenon adsorbs readily in zeolites, and since ^{129}Xe chemical shifts are strong functions of the local environment, this technique is an ideal candidate for a nondestructive, inert probe of the internal properties of zeolites, a fact first exploited by Ripmeester,¹⁹ and Ito & Fraissard.²⁶ Several interactions contribute to the local environment of Xe in zeolites: interaction with the walls; interaction with other adsorbed Xe atoms; and interaction with other adsorbed material. Ito and Fraissard suggested²⁶ an equation that describes the chemical shift of ^{129}Xe in terms of several contributions:

$$\delta = \delta_0 + \delta_S + \delta_E + \delta_M + \delta_{\text{Xe-Xe}} \quad (2.37)$$

where δ_0 is the reference; δ_E and δ_M express the electrical and magnetic effects of cations within the zeolite; $\delta_{\text{Xe-Xe}}$ represents the Xe-Xe interaction which is proportional to the local Xe density inside the zeolite; δ_S characterizes the specific physical interactions between Xe and the wall of the void space where the Xe is adsorbed. The authors indicated that if there is no magnetic effect, and because the influence of the electric field is rather small at room temperature, the δ_S which reflects the structure of the void space can be readily obtained by extrapolation of the $\delta = f[\text{Xe}]$ plot to $[\text{Xe}] = 0$.²⁶

It is worth noting that this empirical correlation has its limitations, and details will be discussed in Chapter Three. Generally speaking, since in an open channel system the ^{129}Xe chemical shift is density dependent, the chemical shift which reflects the xenon-cage wall interactions is obtained by extrapolation of the chemical shift to zero density.

^{129}Xe NMR study of polymer microstructure and dynamics. Due to the high viscosity of amorphous polymers, the mobility of "dissolved" xenon atoms is largely reduced, making it possible to use ^{129}Xe NMR spectroscopy to investigate structural heterogeneities that may exist in amorphous polymer systems. The "solubility" of Xe in many polymers allows measurement of local structural features associated with free volume sites occupied by "dissolved" Xe atoms.^{27,28} At temperatures above the glass transition T_g , mobile polymer segments permit high xenon mobility between different free volume environments, producing a motionally-narrowed ^{129}Xe signal.²⁹ Reduction of the temperature below T_g , traps the xenon atoms in various sites, and thus produces inhomogeneously broadened ^{129}Xe spectral peaks.³⁰

Since xenon atoms have mobility in polymeric systems, ^{129}Xe NMR spectroscopy is used to study dynamic process in these systems. Kentgens *et al.*³¹ performed the first ^{129}Xe 2D exchange spectroscopy (2D EXSY) experiments (technique details are given in Chapter Three) on Xe in linear low density polyethylene (LLDPE) and in polycarbonate systems which display distinct xenon mobilities. The results are shown in Figure 2.9. A spectrum, which consists of a signal extended along the diagonal, indicates the absence of Xe exchange between different sites. Conversely, a circular 2D contour pattern indicates

Figure 2.9 ^{129}Xe 2D EXSY NMR spectra of Xe adsorbed in amorphous polymers (a) Xe in LLDPE. The diagonal spectrum indicates that there is no exchange of Xe among the different local environments during a mixing time of 2s. (b) Xe in polycarbonate. The circular pattern indicates the Xe exchanges among the different sites during mixing time 1s.³⁴

that the Xe atoms samples essentially all the available local sites. A detailed description is given in Chapter Three.

^{129}Xe NMR study of coal micropores. Coal micropore structure shares some structural similarities with the amorphous polymer systems, but usually coal micropore structures are more rigid than those of most amorphous polymers. This character gives the ^{129}Xe NMR applicability to characterize the internal void structure of coals. So far, two papers have been published. Wernett et al.³² observed two peaks in the ^{129}Xe NMR spectrum of xenon adsorbed in Illinois # 6 coals which exhibit different pressure dependences. One was attributed to the xenon "dissolved" in the coal, the other arises from xenon adsorbed in coal micropores. Using the empirical relationship of chemical shift at zero density and the mean free path of Xe in microporous solid,²⁶ an average diameter of 5.2 Å for Illinois # 6 coal micropores was obtained.

Tsiao et al.³³ studied three Argonne Premium coals and the corresponding weathered and oxidized coal samples. The asymmetric broad peak was resolved into sums of symmetric gaussian and lorentzian lines and were attributed to pores of different size or different chemical composition. A model which approximates both the micropore size and swelling characteristics of coals was also proposed. However, neither study addressed the fundamental aspects of the ^{129}Xe NMR spectroscopy of coals.

2.6 References

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Chapter Three:

^{129}Xe NMR Spectroscopy of Xenon in Coal Micropores

3.1 Introduction

As introduced in Chapter Two, the pioneering experiments of Ripmeester¹ and of Ito and Fraissard² have shown that the ^{129}Xe chemical shift of Xe adsorbed in microporous solids can be empirically correlated with the geometrical size of the adsorption site. The data come primarily from two sources: small closed cage systems, and open channel systems. In small closed cage systems, such as clathrates, when Xe atoms are trapped in cages of radii less than 3.4 Å, there is a simple linear correlation between the free radius of the cage and the isotropic ^{129}Xe chemical shift. However, this correlation cannot be accounted for by theoretical considerations based on a binary collision model.³ In open channel systems, the situation is more complicated:

- (a) When cages are interconnected and open to the outside gas phase, inter- and intra-particle Xe exchange may happen. In many cases, the exchange is rapid on an NMR timescale.^{4,5,6} In these cases, the effect of motional averaging must be taken into account.
- (b) Since the ^{129}Xe chemical shift depends on the local density of Xe, the chemical shift arising from the interaction of Xe with the cage wall is obtained by extrapolation of the Xe chemical shift to zero density.² The interpretation of the extrapolated shift in terms of the dimension of cage is not trivial, as there are only empirical correlations, and there are differing opinions on their applicability.^{6,7}

Coal micropores are formed by the irregular arrangement of an interconnected macromolecular network. As a result, coal micropore structure is an irregular channel system of varying degrees of openness. Additional complications may include:

- 1) Coal micropore structure may have an extensive pore size distributions, and thus the ^{129}Xe chemical shift will be distributed. Depending on the details of the distribution, the spectrum may consist of a number of broadened lines.
- 2) The macromolecular framework of coal is deformable to an extent permitted by the distortion of the cross-links from their equilibrium configuration. The flexibility of the micropore structure may permit significant xenon mobility between different sites, which affects all of the ^{129}Xe NMR parameters.

The overall ^{129}Xe NMR chemical shift of Xe adsorbed in coal micropore structure may have several contributions:

- i. Contribution from the interactions of Xe atoms with the walls of the coal micropore structure, which characterizes the size of the pores;
- ii. Contribution from Xe-Xe interactions, which makes the ^{129}Xe NMR chemical shift density dependent;
- iii. Contribution from Xe diffusion, which is fast on the NMR timescale;
- iv. Contribution from the chemical shift anisotropy. Since the interaction between Xe and coal micropore surface is anisotropic, the resulting ^{129}Xe NMR chemical shift is a tensor which is probably modified by dynamic processes.

The aim of this Thesis is to study the factors which affect the ^{129}Xe NMR chemical shift of Xe adsorbed in coal micropores and to interpret the chemical shift in terms of pore size. The investigation involves:

1. establishing a method to obtain meaningful ^{129}Xe NMR spectral data;
2. assessing effects on the ^{129}Xe NMR spectrum by factors other than pore size.
3. proposing an appropriate way of interpreting the ^{129}Xe NMR chemical shift in terms of coal micropore sizes.

3.2 Experimental Considerations

3.2.1 Phase-Cycled Hahn spin echo experiment. Since coal micropores may have an extensive size distribution, the resulting ^{129}Xe NMR signal will also have a very broad, irregular frequency distribution. In the simple one-pulse experiment (Bloch decay), there is a dead time delay (t_d) between the $\pi/2$ pulse and data acquisition period, which is caused by the recovery of the probe circuit and saturation of the preamplifier after an RF pulse. This can cause a frequency-dependent phase shift across the spectrum, which often cannot be removed completely by processing of the data. This results in an uncertainty in the definition of line shape due to a poorly defined baseline. The above problem can be circumvented by using a two-pulse spin-echo experiment developed by Hahn in 1950 to study transverse relaxation processes⁸. The pulse sequence for the Hahn echo is:

$$\pi/2 - \tau - \pi - \tau - \text{Echo}$$

After the second evolution delay (τ), all the chemical shifts are refocused, generating an echo. As all of the chemical shifts are refocused, the associated frequency-dependent phase error introduced by the dead time delay is removed. Thus, a high-fidelity spectrum can be obtained by Fourier transforming the signal starting at the peak of the echo. Figure 3.1 shows the schematic diagram of the two-pulse Hahn spin echo sequence.

Figure 3.1 Schematic diagram of the two-pulse Hahn echo sequence. $\theta_1 = 90^\circ$ and $\theta_2 = 180^\circ$, the dashed regions following the pulse represents the dead time, t_d , of receiver.⁹

Another concern is missetting of the pulse angle in the Hahn echo sequence, which will result in anomalies in the shapes of signals present in the spectrum due to the effects of uninverted residual transverse magnetization. The problem can be solved by proper phase-cycling. In the single-pulse experiment, phase cycling of the pulse can be used to remove the constant offset voltage generated by the electronics and the effects caused by incorrect setting of the quadrature phase-sensitive detectors. In the Hahn echo experiment

with phase cycling, the anomalous effects due to the missetting of pulse angles will cancel each other and a proper echo will be formed regardless of the nominal flip angles of the two RF pulses.

The combination of phase-cycling on the first and second pulses results in sixteen pulse cycles. The relative phases of the two pulses used in Hahn spin echo experiment are listed in reference 9.

3.2.2 Two-dimensional exchange spectroscopy (2D EXSY). As described in Chapter Two, exchange processes affect the ^{129}Xe NMR parameters. 2D EXSY can be used to study the effect of exchange on the Xe-coal micropore system, as it has been used in the study of amorphous polymers.¹⁰

The use of 2D NMR for the study of dynamics was first proposed by Ernst and co-workers.¹¹ The pulse sequence is shown in Figure 3.2.

Figure 3.2 Pulse sequence used in a 2D EXSY experiment.¹¹

Figure 3.3 Vector picture of the 2D EXSY experiment. (a) The magnetization is initially aligned along B_0 (b) A 90° pulse rotates the magnetization into the transverse plane where it (c) evolves for a time t_1 (d) A second 90° pulse rotates the magnetization into the xz plane. (e) During the mixing time the z magnetization undergoes relaxation and exchange (f) Following a third 90° pulse (g) the net magnetization (h) is detected during t_2 .¹¹

There are four periods in the pulse sequence: preparation, evolution, mixing, and detection. The details of the magnetization behaviour during the experiment is shown in Figure 3.3.

In the preparation period the spin system is allowed to come to equilibrium. The first 90° pulse P_1 is applied along the $-x$ axis and flips the net magnetization vector into the x - y plane. Each spin precesses at a characteristic frequency determined by its chemical shift during the evolution period, and this effectively labels each spin. Application of a second 90° pulse P_2 along $-x$ axis rotates the magnetization into the x - z plane. During the mixing time t_m the Xe atoms can undergo exchange and the z -component of magnetization reflects the exchange. Finally, the z -magnetization is rotated to the y axis again by a third 90° pulse P_3 . In the acquisition period t_2 , the magnetization in the xy plane is measured and stored. The acquisition time t_2 is the same as that in the usual 1D NMR experiment. The 2D experiments are made by varying the labeling time t_1 , and the measured magnetization is then a function of both t_1 and t_2 :

$$M = M(t_1, t_2) \quad (3.1)$$

Double Fourier transformation of this time domain function gives a 2D spectrum.

$$S(\omega_1, \omega_2) = \iint M(t_1, t_2) e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} dt_1 dt_2 \quad (3.2)$$

Consider the simplest case: chemical exchange between two sites A and B, in which nuclei are characterized by the precession frequencies ω_A and ω_B . During the labeling period, nuclei that are in site A will contribute a component $\exp(i\omega_A t_1)$ to $M(t_1, t_2)$. If during the mixing period t_m some of these nuclei exchange to site B, they will precess at

frequency ω_B during the acquisition period and will contribute a component $\exp(i\omega_B t_2)$ to $M(t_1, t_2)$. Double Fourier transformation will then produce a peak at $\omega_1 = \omega_A$ along the first frequency coordinate and at $\omega_2 = \omega_B$ along the second frequency coordinate. The peak is referred to as an off-diagonal or cross peak. Those nuclei that do not exchange during t_m contribute $\exp(i\omega_A t_1)$ and $\exp(i\omega_A t_2)$ to the magnetization, and they produce a peak at $\omega_1 = \omega_A$, $\omega_2 = \omega_A$, i. e., the diagonal peak. The same description holds for the nuclei starting in site B.

3.2.3 T_1 experiment. Information about the spin-lattice relaxation time can be used to choose the appropriate time delay between successive pulses and it can also provide information about exchange processes. The measurements of T_1 were made by means of inversion recovery experiments, using the pulse sequence:¹²

$$(\pi)_x - \tau - (\pi/2)_x - \text{acquire} - \text{delay}$$

A 180° pulse inverts the spin magnetization to the -z direction in the rotating frame, and this is followed by spin-lattice relaxation during the variable τ period. The magnetization is then read by a subsequent 90° pulse. The T_1 values were extracted from the dependence of the intensity at the resonance peak frequency as a function of the delay time τ , and calculated using the equation:

$$M_z = M_0 - C \exp(-\tau/T_1) \quad (3.3)$$

where M_0 is the intensity of the fully relaxed magnetization, M_z is the observed intensity and C is a constant. Figure 3.5 is a typical fit of the signal intensity versus τ obtained in a

Figure 3.4 A typical fit of signal intensity versus delay time τ for a T_1 measurement of a coal sample. Peak position at 171 ppm.

T_1 experiment of Xe adsorbed in a coal sample.

3.3 Experimental Section

3.3.1 Materials. Coal sample A was obtained from Alberta Power; sample B was from Ortech. Both samples A and B came from same mining source but were subjected to different physical processes. Coal sample C was from the Argonne Premium Coal Sample Program (ACPS).¹³ Table 3.2 summarizes the properties of the three samples.

Figure 3.6 55.3 MHz static ^{129}Xe NMR spectra of Xe adsorbed in coal sample A.

Loading unit: 10^{-5} moles/g.

3.3.2 Sample treatment. The raw coal samples are the samples as received without any treatment.

Some samples were prepared to study the effect of different drying techniques.

The treatment was as follows:

- 1) vacuum drying at room temperature;
- 2) vacuum drying at 105 °C;
- 3) air drying at 105 °C;
- 4) freeze drying;
- 5) microwave drying.

Some samples also were prepared to study the effect of oxidation. These were prepared by putting the raw coal samples in an oven at 105 °C for a month.

3.3.3 Preparation of Xe-Coal Samples.

1) Raw coal samples: the samples were weighed and packed in pyrex glass tubes (o.d. 10 mm). The tube was attached to a vacuum manifold for sample outgassing at 10^{-5} Torr. Before introduction of Xe gas, the coal sample was heated slowly to 105 °C and then maintained under vacuum at this temperature for about three hours in order to remove completely the water present in the pores. After cooling to ambient temperature (21 °C), a measured amount of Xe gas (99.995%) was condensed into the tube with liquid nitrogen. The tube was then flame-sealed. The weight of samples out-gassed at 21 °C and 105 °C are corrected for residual water content by subtracting the weight loss on heating similar samples from 21 °C to 105 °C.

Figure 3.5 Diagram of high-vacuum glass manifold

2) Samples for the drying technique study: the samples were weighed and packed in pyrex tubes, then attached to the vacuum manifold. In order to preserve the water content and pore character of the samples during sample loading, the air was removed by freeze-pump-thaw cycles. A measured amount of xenon gas was then condensed into the sample tube which was flame-sealed.

3) Samples for the oxidation effect study: the same as for the raw coal samples.

3.3.4 ^{129}Xe NMR Experiments. ^{129}Xe NMR spectra were recorded at a frequency of 55.3 MHz on a Bruker MSL-200 spectrometer. A solid-state probe with horizontal

solenoid geometry (o.d 10 mm samples) was used. Magic-angle spinning experiments at room temperature were carried out with a 7 mm pencil probe (Chemagnetics). Variable temperature experiments were done by using a conventional gas-flow system and a Bruker BVT-1000 temperature controller. The 90° pulse lengths were between 5 and 7 μ s and the recycle delay time was 1s. The spectral width was 30 KHz. For most of the spectra 512 datum points were accumulated which were zero filled to 1 K datum points, and a 100 Hz Gaussian line-broadening was applied before Fourier transformation (FT). 5000 to 60000 scans were acquired. All spectra were referenced to a standard Xe-NaY zeolite sample which had a chemical shift value of 71.1 ppm.

2D EXSY spectra were acquired at 83.0 MHz on a Bruker AMX-300 spectrometer with a solid-state probe. The 90° pulse length was between 4.5 and 7 μ s, and the typical recycle delay time was between 0.1 and 0.5 sec. The pulse sequence for the exchange experiment was $(\pi/2 - t_1 - \pi/2 - t_m - \pi/2 - t_2)_n$. Typically, 64 and 128 points were acquired in the t_1 and t_2 dimensions, respectively, with 20 ms increments and 256 scans per t_1 value. During data processing, the t_1 dimension was zero filled to 128 data points and a 80 Hz Gaussian line-broadening was applied in both dimensions. The reference sample was the same as used in 1D experiments.

3.4 Results and Discussion

3.4.1 General description of ^{129}Xe NMR spectra. Typical ^{129}Xe NMR spectra of xenon adsorbed in the three coal samples A, B, and C are shown in Figures 3.6, 3.7, and

3.8 respectively. The Xe loading for each spectrum is given in the figure caption with the loading level increasing from bottom to top. For samples A and B, two peaks are evident. The peak near 0 ppm arises from free Xe gas interacting with the external surface of the sample particles which can be used as an approximate internal chemical shift reference. In sample C, two broad, resolved peaks (region I and region II) were observed in addition to the free Xe gas line, which may be indicative of two different pore size regions. The main peaks observed for sample A and B are quite broad, and may reflect a micropore size distribution in the coal. This conjecture is discussed in the following sections. From Figure 3.6 and 3.7, it can be seen that for sample A and B the broad peak shows some asymmetry at low loading levels, while it is quite symmetric at high loading levels. From Figure 3.8, the linewidths of the two main peaks in sample C are narrow compared to those of the samples A and B, and the two peaks overlap at low loading levels. As a result, the linewidth for the individual pore region can not be defined at low loading levels. For sample A, B and region I of sample C, the chemical shift of the peak maxima generally increased with the loading level, which is the typical character of Xe adsorbed in open channel systems. The chemical shift of the peak maximum of the region II in sample C is independent of Xe loading.

For sample A and B, the linewidth of the broad peak decreases with increasing loading level, and this, together with the highly symmetric gaussian lineshape in the spectrum of high loading sample suggests that there is a certain effect which broadens the spectral fine structure details in highly loaded Xe samples. Possible explanations can be the

Figure 3.6 55.3 MHz static ^{129}Xe NMR spectra of Xe adsorbed in coal sample A.

Loading unit: 10^{-5} moles/g.

Figure 3.7 55.3 MHz static ^{129}Xe NMR spectra of Xe adsorbed in coal sample B.

Loading unit: 10^{-5} moles/g.

Figure 3.8 83 MHz static ^{129}Xe NMR spectra of Xe adsorbed in coal sample C.

Loading unit: 10^{-5} moles/g.

swelling of the coal, and the effect of Xe exchange (*vide infra*).

3.4.2 Spin-lattice relaxation time. For all three samples the spin-lattice relaxation time T_1 of the main peak is given in Table 3.2. The T_1 values for all samples are short, falling in the range from 15 ms to 144.6 ms. The T_1 of gaseous Xe is quite long;¹⁴ it is often reduced when Xe is adsorbed in a microporous solid due to the collision with the surface of solids. The T_1 values are especially short for samples A and B, and this is probably due to the relatively large iron content in the two samples, which induces efficient paramagnetic relaxation.¹⁵

Table 3.2 Spin-lattice relaxation time T_1 of three coal samples.

Samples	Sample A	Sample B	Sample C peak I	Sample C peak II
T_1 (ms)	15.0	21.5	116.8	144.6
δ (ppm) ^a	171	170	174	110
Std. Dev. ^b	2.3×10^{-2}	5.5×10^{-2}	4.2×10^{-2}	2.5×10^{-2}

a) relative to Xe gas at zero pressure $\delta = 0$ ppm. b) standard deviation of fitting.

According to the T_1 values, the recycle time chosen for both 1-D and 2-D experiments (0.1 to 1s) are long enough for all of the magnetization of ^{129}Xe in the different sites to be re-established between successive pulse trains.

3.4.3 Effect of Xe chemical exchange. In open channel systems, a major concern about the application of ^{129}Xe NMR spectroscopy to the study of void space of microporous solids is the presence of inter- and intra-particle chemical exchange of Xe atoms. In order to interpret chemical shifts in terms of pore size, it is important to know how well a xenon atom is localized in the structure. For instance, Karger and coworkers have shown that xenon exchange in NaCa-A, Na-X, and Na-Y zeolites is sufficiently fast at room temperature to average xenon interactions over thousands of zeolite cages on a time scale of 10^{-3} s, which is similar to the timescale of 1D ^{129}Xe NMR experiments.^{16,17} The effects of inter- and intra-particle Xe exchange on NMR parameters (chemical shift, linewidth and relaxation time) can be described as follows:

(i) *Inter-particle exchange of Xe.* If xenon atoms can exchange rapidly between particles of a powdered solid with internal pore space, then certainly rapid exchange will occur between the adsorbed and gaseous Xe, as observed for NaY zeolite and Vycor glass.¹⁸ The system probed by Xe then includes both the surfaces of the internal pore space and the void space between particles. In this case, the extraparticle Xe plays an important role in all of the NMR parameters. The observed chemical shift, linewidth and relaxation time then depend on the particle size distribution and bulk density of the solid phase.¹⁸

The existence of interparticle Xe exchange is determined by the diffusion pathlength of a Xe atom during its lifetime within a particle. The lifetime of a xenon atom within a particle is defined as t_1 , and the related diffusion pathlength is taken to be r_1 . The parameter which defines the criterion for fast and slow exchange on an NMR timescale is

given by $t_c = [2\pi(\delta_s - \delta_g)]^{-1}$, where the δ_s and δ_g are the xenon chemical shifts in the adsorbed and gas phases respectively. Three kinds of exchange situations can arise as follows:¹⁸

1. Diffusion pathlength r_1 is much smaller than the particle size, i.e., no exchange between adsorbed Xe and gaseous Xe. In this situation $t_1 > T_1$ (adsorbed or gas) and $t_1 > t_c$ (vide supra). The measured chemical shift, linewidth and relaxation time truly reflect the values for xenon in the two phases.
2. Diffusion pathlength is such that exchange is slow, but of the same order as the xenon T_1 (adsorbed or gas). $T_1 > t_1 > t_c$. Again the observed chemical shift values should be equal to the actual values for the gas and adsorbed phases, but the spin-lattice relaxation times for xenon in the two phases will be complex, and exchange broadening of the resonance line may occur.
3. Diffusion pathlength is much greater than particle size, i.e., exchange between the two phases is fast. In this case $T_1, t_c > t_1$; a single line is seen at a chemical shift value which is a weighted average for the two phases. The linewidth may again show exchange broadening.

Information about the lifetime of a Xe atom within a particle can be obtained by following Xe uptake into coal micropores as a function of time. This is done by measuring the ratio of the integrated intensity of the two Xe lines for xenon inside and outside the particles as a function of time after Xe was sealed into the sample tube.

Figure 3.9 shows typical spectra of a Xe uptake experiment. It clearly shows that the

Figure 3.9 55.3 MHz static ^{129}Xe NMR spectra of Xe uptake as a function of time.

Coal sample A with loading: 60×10^{-5} moles/g.

Figure 3.10 Fraction of Xe adsorbed into coal micropores as a function of time.

number of Xe atoms adsorbed into coal micropores increases with time. The curves in Figure 3.10 show the fraction of Xe adsorbed into coal micropores as a function of time for the three samples. The results of curve fitting for coal samples A, B and peak I of sample C shows that Xe uptake into the coal micropores can be fit by an exponential function with quite a large time constant relative to the T_1 of adsorbed Xe and t_c (Table 3.3).

Table 3.3 Time constants for Xe uptake into coal micropores.

Samples	A	B	C (peak I)
Time constant (hrs)	7.67	7.74	3.23
Std. Dev. ^a	0.84	1.04	1.05

a) standard deviation of fitting.

The results indicate that there are significant barriers to Xe diffusion into the coal micropores, and it implies that once Xe is adsorbed in coal micropores the lifetime of Xe within a particle will be much longer than the T_1 (adsorbed or gas phase) and t_c .

Therefore, the diffusion pathlength of Xe within a particle should be much smaller than the particle size. Consequently, it can be concluded that on an NMR timescale the effect of Xe exchange in these coal systems is limited to sites within coal particles.

Another convincing piece of evidence in agreement with the above conclusion comes from 2D EXSY results, which shows no coupling between the adsorbed and gas Xe in a mixing time of 3 ms (Figure 3.11-3.12).

The results also show that the uptake of region II of sample C, which is of larger pore size, is quite fast. This clearly indicates a much smaller diffusional barrier for region II of coal sample C.

Figure 3.11 ^{129}Xe 2D EXSY spectrum of Xe adsorbed in coal sample A. Mixing time 3 ms.

Figure 3.12 ^{129}Xe 2D EXSY spectrum of Xe adsorbed in coal sample C. Mixing time 3 ms.

An interesting feature in the spectra for the Xe uptake experiment (Figure 3.9) is that the chemical shift (peak maximum) decreases as the time increases. This can be explained by swelling of the coal. As time increases, more Xe enters into coal micropores, and causes the coal matrix to swell. Since the chemical shift is inversely related to the pore size, the chemical shift is, therefore, larger at the beginning of the uptake process, then becomes smaller due to the swelling process.

(ii) *Intra-particle exchange of Xe.* When a Xe atom can sample a number of sites within a particle on the appropriate NMR timescale, then the NMR spectrum reflects only the average local environment sampled by a Xe atom. Such averaging effects will "wash out" any fine structure due to structural inhomogeneities. As a result, the utility of ^{129}Xe NMR for obtaining information on structural heterogeneities will rely on the presence of sufficiently slow xenon exchange between distinct trapping sites within a particle. For instance, resolution of two lines separated by 10 ppm at 4.7 Tesla (^{129}Xe resonance frequency 55.3 MHz) requires that the characteristic Xe exchange time between these two trapping sites be slow compared to 1.8×10^{-3} s, which is the reciprocal of peak separation in Hz.

Depending on the exchange rate, intraparticle xenon exchange can be studied by variable temperature experiments. Reducing the temperature decreases the thermal energy of adsorbed xenon which in turn increases the lifetime of Xe in each trapping sites. Figure 3.13 shows the spectra of a high-loading sample at different temperatures; as the temperature decreases, the linewidth of the broad peak increases.

Figure 3.13 ^{129}Xe NMR spectra of Xe adsorbed in coal micropores at different temperatures. Sample A with loading: 60.0×10^{-5} moles/g.

The plot of linewidth as a function of temperature (Figure 3.14) shows that the linewidth increases as the temperature decreases, and reaches an equilibrium value at ca. 213 K. This indicates that the intraparticle Xe exchange rate decreases as the temperature decreases, and it probably reaches the slow limit, in which the exchange becomes slow on the NMR timescale, at temperature ca. 213 K. Low temperature 2D EXSY results confirm this (*vide infra*).

Therefore, Xe atoms do exchange between different trapping sites at temperatures above 213 K, and only an average answer for the pore sizes in three coals can be expected

Figure 3.14 Linewidth of ^{129}Xe NMR signal of Xe adsorbed in coal micropores as a function of temperature. Sample A with loading, 60×10^{-5} moles/g.

A contributing factor to the trend of increasing linewidth as the temperature decreases may be that at low temperature the deformable coal micropore structure becomes more rigid which limits the mobility of xenon atoms. This effect may become more important in samples highly loaded with Xe.

A more quantitative study of Xe intraparticle exchange is possible by applying 2D EXSY NMR experiments. Some of the lines in a 2D contour plot reflect the presence of cross-peaks resulting from exchange of Xe between trapping sites with different chemical shifts. Consequently, the shape of the contour plot reflects the magnitude of Xe exchange between different trapping sites.

Figure 3.15 Schematic representation of a hypothetical 2D EXSY contour plot.

Figure 3.15 is a schematic presentation of a hypothetical 2D EXSY contour plot which illustrates how the shape of plot provides information on exchange. The four black dots along the diagonal line represent the chemical shifts of four sites with distinct chemical shifts; the six stars represent the intensity of cross-peaks between close (chemical shift) trapping sites; and the six circles represent the cross-peaks between trapping sites with larger chemical shift differences. In the figure, the contour formed by the cross-peaks of close trapping sites is flatter than that related to the more separated trapping sites.

Therefore, the extent of exchange can be conveniently quantified for comparison purposes by the ratio of short (a) and long (b) axes of the ellipses formed by the contour lines.

Figure 3.16 is a typical ^{129}Xe 2D EXSY spectrum of Xe adsorbed in coal micropores. Since the distribution of coal micropore size appears to be a continuous function, the 2D contour plot consist of lines with elliptical shape.

Table 3.4 lists some ratios of the two axis (a/b) of the ellipses of 2D EXSY contour plots. The results were obtained from the samples with different Xe loading and the same sample at different experimental temperature or with a different mixing time.

As shown in Table 3.4, several factors which determine the magnitude of intra-particle exchange can be discussed as follows:

1) *loading level*. As shown in the table, when the mixing time and temperature are the same, increasing the loading level from 5.9×10^{-5} to 60×10^{-5} , the a/b ratio changes from 0.27 to 0.43 for sample A and 0.28 to 0.46 for sample B. Clearly, intra-particle Xe

Figure 3.16 Typical ^{129}Xe 2D exchange spectrum of xenon adsorbed in coal micropores. Sample A with loading: 60×10^{-5} moles/g and mixing time 3 ms.

Table 3.4 Ratios of the two axes of ellipses formed by 2D EXSY contour lines.

Sample	Loading (moles/g)	Temperature (K)	Mixing time (ms)	a/b ratio
A	60×10^{-5}	293	3	0.43
A	5.0×10^{-5}	293	3	0.27
A	60×10^{-5}	293	15	0.62
A	60×10^{-5}	213	3	0.22
B	66×10^{-5}	293	3	0.46
B	5.0×10^{-5}	293	3	0.28

exchange is much less significant in the low-loading (L) sample than in the high-loading (H) sample. Figure 3.17 shows 2D EXSY contour plots for the sample with different loading levels. Consequently, L samples will be the best for giving significant chemical shift information of Xe atoms trapped in different pore sizes. The most likely explanation for the loading-dependent exchange magnitude is that the coal matrix swells as the Xe density increases. Another contributing factor may be that Xe-Xe interactions are weaker than the Xe-wall interactions. These results are consistent with the trend of the loading-dependent chemical shift curves (see section 3.4.5). The fact that xenon exchange rates are

minimal at low loading is of great importance, since the chemical shift which characterizes the interaction of Xe with the cage walls is obtained by extrapolation to zero loading.

2) *Temperature.* On using the same sample, keeping the same mixing time, but reducing the temperature, the a/b ratio changes from 0.62 to 0.22 (Figure 3.18). This result suggests that when $T < 213$ K, intra-particle Xe exchange slows down to its slow limit.

3) *The mixing time.* Increasing the mixing time allows the xenon to sample more sites. As shown in Table 3.3 (sample A with loading 60×10^{-5} moles/g), when the mixing time is increased from 3 ms to 15 ms, the a/b ratio increases from 0.43 to 0.62 (Figure 3.19). When the mixing time is increased from 3 ms to 15 ms, exchange even occurs between the two different pore size regions of sample C (Figure 3.20).

The above results indicate that only at low temperatures and under low Xe loading conditions will the spectrum reflect the chemical shifts of Xe trapped in the distinct sites. Since room temperature low loading 2D EXSY spectra show minimal exchange, the spectra of room temperature low loading samples should also give a satisfactory presentation of the chemical shifts of Xe trapped in the coal micropore structure.

It is also clear that ^{129}Xe 2D EXSY NMR spectroscopy can be a useful tool to study diffusion processes in coals. Information of diffusion rates can be obtained by fitting the dependence of the ratio of cross peak intensity to diagonal peak intensity ($I_{\text{cross}}/I_{\text{diagonal}}$) on the mixing time. Also, determining the exchange rate as function of temperature can yield information on the activation energy of diffusion.

Figure 3. 17 ^{129}Xe 2D EXSY NMR contour plots of xenon adsorbed in coal sample A at different Xe loadings: (a) 5.0×10^{-5} moles/g; (b) 6.0×10^{-5} moles/g. Mixing time is 3 ms for both samples

Figure 3. 18 ^{129}Xe 2D EXSY NMR contour plots of Xe adsorbed in coal sample A at different temperatures: (a) 293 K; (b) 213 K. Mixing time is 3 ms for both. Sample loading: 60×10^{-5} moles/g.

Figure 3. 19 ^{129}Xe 2D EXSY NMR contour plots of xenon adsorbed in coal sample A with different mixing times: (a) $t_m = 1.5$ ms, (b) $t_m = 15$ ms. Sample loading: 60×10^{-5} moles/g.

Figure 3. 20 ^{129}Xe 2D EXSY contour plots of Xe adsorbed in coal sample C. Xe atoms exchange between two different pore size regions as the mixing time increase from (a) $t_m = 0.5$ ms to (b) $t_m = 15$ ms. Sample loading: 60×10^{-3} moles/g.

3.4.4 Effects of Chemical Shift Anisotropy. To date, empirical correlations of ^{129}Xe chemical shifts simply correlate the isotropic chemical shift with the void space of microporous solids.^{3, 7, 19, 20} It is clearly impossible that the complete 3-dimensional pore structure should be interpretable in terms of a single isotropic chemical shift. The short range and anisotropic nature of Xe-surface interactions have been demonstrated in a ^{129}Xe chemical shift *ab initio* calculation for a Xe-H₂O pair, with the Xe atom approaching the oxygen atom along the symmetry axis.¹⁸ Therefore, there are obvious limitations in the interpretation of an isotropic chemical shift in terms of 3-dimensional structure.

In the closed cage system of clathrates, chemical shift anisotropy manifests itself clearly in the ^{129}Xe NMR spectrum with values for up to $\Delta\delta = 45$ ppm, and only becomes isotropic in cages with cubic symmetry.³ In open channel systems such as zeolites, chemical shift anisotropy was observed for Xe adsorbed in the small ellipsoidal channels of SAPO-11 and AlPO₄-11,^{21, 22} also the ZSM-12.²³ In many cases, a significant chemical shift anisotropy is not observed; this then must be due to the presence of dynamic exchange of Xe atoms among a number of sites which imposes a roughly spherical symmetry on the diffusion path, or by the exchange between the gas phase and randomly oriented particles. Both these effects average the chemical shift tensor to its isotropic value.²²

The coal micropore structure has been proposed to be a highly anisotropic, interconnected slit-like pore system. Since the spectrum of Xe adsorbed in the three coal

Figure 3.21 55.3 MHz static and spinning ^{129}Xe NMR spectra of Xe adsorbed in the coal micropore structure. Sample A with loading: 40.0×10^{-5} moles/g.

samples shows a relatively large chemical shift, and the uptake of Xe gas is quite slow, it is likely that these sites are relatively "tight" for Xe atoms. For such small-pore systems, there is then quite a good possibility for the presence of chemical shift anisotropy which may contribute to the width of the broad line. The anisotropy contribution can be checked by comparing the spectrum obtained with and without magic angle spinning. Figure 3.21 shows the ^{129}Xe NMR static and spinning spectra of coal sample A. The two spectra do not show significantly different linewidths, indicating that the chemical shift anisotropy does not contribute significantly to the linewidth. The most likely explanation is that there is sufficient motion of the Xe atoms within the pore system which averages the individual shielding tensor components. The effect of motional averaging over the irregular pore surface must approximate spherical averaging, much the same as observed in solid polymers and zeolites.^{22,24}

Similarly, the dipolar coupling between Xe atoms, and between Xe atoms and protons in the pore walls can be eliminated as a source of line broadening. These interactions are expected to be quite weak and would have been eliminated by application of MAS if they had been significant.

Since the chemical shift anisotropy and dipolar broadening are not significant, the Xe spectra can be interpreted in terms of only isotropic chemical shifts with some confidence.

3.4.5 The ^{129}Xe NMR Chemical Shift As a Function of Xenon Loading. As discussed above, the intraparticle Xe exchange is fast enough to average the chemical shift

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anisotropy and dipolar interaction, but would not appear to contribute significantly to the linewidth at low loading. Therefore, the 1D static ^{129}Xe NMR spectra can be interpreted in terms of only isotropic chemical shifts, and the width of the broad line reflects the distribution of isotropic chemical shifts.

We use an analogue of eq. (2.37), which was used to describe the chemical shift behaviour in zeolites, and assume that the magnetic effect and the influence of electric fields can be neglected for the Xe-coal system. Also to a good approximation, the asymmetry of the broad line for low loading spectra of samples A and B can be ignored (i.e. the peak maxima were simply taken as the average chemical shift). The data of the three curves in Figure 3.22 (sample A, B and region I of sample C) can then be fitted to a second order polynomial function which is expressed as:

$$\delta(L) = \delta_0 + \delta_1 L + \delta_2 L^2 \quad (3.2)$$

where δ is the average chemical shift, L is Xe loading level, and δ_0 , δ_1 , δ_2 are coefficients obtained from fitting the data to eq (3.2). In Figure 3.22, most of curves show that the chemical shift varies linearly with Xe loading in the low loading region (ca. $\leq 30 \times 10^{-5}$ moles/g), but non-linearly in the high loading region as pointed out previously. The curvature in the high loading region has been suggested to be due to the swelling of the coal matrix, as the decreasing chemical shift seems to indicate increasing pore volume. This also is consistent with the observations of the uptake and exchange experiments. The chemical shift of Peak II of sample C, which reflects a larger pore size region, is independent of Xe loading. An explanation is that exchange occurs between the adsorbed

Figure 3.22 ^{129}Xe NMR chemical shift as a function of Xe loading for three coal samples.

and gaseous Xe within this larger pore.²⁴

The coefficients of eq. (3.2) can be assigned as follows: δ_0 is due to Xe-pore surface interactions, δ_1 is due to the Xe-Xe interactions, and δ_2 is a parameter which accounts for the swelling of coal structure. Table 3.5 lists the three coefficients for the three coal samples.

Table 3.5 The coefficients of Eq.(3.2) for three coal samples.

Sample	δ_0	δ_1	δ_2	Std. Dev. ^a
A	126.3	1.2	-6.2×10^{-3}	1.9
B	127.6	0.92	-2.5×10^{-3}	3.4
C peak I	144.9	0.84	-4.9×10^{-3}	0.66

a) standard deviation of fitting.

Since the data at high Xe loading are affected by the swelling of the coal, another way to obtain the chemical shift which reflects the Xe-pore surface interactions is to use just the low loading data (ca. below 30×10^{-5} moles/g) linearly extrapolated to zero loading (Table 3.6). The results of the two procedures are the same within experimental error.

Table 3.6 The chemical shift δ_0 by linear extrapolation to zero loading.

Sample	A	B	C peak I
δ_0 (ppm) ^a	128	131	150

a) estimated uncertainty is ± 5 ppm.

3.5 Interpretation of Chemical Shift in Terms of Pore Size

To interpret the extrapolated chemical shifts in terms of pore size, the empirical correlations to be used should be specified. For open channel systems, there is no universal empirical correlation of the ^{129}Xe NMR chemical shift with pore dimensions.^{2,4,20}

Fraissard *et al* proposed a hard-sphere model.^{2,4} In this model the Xe atom was treated as a rigid sphere which collides elastically with the wall of the void space of zeolites. The extrapolated chemical shift is then related to the mean free path of a Xe atom imposed by the structure as:

$$\delta_s = 243 [2.054 / 2.054 + L] \quad (3.3)$$

where the δ_s is extrapolated chemical shift, L is mean free path of a Xe atom within the structure. The mean free path in turn was used to calculate the dimension of pore. The obvious drawback of this model is that it ignores surface-wall interactions. Also according to the eq. (3.3) the maximum possible shift is 243 ppm, although experimental shifts considerably larger have been measured.³ The Xe-O Lennard-Jones potential model for

Figure 3.23 Correlation of ^{129}Xe isotropic NMR chemical shift with the free-space radius available to the xenon atom.³

zeolites⁶ shows that the Xe atom does not sample the cage space uniformly when the cage dimension is considerably larger than the van der Waals diameter of the Xe atom and simple correlations should not be expected. In a large cage or pore, the Xe atom spends more time near the cage surface than in the cage center. The strongest trapping sites are those closely matching the xenon van der Waal's dimension of 4.4 Å.

From Table 3.6 the linearly extrapolated chemical shifts (δ_0) of the three coal samples fall in the small-pore region, and the correlation established for the clathrate cages can be used as a reasonable approximation.³ Figure 3.23 is the calibration curve for the extrapolated chemical shift and the pore size. Table 3.7 lists the mean pore sizes and pore distribution of three coal samples using the empirical correlation shown in Figure 3.23.

Table 3.7 The average pore size and pore size distribution width of three coal samples obtained by using the Xe-clathrate cage empirical correlation.

Sample	δ_0 (ppm) ^a	radius(Å) ^b	distribution width($\pm$ Å)
A	128	3.10	0.36
B	132	3.07	0.36
C	150	2.98	0.25

a) estimated uncertainty ± 5 ppm.

b) pore size distribution uncertainty ± 0.03 Å.

3.6 Applications

3.6.1 Effect of drying techniques. Coal sample A was subjected to different drying techniques and the pore sizes were studied by ^{129}Xe NMR spectroscopy. Table 3.8 gives the description of samples (for the experimental details see section 3.3).

Table 3.8 Description of samples for the study of the effect of drying techniques

Sample name	Description
RAW	raw coal without treatment
VDRT	vacuum dried at room temperature
VDOH	vacuum dried at 105 °C
ADOH	air dried at 105 °C
FRD	freeze dried
MVD	microwave dried

The extrapolated chemical shift is indeed a sensitive indicator of pore size. Figure 3.24 shows the ^{129}Xe NMR chemical shifts of coal samples treated in different ways as a function of Xe loading. Translation of the extrapolated chemical shift gives the mean pore size for different samples (Table 3.9).

The results show the order of mean pore size follows the order: VDRT > ADOH > MVD~VDOH > FRD > RAW. The trend appears to be in reverse order of residual water

Figure 3.24 ^{129}Xe NMR chemical shifts as a function of sample loading for the different coal samples.

Table 3.9 The extrapolated chemical shift and average pore size of different samples.

Samples	Extrapolated chemical shift (ppm) ^a	Average pore radius (Å) ^b
RAW	194	2.57
VDRT	134	3.04
VDOH	148	2.96
ADOH	140	3.00
FRD	171	2.86
MVD	150	2.97

a) estimated uncertainty ± 5 ppm. b) pore size distribution uncertainty ± 0.03 Å.

Table 3.10 The residual water content of the different samples

Samples	Residual water content (wt%, dry basis)
RAW	22.0
VDRT	3.87
VDOH	4.11
ADOH	3.41
FRD	7.47
MVD	5.59

content (Table 3.10), only the VDOH sample is an exception. Since the mean pore size correlates inversely with the residual water content, the measurements reflect the effectiveness of the drying treatment. It seems that water and Xe compete for the same pore space. Probably the basic pore structure has not been changed by the treatment. The VDOH sample treatment is the most aggressive, and it may have caused the pores to shrink slightly.

3.6.2 Effect of oxidation. The effects of oxidation on the pore structure and swelling character have also been examined (for the experimental details see section 3.3).

Figure 3.25 shows the ^{129}Xe chemical shifts as a function of sample loading for both the raw and oxidized coal samples. The extrapolated chemical shifts and the interpreted pore sizes are listed in Table 3.11. The mean pore size of oxidized coal samples A and B are slightly smaller than for the raw coal samples suggesting that the free pore volume shrinks slightly on oxidation. Another interesting feature observed in the Figure 3.25 is that the curvature in the high loading range is much less significant in the oxidized coal samples as compared to the raw coal samples. This indicates that oxidation has made the coal structure less capable of swelling, perhaps due to the forming of cross-links in the coal polymer structure. The feature is reflected in the δ_2 of Eq. (3.2) (Table 3.11). It is clear that δ_2 could be used as an index to determine the swelling capability of coals.

Figure 3.25 ^{129}Xe NMR chemical shifts as a function of Xe loading of different coal samples.

Table 3.11 Summary of data for oxidation effects study

Samples	δ_0^a	Pore radius ^b (Å)	δ_2	a/b ratio
Raw coal A	128	3.10	-6.19×10^{-3}	0.44
Oxidized A	134	3.06	-3.79×10^{-3}	0.34
Raw coal B	132	3.07	-2.53×10^{-3}	0.46
Oxidized B	137	2.94	-1.64×10^{-3}	0.36

a) estimated uncertainty ± 5 ppm. b) pore size distribution uncertainty ± 0.03 Å.

2D EXSY results also show the smaller magnitude (a/b ratio see section 3.4.3) of intraparticle exchange of adsorbed Xe due to the increase of coal rigidity which in turn decrease the mobility of Xe atoms.

3.7 Summary and Future Work

1. *The experimental considerations.* All three coal samples studied show very broad resonance lines, and a meaningful ^{129}Xe NMR spectrum can only be obtained by using a phase-cycled two pulse spin-echo experiment. The T_1 value for the three coal samples are short (in range of ms), and the pulse recycle delay time chosen for both 1D and 2D experiments (0.1 to 1 s) are suitable for obtaining quantitative data.

2. *The factors which affect ^{129}Xe NMR spectra.* The results of Xe uptake experiments indicate that this process is quite slow (hours). This, together with 2D EXSY NMR results show that on the NMR timescale the Xe exchange effects are limited to the intraparticle exchange. The 2D EXSY NMR experimental results demonstrate that the intraparticle exchange effects are smallest for low loading.

MAS results show the effect of Xe dynamic averaging is sufficient enough to eliminate the contribution of chemical shift anisotropy and dipolar coupling, which allows the interpretation of the ^{129}Xe NMR spectrum in terms of only isotropic chemical shifts.

Temperature variation results show a relatively weak temperature dependence of the ^{129}Xe NMR chemical shifts. This again indicates that the xenon atoms do not sample large void spaces.

3. *The results for coals.* Using the empirical correlation of ^{129}Xe isotropic chemical shifts with the radius of the free-space volume available to the xenon atom, average radii of 3.10, 3.07 and 2.98 Å were obtained for coal samples A, and B and the small pore region of sample C respectively.

The long loading times suggests that Xe reaches the coal micropores after diffusing through tight bottlenecks or the coal matrix itself.

For coal samples A and B different drying techniques do not seem to affect pore size, the apparent decreased pore size is due to adsorbed water, and xenon and water compete for the same pore space. Oxidation of the coal inhibits coal swelling, but doesn't affect pore sizes significantly.

Two pore size domains were identified for coal sample C: the micropores similar to samples A and B; and a larger pore which shows an unusual loading dependence which does not allow a pore size estimate without additional studies. The 2D EXSY NMR results indicate that the two types of pore are linked on a timescale of msec, so that the larger pores play an important role in gas transport. It is shown that the time for Xe uptake into sample C is shorter than that for samples A and B.

In summary, the ^{129}Xe NMR spectroscopy can be a useful technique in the study of coal micropore structural features which normally are not observed with standard BET methods or other techniques.

Possibilities for future work:

- 1) to further understand the Xe dynamics in coals, which can be done by measuring diffusion constants to obtain the diffusion path length of Xe in coals.
- 2) to develop 2D EXSY NMR to measure the activation energy for diffusion between different xenon sites in coals.
- 3) to develop quantitative correlations of the δ_2 parameter in eq. (3.2) for use as a coal swelling index.
- 4) Examination of coals of other rank by ^{129}Xe NMR spectroscopy.

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