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OBJECTIVE: The objective of this project was to apply recently developed, state-of-the-art nuclear magnetic resonance (NMR) techniques to examine in situ changes in the chemical structure and molecular/macromolecular motion in coal as the temperature is increased above room temperature. Although alterations in the chemical structure of coal have been studied previously by $^{13}$C NMR, using quenched samples, the goal of this project was to examine these chemical structural changes, and changes in molecular/macromolecular mobility that may precede or accompany the chemical changes, at elevated temperatures, using modern $^{13}$C and $^1$H NMR techniques, especially $^1$H dipolar-dephasing techniques and related experiments pioneered in our laboratory for examining pyridine-saturated coals.

OVERALL PLAN: The initial plan envisioned for this project consisted of the following four primary segments (1-4) and related efforts (5) on matters relevant to the first four tasks.

1) $^1$H NMR characterization of coal structure and mobility as a function of temperature variation over a temperature range (30°-240 °C) for which substantial chemical transformations were not anticipated.

2) $^1$H NMR characterization of coal structure, mobility and conversion as a function of temperature variation over a temperature range (240°-500 °C) for which chemical transformations of coal are known to occur.

3) $^{13}$C NMR investigation of coal structure/mobility as a function of temperature over a temperature range (30°-240 °C) for which substantial chemical transformations were not anticipated.

4) $^{13}$C NMR investigation of coal structure, dynamics and conversion as a function of temperature variation over a range (240°-500 °C) for which chemical transformations of coal are known to occur.

5) Related matters relevant to the first four tasks.
   a) $^1$H CRAMPS NMR characterization of oil shales and their kerogen concentrates.
   b) Improved quantitation in $^{13}$C MAS characterization of coals.

The small effort 5a was carried out because kerogens in one sense represent the extrapolation of coal structures to lower percent aromatic carbon, so understanding kerogen structures and NMR spectra might be expected to help the interpretation of coal spectra, especially under conditions (higher temperatures) in which the sp$^3$/sp$^2$ ratio is decreased. The small effort 5b was carried out in anticipation of improving $^{13}$C NMR quantitation under
conditions (high temperatures) under which cross polarization dynamics might dramatically effect the ability to quantitate structural features.

Although the total efforts represented in 5a and 5b were small, both resulted in papers, one published and one almost ready to be submitted for publication (vide infra).

PERSONNEL: In addition to the P.I. (Gary E. Maciel), the main participants in this project were Dr. Antoni Jurkiewicz (now in a staff position at DOE's Pacific Northwest Laboratory) and Jincheng Xiong (whose Ph.D. thesis, which is attached to this report, is based on this project). In addition, Ph.D. student David Keeler participated in this project.

PUBLICATIONS RESULTING FROM THIS PROJECT

Published or Submitted


(2) Jincheng Xiong, "In Situ Variable-Temperature $^1$H Solid-State NMR Studies of Molecular Structure and Dynamics in Coals," Ph.D. Dissertation, Colorado State University, 1996.

(3) Jincheng Xiong and Gary E. Maciel, "In-Situ Variable-temperature High-Resolution $^1$H NMR Studies of Molecular Dynamics and Structure of Coal," Energy and Fuels, submitted.


(5) Antoni Jurkiewicz, David Keeler and Gary E. Maciel, "High Resolution $^1$H NMR Investigation of Oil Shales by the $^1$H CRAMPS Technique," Energy and Fuels, manuscript being finalized for submission.

Papers in Preparation

(6) Jincheng Xiong and Gary E. Maciel, "Reexamining the Molecular/Macromolecular Structural Model of Coal: A Variable-temperature $^1$H CRAMPS Study of Pyridine-Saturated Coal," Energy and Fuels, manuscript in preparation.


WORK CARRIED OUT. RESULTS

TASK 5.

As indicated above, both tasks 5a and 5b resulted in papers. In task 5b efforts were focused on a continuing effort in evaluating and improving the analytical reliability of $^{13}$C NMR measurements on coal. To this end, studies were performed on eight Argonne Premium coals, using the non-overlapping carbonyl peak of 4-(N-methylpyrrolidino)bicyclo[3.2.1]octan-8-one triflate as an intensity reference. $^{13}$C spin-lattice relaxation times measured by cross polarization (CP) detection were found to depend on the CP contact time. A series of experiments with different CP contact times yielded observed $^{13}$C spin-lattice relaxation times that are significantly larger than those reported in the literature. To insure quantitation in DP-MAS (DP = direct polarization), one needs to know only the largest $T_1^C$ value. These values were derived from plots such as those shown in Figures 1 and 2. The $T_1^C$ results are summarized in Table 1 for all the Argonne Premium Coals.

Carbon spin counting experiments performed by using direct polarization instead of CP yielded spectra shown in Figure 3 and numbers for the fraction of carbon spins that can be observed that are 81-97% of those present in the sample (Table 2). A relationship was observed between the number of unpaired electron spins and the fraction of $^{13}$C spins detected. The role of unpaired electron spin dynamics on the effective electron magnetic moment was considered and the corresponding influence on $^{13}$C NMR detection was examined. This study was summarized in paper (1) in the publication list.

The "high-resolution" $^1$H NMR study of oil shales and their kerogen concentrates, the first of its kind, was carried out by the CRAMPS technique. The spectra obtained directly via CRAMPS are shown in Figure 4. Drawing upon our prior experience with coals, the effects of $^1$H-$^1$H dipolar dephasing and of saturation with perdeuterated pyridine were examined (e.g., Figure 5). Correlations with previously published $^{13}$C CP-MAS studies were examined. Additional structural/dynamical details not evident from the $^{13}$C results were obtained. This study is summarized in paper (2) in the List of Publications.

TASKS 2-4.

In the original planning for this project, we estimated that the division of efforts required in the three-year project would be as follows: task (1), 45%, task (2) 10%, task (3) 10%, task (4) 25%, task (5) 10%. The reason why task (1) was estimated to require (and deserve) the greatest effort is that we knew there would be an extensive set of time-domain $^1$H NMR experiments to elucidate the molecular/macromolecular dynamics in coal over the 25 °C - 240 °C temperature range, and that these potentially important experiments would require extensive data treatment and interpretation; in this temperature range, the main effects of temperature variation were expected (and found) to be motional effects, rather than chemical transformations. $^{1}$H NMR techniques were expected to provide the best avenues for elucidating these motional changes. For this reason $^{13}$C NMR experiments were not expected to be as useful over this temperature range (task 2).
Figure 1. $^{13}$C spin–lattice relaxation magnetization decays of the aromatic peak of Pocohontas no. 3 coal, recorded with two different CP contact times (CT).

Figure 2. Plots of the spin–lattice relaxation time constant ($T_{1S}$) of the slowly relaxing component of the aromatic peak vs the CP contact time for Argonne Premium coals: (A) Pocohontas no. 3 (B) Lewiston-Stockton, (C) Blind-Canyon, (D) Upper-Freeport, (E) Illinois no. 6, (F) Pittsburgh no. 8, (G) Buelah-Zap, and (H) Wyodak-Anderson.
Figure 3. $^{13}$C DP-MAS spectra of Argonne Premium coals obtained with the $^{321-13}$CO intensity reference (217 ppm): (A) Lewiston-Stockton, (B) Pocohontas no. 3, (C) Blind-Canyon, (D) Wyodak-Anderson, (E) Upper-Freeport, (F) Illinois no. 6, (G) Buelah-Zap, and (H) Pittsburgh no. 8.

For the higher temperature range (240°-500 °C), the extensive chemical transformations that are known to occur might be expected to overshadow, and to some extent obscure, changes in molecular dynamics. For this reason, $^1$H NMR experiments over this temperature range (task 3) were not expected to be worthy of the extensive experimental or interpretative efforts required, and justified, for task (1); since $^{13}$C NMR techniques are excellent for elucidating chemical transformations, task (4) was considered potentially very important and worthy of an extensive effort. However, the number and sophistication of worthwhile $^{13}$C NMR experiments in task (4) and the sophistication of the data treatment, were expected to be substantially less than for the $^1$H NMR experiments of task (1).
Table 1. $^{13}$C Spin–Lattice Relaxation Times of Argonne Premium Coals

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<th>aliphatic</th>
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<tr>
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<td>$T_{1\text{Fmax}}$ (s)</td>
<td>$T_{1\text{Smax}}$ (s)</td>
</tr>
<tr>
<td>Upper-Freeport</td>
<td>9.0</td>
<td>67</td>
</tr>
<tr>
<td>Wyodak-Anderson</td>
<td>0.28</td>
<td>5.6</td>
</tr>
<tr>
<td>Illinois no. 6</td>
<td>4.6</td>
<td>32</td>
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<tr>
<td>Pittsburgh no. 8</td>
<td>7.5</td>
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<tr>
<td>Pocohontas no. 3</td>
<td>6.5</td>
<td>59</td>
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<tr>
<td>Blind-Canyon</td>
<td>1.8</td>
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<tr>
<td>Lewiston-Stockton</td>
<td>4.8</td>
<td>42</td>
</tr>
<tr>
<td>Buelah-Zap</td>
<td>0.30</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$T_{1\text{Fmax}}$: maximum value of the $^{13}$C spin–lattice relaxation time of the fast-relaxing component, determined as a function of the CP contact time (CT).

$T_{1\text{Smax}}$: maximum value of the $^{13}$C spin–lattice relaxation time of the slowly relaxing component, determined as a function of the CP CT.

$A_F$, fraction of fast-relaxing component, determined by extrapolation of the plot of $A_F$ vs CT.

Table 2. Aromaticity ($f_a$) and Percent of $^{13}$C Spins Observed ($C_{obs}$) in Argonne Premium Coals as Determined via $^{13}$C DP-MAS NMR

<table>
<thead>
<tr>
<th>sample</th>
<th>this study</th>
<th>$C_{obs}$ (%)</th>
<th>$f_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ref 13</td>
<td>ref 14</td>
</tr>
<tr>
<td>Upper-Freeport</td>
<td>96 ± 3</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Wyodak-Anderson</td>
<td>89 ± 5</td>
<td>95</td>
<td>58</td>
</tr>
<tr>
<td>Illinois no. 6</td>
<td>97 ± 3</td>
<td>85</td>
<td>72</td>
</tr>
<tr>
<td>Pittsburgh no. 8</td>
<td>81 ± 3</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>Pocohontas no. 3</td>
<td>87 ± 6</td>
<td>90</td>
<td>82</td>
</tr>
<tr>
<td>Blind-Canyon</td>
<td>93 ± 7</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Lewiston-Stockton</td>
<td>92 ± 6</td>
<td>75</td>
<td>84</td>
</tr>
<tr>
<td>Buelah-Zap</td>
<td>90 ± 5</td>
<td>95</td>
<td>65</td>
</tr>
</tbody>
</table>
Tasks (1) and (3) require different probe technology (pushing conventional gas-flow heating technology to a challenging level) than tasks (2) and (4) (rf heating or laser heating). In addition, the higher temperature range (240°-500 °C) of tasks (2) and (4) requires more difficult temperature measurement techniques not yet well developed.

In parallel with the demanding, extensive and valuable task (1) effort was a parallel, and partially successful, effort in developing the technology required for the higher-temperature tasks. However, by the beginning of the third year of this project, it became clear that there would not be sufficient time or resources during the final year to complete all of the first four tasks satisfactorily. Accordingly, it was decided to emphasize task (1), make a modest effort toward task (2) and leave the corresponding 13C NMR studies (tasks (3) and (4)) to a subsequent period. It was hoped that tasks (3) and (4) would constitute the basis for a follow-up UCR project; however, recent changes in the UCR program now make that essentially impossible, so an attempt will be made to secure support for tasks (2), (3) and (4) from EPRI.
Figure 5. Proton CRAMPS dipolar-dephasing spectra of the New Albany oil shale composite. (A) C₅D₅N-treated sample, arbitrary scaling. (B) C₅D₅N-saturated sample, absolute intensities. (C) Untreated sample, arbitrary scaling. (D) Untreated sample, absolute intensity.

**TASK 1.**

Determined to focus a thorough effort on task (1), and thereby insure a successful project, rather than a superficial survey of all four tasks, we carried out the first systematic *in situ* variable-temperature $^1$H CRAMPS study of untreated coal and C$_5$D$_5$N-saturated coal samples.
between 25 °C and 230 °C. Major advances of previously existing \(^1\)H CRAMPS experimental methods and techniques were made to improve the reliability, robustness and efficiency of these techniques. New time-domain NMR experiments based on \(^1\)H CRAMPS techniques, including a new two-dimensional proton spin-exchange experiment, were developed and applied to in situ variable-temperature studies of coal. The main scientific issue on which this work focused is how non-covalent associative bonds are affected at the molecular level by thermal treatment and solvent saturation. The molecular structural and dynamical changes induced in coal by thermal treatment and solvent saturation were monitored with various time-domain and two-dimensional NMR experiments based on \(^1\)H CRAMPS.

We found that pyridine saturation can dramatically promote molecular motion, even at room temperature, while thermal treatment alone is much less effective in promoting molecular motion even at 230 °C. However, for pyridine saturated coal, a moderate increase in temperature can significantly enhance the molecular mobility of coal. A new model for explaining the enhancement of molecular mobility induced by thermal treatment and solvent saturation was proposed and discussed in terms of our new experimental results.

Correlations among molecular structure, molecular mobility and solvent-extraction components were established through comparative variable-temperature \(^1\)H CRAMPS studies on the C5D5N-saturated premium 601 and its pyridine-extraction residue. A critical review of the molecular/macromolecular (M/M) structural model of coal was made on the basis of our new results. The nature of the molecular phase and macromolecular phase in coal and the relationships between the M/M structural model and molecular mobility, as detected experimentally by NMR, were re-examined. We developed a coherent view of the molecular structure and dynamics of coal on the basis of the new experimental results. Many discrepancies in the literature on these issues are well resolved by this view, and the resolution enhancement due to solvent saturation is satisfactorily explained.

Time-domain experiments, including proton dipolar-dephasing experiments and the measurements of proton spin-lattice relaxation times in the laboratory frame and in the rotating frame, have not only provided molecular dynamical information on coal over a large range of time scales, but have also revealed the extremely large structural heterogeneity existing in coal over a broad range of spatial dimensions from 4 Å to 350 Å. The structural heterogeneity in coal was also directly addressed in this work by the first 1D and 2D spin-exchange studies of coal based on \(^1\)H CRAMPS detection. Information on the spatial distribution of different types of structural units in coal in terms of chemical shifts and molecular mobilities was obtained from this study. In particular, a new 2D \(^1\)H,\(^1\)H spin-exchange technique was developed in this work for probing complicated spin-exchange pathways among protons with different mobilities and chemical shifts. This new 2D spin-exchange experiment has also proved to be very useful for studying intramolecular spin exchange among protons in highly mobile structures of C5D5N-saturated coals. Information on the degree of substitution of aromatic rings of the mobile structures in C5D5N-saturated coals was obtained from such studies.

Details of this extensive task (1) effort are described in papers (3) - (8) in the list of Publications Resulting from this Project (vide infra) and in the remainder of this report.
1H NMR Characterization of Coal Structure and Dynamics over the Temperature Range, 25-230°C

Introduction

In previous NMR studies of coal, two very important issues have not been addressed or fully exploited. One major lack in previous studies has been temperature effects on non-covalent bonds. This subject is of great importance from the standpoint of both fundamental and applied research. The M/M model is based on the 1H-1H dipolar-dephasing behaviors of protons in environments of different molecular mobilities. Molecular mobility is highly temperature-dependent. Most previous NMR studies were carried out at room temperature, trying to correlate molecular mobility (e.g., the fraction of the Gaussian dephasing component) at only one temperature with the molecular structure of coal. It is no wonder that many discrepancies exist in the literature based on this approach. In particular, no in situ high-resolution NMR studies at a temperature close to solvent extraction temperatures have been reported. It is well known that the extraction yield is sensitive to extraction conditions. Correlating NMR studies at room temperature with solvent extraction experiments is certainly not an easy task. From the practical point of view, the understanding of temperature effects of non-covalent bonds below 300 °C would be key to developing low-temperature coal conversion technology.

Another major lack of emphasis in previous studies is the correlation between molecular structure/molecular mobilities and secondary interactions with the environment within coal. It is conceivable that different molecular structural units will manifest different mobilities even in a similar chemical and physical environment. For example, methyl groups tend to undergo rapid internal rotation at room temperature.

Most previous NMR studies of coal have been limited to wide-line 1H techniques. The extremely valuable chemical shift information of NMR was lost in these studies. A fundamental question that arose from such studies is whether the observed multiple-dephasing components are due to different mobilities of the same kind of structural unit or are simply contributions from different structural units with their own characteristic molecular mobilities. An equally important practical question is what kind of structural units in coal can be effectively mobilized and are thus selectively extracted in solvent extraction experiments.

These problems can be addressed by a high-resolution solid-state 1H NMR technique called CRAMPS (combined rotation and multiple-pulse spectroscopy), which was introduced by Gerstein and coworkers. Chemical shift information can be extracted from this technique by removing two major line broadening effects that dominate a wide line 1H NMR spectrum: the dipolar interaction and chemical shift anisotropy. The power and potential of this technique for coal studies have been demonstrated in extensive 1H CRAMPS studies of coal samples carried out at room temperature by this research group. In particular, dramatic resolution enhancement was observed for some C6D4N-
saturated bituminous coals. Dipolar-dephasing experiments based on \(^1\)H CRAMPS detection have been successfully used to correlate molecular mobilities with molecular structure at room temperature. But a correlation between solvent extractable components and molecular mobility were not well established, as the experiments were carried out only at room temperature, because great technical difficulties are involved in implementing the CRAMPS technique at other temperatures.

The application of the \(^1\)H CRAMPS technique in coal studies has been limited to very few groups in the world. Dipolar dephasing experiments based on \(^1\)H CRAMPS detection used in the previous work have also suffered from phase and baseline distortions that may severely affect spectral quantitation on some coal samples. Experiments and data analysis procedures needed to be improved to assure reliability and robustness of this technique.

To our knowledge, all the previous \(^1\)H CRAMPS studies on coal have been limited to room temperature studies. Time-domain experiments on coal based on \(^1\)H CRAMPS detection have been limited only to dipolar-dephasing experiments in previous studies. A large array of time domain experiments based on \(^1\)H CRAMPS techniques has not previously been exploited in coal studies.

In this work, we carried out the first systematic variable-temperature (VT) in situ \(^1\)H CRAMPS studies of untreated coal and C\(_5\)D\(_5\)N-saturated coal samples between 25 \(^\circ\)C and 230 \(^\circ\)C. Major enhancements on previously existing experimental \(^1\)H CRAMPS methods and techniques have been made to improve the reliability and robustness of these techniques. New time-domain NMR experiments based on \(^1\)H CRAMPS techniques, including a new two-dimensional spin-exchange experiment, have been developed and applied to variable-temperature studies of coal.

A main scientific issue in this work is how non-covalent associative bonds are affected by thermal treatment and solvent saturation at the molecular level. We have aimed at improving our fundamental understanding of this issue at the molecular level through various time-domain and two-dimensional NMR experiments. Correlations among molecular structure, molecular mobility and solvent-extraction components have been established. The origins of many discrepancies in the literature have been found. A critical review of the M/M model has been made on the basis of our new experimental results.

\(^1\)H CRAMPS Studies of Untreated Coal at Temperatures between 25 \(^\circ\)C and 230 \(^\circ\)C

Thermally induced changes in coals are of interest from the stand point of both basic theoretical and applied research. The study of structural and dynamic changes during thermal activation could shed some light on the nature of the complex structure of coals. Such knowledge could be used to refine the current structural models of coals. The knowledge gained from such a study could also be useful for improving prospects and efficiencies of coal conversion.
The thermal transformation of coal can be studied by the “equilibrium method” and the \textit{in situ} method. In an “equilibrium method”, a coal sample is heated to a certain temperature for a certain period of time, then cooled down to room temperature for analysis. Such a method is useful for determining the permanent structural changes that occur in coals and requires no special high temperature capability in an analytical instrument. However, an \textit{in situ} method of observation is required to measure transient, non-equilibrium intermediate states during the thermal transformation.

To monitor the dynamic change of coal with the temperature, an \textit{in situ} method must be used\textsuperscript{26}. Many thermal analysis techniques have been used for the \textit{in situ} study of coals. Some of the techniques are based on macroscopic thermodynamic properties such as heat flow (differential scanning calorimetry and differential thermal analysis), mass (thermogravimetric analysis) and dimension (thermomechanical analysis). Other techniques include analysis of evolved products using evolved gas analysis (EGA), combined gas chromatography-mass spectrometry (GTMS), and emission and adsorption Fourier transformation infrared spectroscopy (FTIR).

Of the various analytical methods available, NMR spectroscopy has proved to be of special importance in coal research\textsuperscript{27,28}. It provides both structural and dynamic information on coal at the molecular level. \textit{In situ} high temperature \textsuperscript{1}H NMR techniques were used to study thermal transformation of coals by Sanada et al.\textsuperscript{25}, and by Barton and coworkers\textsuperscript{26}. Proton density and \textsuperscript{1}H NMR line width were monitored at temperatures between 200 °C and 450 °C in their studies. The change of line width with temperature was attributed to the thermoplastic properties of coals, and was used to correlate other coal properties such as maximum vitrinite reflectance and Hardgrove grindability index (HGI). All these studies were carried out at low magnetic field strength (38 MHz and 20 MHz \textsuperscript{1}H Larmor frequency) using \textsuperscript{1}H wide line techniques. Thus, they could not monitor details of structural changes in coal with variation in temperature due to line-broadening caused by strong proton dipolar interactions. The proton CRAMPS (combined rotation and multiple-pulse spectroscopy) technique now provides the capability of obtaining high resolution \textsuperscript{1}H spectra of rigid solids by means of multiple-pulse averaging of proton dipolar interactions combined with averaging of chemical shift anisotropy (CSA) by magic angle spinning (MAS)\textsuperscript{29-31}. \textit{In situ} high temperature \textsuperscript{1}H CRAMPS techniques, combined with various time-domain experiments, should provide detailed structural and dynamic information on the thermal transformation of coal. This is demonstrated in this work, which is the first systematic \textit{in situ} high-temperature \textsuperscript{1}H CRAMPS study of coal.

There are both technical and scientific reasons for focusing on the temperature range of 25 °C - 250 °C for coal study. On the technical side, this temperature range is readily accessible to us with a commercial (Chemagnetics) \textsuperscript{1}H CRAMPS variable temperature (VT) probe (-100 °C to 250 °C) already in our laboratory. A CRAMPS probe capable of working at a temperature higher than 250 °C is not commercially available, and has not been demonstrated previously. In terms of coal science, an understanding of coal over this temperature range is also important for us to refine or modify the current structural model of coal. In this temperature range, structural changes in coals will be mainly
caused by changes in secondary (Van der Waals) interactions, as the primary (covalent) interactions are largely unchanged at temperatures below 300 °C. Thermal activation below 250 °C should dramatically change the properties of the molecular component of coal, but leave the three-dimensional macromolecular framework essentially unchanged.

In this work, we examined the experimental results of in situ variable temperature 

\[ ^{1}H \] CRAMPS studies on three types of Argonne premium coals at temperatures between 25 °C and 230 °C. The three Argonne Premium coals used in this work are: Illinois #6 (premium coal 301) and Utah Blind Canyon (premium coal 601) coals which are both high volatile bituminous (HVB) coals, and Pocahontas coal (premium coal 501) which belongs to the low volatile bituminous (LVB) coal category\(^{33,34}\). Various time-domain experiments based on 

\[ ^{1}H \] CRAMPS detection were used to probe the detailed structural and dynamic changes of coal in this temperature range.

To reduce the effect of residual water on the 

\[ ^{1}H \] CRAMPS spectra of coals, the coal samples were evacuated to about 10\(^{3} \) Torr for approximately 24 hours at room temperature, and stored in a glove box under a N\(_{2}\) atmosphere. Prior to a 

\[ ^{1}H \] CRAMPS experiment, the coal sample was packed in a home-made Pyrex glass spinner designed for the Chemagnetics 5 - mm Pencil type MAS module. The glass spinner is made from a thick-wall Pyrex NMR tube (Wilmad, 502pp). As shown in Figure 1, the glass tube is sealed in the middle with a torch, while both ends of the glass tube are still open. Such a glass spinner is specifically designed for air-sensitive samples and/or samples that need to be sealed so that their volatile components are kept in the NMR tube for analysis. The open end of the spinner on the sample-loading side can be easily sealed with a Teflon rod that makes a snug fit in the sample tube. If an absolutely air-tight seal is required, a glass rod with a diameter slightly smaller than the internal diameter of the spinner can be inserted into the spinner to confine a sample to its position; the spinner can then be sealed either with Epoxy or a torch. Epoxy is much easier to use, and its use makes it easier to get a symmetrical seal for magic-angle spinning.

\[ ^{1}H \] CRAMPS Experiments Based on BR-24. All 

\[ ^{1}H \] NMR experiments were performed on a severely modified NT-200 NMR instrument operating at a proton NMR resonance frequency of 187 MHz\(^{35}\). Modification and redesign on both hardware and
software have been made in this work to enhance the performance and stability of the spectrometer. The BR-24 pulse sequence was used in most of the \(^1\)H CRAMPS experiments\textsuperscript{36}, the use of other multiple-pulse sequence will be specifically indicated where appropriate. For experiments based on BR-24 detection, a 108 \(\mu\)s cycle time and a 90° pulse width of 1.2-1.3 \(\mu\)s were used. The number of BR-24 cycles used in the experiments was between 128 and 512, depending on the required resolution of the CRAMPS spectra. The recycle delays were 3-10 seconds. The sample spinning speeds were between 1.4 kHz and 2.0 kHz.

For measuring rotating-frame spin-lattice relaxation based on \(^1\)H CRAMPS detection, a home-built 8-level RF amplitude control unit was used to switch the RF amplitudes between the spin-lock period and the CRAMPS detection period during the experiment. The field strength of the spin-lock field was measured from the 90° pulse width in a multiple pulse tune-up experiment. We used two spin-lock field strengths of 93 kHz and 46 kHz in this work.

In CRAMPS experiments, the probe, transmitter amplifiers, and the matching network between the amplifier and probe are all carefully tuned for best performance. However, the impedances of electronic components in a probe will change with a change in the temperature in a VT experiment. Maintaining the best tuning condition for CRAMPS is critical for VT CRAMPS experiments. In our experience, even just a change of a sample in the probe at the same temperature could also result in significant impedance change in the probe, which may cause the CRAMPS performance to deteriorate. We used a RF sweeper to check and retune the impedance of the probe each time we changed a sample or sample temperature. This method is convenient and works very well.

\(^1\)H CRAMPS Experiments Based on the CMG-48. CMG-48 is one of the most efficient pulse sequences for time-suspension experiments\textsuperscript{37,38}. In a time-suspension experiment, both homogeneous and inhomogeneous broadening are refocused. The time evolution of a spin system in a time-suspension experiment should ideally be suspended, if the pulse sequence is perfect and there is no random modulation of the system. Such experiments have been mainly used for solid-state NMR imaging of nuclei with strong homonuclear dipolar couplings (e.g. \(^1\)H, \(^19\)F)\textsuperscript{37,38}. In this work, we have, for the first time, exploited the potential of CMG-48 in applications other than imaging. In particular, we used CMG-48 to estimate line broadening combinations in a CRAMPS experiment. We also used this pulse sequence in VT experiments to investigate line-broadening contributed from random motion, or incoherent sources.

A 90° pulse width of 1.3 \(\mu\)s and a cycle time of 216 \(\mu\)s were used for CMG-48. As the NMR signal from a CMG-48 experiment will be close to the RF carrier frequency, quadrature detection is preferred. As we had only a single-channel phase detector for the \(^1\)H NMR signal, we designed and implemented a pseudo quadrature detection scheme to acquire the quadrature data set for the CMG-48 experiment. In this scheme, the preparation pulses of CMG-48 multiple pulse cycles went through a CYCLOPS phase
cycling, just as in a normal quadrature detection experiment. The data acquired with the phases of the preparation pulses in quadrature are stored and accumulated in different locations of computer memory. The acquired time domain data are the same as obtained using a normal quadrature detection method, except that there is no S/N gain of $\sqrt{2}$ for this detection scheme.

Another hardware requirement of CMG-48 experiment is the use of RF phases other than integer multiples of 90°. A small angle phase shift at every half cycle of all the RF pulses of the CMG-48 sequence introduces a error term for “second averaging” of high order residual terms of the average Hamiltonian. We used a PTS-300 frequency synthesizer equipped with a digital phase shifter to realize a 45° phase shifting of all the RF pulses in every half cycle of the CMG-48 sequence. The relative RF phases of pulses in CMG-48 are still controlled by the home-built transmitter phase shifter for CRAMPS experiments. The digital phase shifting was performed on the local oscillator (LO) of the $^1$H transmitter (167 MHz); the relative phases of RF pulses were set through the intermediate frequency (IF) section of the transmitter (20 MHz). This setup is very flexible. The basic phase of a group of RF pulses can be changed easily relative to the basic phase of another group of pulses without affecting the relative phases of pulses within each group. As the LO frequency of the transmitter was the same as the LO frequency of the new homemade receiver phase shifter, such setup maintained the relative phase between the receiver and the preparation pulses of CMG-48, even though the phase of the LO signal changed every half cycle of the CMG-48 sequence. To further simplify the pulse programming, the AdNic Box was used as a slave of the spectrometer pulse programmer, to control phase shifting of the PTS-300 synthesizer. The phase control codes for the PTS-300 synthesizer were stored in the EPROM of the AdNic Box.

**Temperature Calibration.** A Chemagnetics variable-temperature (VT) CRAMPS probe was used in this work. Variable temperature is achieved with an external heater in which the VT gas is heated to a certain temperature prior to being delivered to the center of the MAS spinner. A platinum resistance temperature device (RTD) is located several centimeters upstream from the sample. The RTD is used to measure the temperature of the VT gas prior to contact with the MAS spinner and provides a feedback for a temperature controller. The fluctuation of the temperature of the VT gas is within ±0.5 °C of the setting of the temperature controller.

In the VT CRAMPS probe, the drive and bearing gases for magic-angle sample spinning are always at room temperature; the variable-temperature gas used to heat or cool the sample is essentially confined in the housing of the MAS spinning module of the probe. This design avoids spinning problems usually encountered when using a VT gas for drive and bearing purposes. It also minimizes electronic tuning changes of the probe circuit with the temperature variation. A room-temperature purge gas is also used in the probe to keep all the probe parts except the inside of the spinning module at room temperature. However, the room-temperature drive and bearing gases can enter into the sample chamber of the spinning module, and may change the temperature of the VT gas.
around the sample to a certain extent. This effect will certainly depend on the pressures (or flow rates) of the drive and bearing gases relative to the VT gas.

As it is impossible for a normal temperature sensor to have a direct thermal contact with a sample under magic-angle spinning, the measurement of the sample temperature is nontrivial. Various gas streams used in a MAS probe for sample rotation and temperature regulation, as just discussed, make the temperature measurement even more complicated. It would be better to use some NMR parameter(s) of a sample for temperature calibration. Chemical shifts of many compounds are very sensitive to temperature and have been used for calibration of the sample temperature in NMR experiments. One of the most famous examples of chemical shift thermometry, using the $^1$H NMR spectra of methanol and ethylene glycol, was discovered by Van Geet in 1968 and 1970. The peak separation between the aliphatic and hydroxyl protons in both methanol and ethylene glycol were calibrated between $-95 \degree C$ and $145 \degree C$ at 60 MHz by Van Geet. More recently, Becker et al. calibrated these compounds at 220 MHz, and concluded that the Van Geet equation could be scaled to higher fields without significant increase in error. In the work discussed in this thesis, ethylene glycol was used to calibrate the temperature between $25 \degree C$ and $150 \degree C$. We used a more recent calibration equation obtained by Ammann et al. The chemical shift difference $\Delta \delta$ (ppm) between the aliphatic protons and hydroxyl protons can be related to the absolute temperature ($T$) according to the following empirical equation:

$$T(K) = 466.5 - 102.00 \Delta \delta, \quad 273K \leq T \leq 416K.$$  \hspace{1cm} (1)

For temperature calibration between $150 \degree C$ and $250 \degree C$, we used the melting points (M.P.) of several organic compounds, including hexamethylbenzene (M.P. 168 $\degree C$), 4-ethoxylbenzoic acid (M.P. 198 $\degree C$) and 4-hydroxybenzoic acid (M.P. 214 $\degree C$).

A typical temperature calibration curve is shown in Figure 2. The calibration curve was obtained under a VT gas pressure of 10 psi, a driving gas pressure of 3 psi, a bearing gas pressure of 6 psi, and a purge gas pressure of 5 psi. The sample temperature, measured by the two methods described above, and the gas temperature readout from the RTD are correlated by a good linear relation. The temperature difference between the sample and the RTD readout also increases linearly with the temperature. Under this
calibration condition, the temperature differences were 7 °C and 20 °C at sample temperatures of 100 °C and 200 °C, respectively. Considering the various factors that are related to the temperature calibration, we estimate the errors of the sample temperatures measured in this work to be within ± 2 °C.

**Line Broadening Mechanisms of ′H CRAMPS Spectra of Coal.** Figure 3 shows ′H CRAMPS spectra of three Argonne premium coals at room temperature. One general characteristic of these spectra is that they each consists of two broad contributions. The band that is centered at about 1-3 ppm is associated with protons attached to aliphatic carbons, and the band centered around 6-8 ppm is due to protons attached to aromatic carbons. The two bands can be separated by a computer deconvolution program developed by the author, as shown in Figure 3. From the deconvolution, it is possible to obtain quantitative information on the populations of aliphatic and aromatic protons. As the two bands are broad, the accuracy of quantitation depends very critically on the quality of ′H CRAMPS spectra, especially the flatness of the baseline and the absence of rotor line interferences.

To avoid baseline distortions and “pedestals”\(^{46}\), well-calibrated composite preparation pulses before the multiple pulse cycles were used in this work so that the proton magnetization spin-locked along the effective field of average Hamiltonian is minimized. The receiver phase was also optimized to minimize “pedestals”.

The apparent resolution of ′H CRAMPS spectra of typical coals is much lower than the resolution of typical rigid crystalline solids. The main line broadening mechanism is presumably due to anisotropic bulk susceptibility effects and the dispersion of isotropic chemical shifts due to the complex chemical structures of coal. We demonstrate this point experimentally with a so-called “time-suspension” experiment and a two-dimensional spin-exchange experiment.

In a time-suspension experiment, both homogeneous and inhomogeneous broadening are refocused, and the line-width obtained would ideally be contributed only from random motion, or incoherent sources. CMG-48 is one of the most efficient time-suspension pulse sequences available\(^{37,38}\). According to an analysis based on

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**Figure 3** ′H CRAMPS spectra of premium coal (a) 301, (d) 501, (e) and 601 obtained at 25 °C. The corresponding spectral deconvolutions are shown in (b), (d) and (f). The BR-24 pulse sequence was used with a cycle time of 108 μs and a 90° pulse width of 1.2 - 1.3 μs. Each spectrum was acquired with 200 scans and a recycle delay of 3 s. The MAS rates were between 1.5 and 1.8 kHz.
the average Hamiltonian theory, CMG-48 can eliminate the homonuclear dipolar coupling to the second order, just as with BR-24. In addition, the chemical shift effects are also eliminated to the second order by CMG-48. With CMG-48, the NMR line broadening effects of dipolar coupling and chemical shifts are minimized so that the $^1H$ NMR line shape of a solid is transformed into a single narrow line. In addition to the contribution from random motion, the line-width obtained from CMG-48 is also dependent on the higher order residual dipolar coupling, residual chemical shifts and their cross terms. As CMG-48 and BR-24 are roughly equivalent in their ability to average dipolar coupling, the line width difference between the two pulse sequences will come mainly from coherent inhomogeneous interactions, including anisotropic bulk susceptibility and isotropic chemical shift dispersion. For a rigid solid such as monoethyl fumarate, the full line-width at half height (FWHH) from CMG-48 is only 7 Hz, while the FWHH of the ethylenic protons in a BR-24 spectrum is about 42 Hz. In Figure 4 we show a CMG-48 spectrum of Argonne Premium coal 601, along with its BR-24 spectrum. The line-width from CMG-48 is clearly much smaller than that from the BR-24 spectrum. The FWHHs of aliphatic and aromatic protons in the BR-24 spectrum are 220 Hz and 530 Hz, respectively, based on peak deconvolution. The FWHH from CMG-48 is only 30 Hz. This result demonstrates that the line-widths of BR-24 spectra of coal are mainly contributed from inhomogeneous broadening. This also implies that higher magnetic field will not be a big help in improving CRAMPS resolution.

The two-dimensional spin-exchange experiment provides another means for addressing the contributions of homogeneous and inhomogeneous line broadening mechanisms. If a line is broaden by an inhomogeneous source, a narrow portion of the line can be selectively inverted or saturated in the preparation period of a 2-D exchange experiment. If one keeps the mixing period short, so that no substantial spin-exchanges occur among spins of different chemical shifts during this period, then the narrow portion of the line that is inverted would be detected at the same frequency as encoded during the evolution period. In a 2-D contour plot of the doubly Fourier transformed spin-exchange data, a broad line will show up as a narrow ridge along the diagonal, if inhomogeneous broadening is dominant. The 2-D spin-exchange experiment is in this case actually used as a kind of chemical shift self correlation experiment. Such experiment was successfully
used to analyze the line broadening mechanisms of solid-state NMR spectra of rare spins (e.g., $^{13}$C$^{47,48}$). For abundant spins such as protons, multiple-pulses must be used in both preparation period and detection period in order to get high resolution. As proton spin diffusion is very efficient in rigid solids, the evolution period should be kept very short to avoid complications from spin diffusions among spins with very close chemical shifts.

The $^1$H 2-D spin exchange and/or diffusion experiment based on MREV-8 was used previously by Caravatti et al. to study miscibility in polymer blends$^{49}$. We used a $^1$H 2-D spin exchange pulse sequence based on BR-24. The main difference of our pulse sequences from that based on MREV-8$^{49}$ is the use of preparation pulses and composite pulses before and after multiple-pulse cycles. The preparation pulses and composite pulses are used to maximize the detected signal and minimize the distortions caused by magnetization spin-locked along the effective field of a multiple-pulse sequence. One thing that may be worth mentioning is that the composite pulses used after the evolution period are used to select one component of the magnetization for rotation back to the z direction. One may visualize the function of the composite pulses in two steps. The first step is to convert the magnetization processing along the effective field of a multiple-pulse sequence back to xy plane; the second step is to flip the x or y component of the magnetization to z direction, just as in a standard 2-D exchange experiment. As the sequence here is used to estimate the line broadening effects of BR-24, any extra deterioration of resolution in a 2-D experiment should be avoided. This means that pure absorption-mode 2-D spectra are desirable. For the pulse sequence with single channel detection, pure 2-D absorption spectra can be obtained easily by placing the carrier frequency of the proton transmitter on one side of the whole spectral region, and using proper data processing procedures. For the quadrature detection scheme, the time proportional phase increment (TPPI) method can be used for the preparation pulse to obtain pure 2-D exchange spectra$^{30}$.

As an example, a contour plot of 2-D exchange spectrum of Angonne Premium coal 601 is shown in Figure 5. The spectrum was obtained at 25 $^\circ$C with the pulse sequence described above. The elliptical shape of the peak along the diagonal proved that the line widths observed in $^1$H CRAMPS spectra of coal are largely due to inhomogeneous broadening. Figures 5b and 5c are slices cut along the second dimension. Comparing the slices with the BR-24 spectrum shown in Figure 5a, the line widths of both aliphatic and aromatic proton peaks in the slices are much narrower than that in the BR-24 spectrum. The FWHHs of aliphatic and aromatic proton peaks in the slices are only 110 Hz and 160 Hz, respectively.

Both the time suspension experiment and the 2-D spin exchange/diffusion experiment proved that the line widths of $^1$H CRAMPS spectra of coal are mainly due to inhomogeneous broadening. Such inhomogeneous broadening includes anisotropic bulk susceptibility effects due to the extremely heterogeneous nature of coal samples from the point of view of magnetic susceptibility, and dispersion of isotropic chemical shifts due to the very complex chemical structure of coal. It is difficult to separate these two contributions experimentally. As the $^1$H CRAMPS spectra of coal spread over a very
broad range of resonance frequencies that are much larger than the usual chemical shift range of protons, bulk susceptibility effects may be a larger contributor to the line width than the isotropic chemical shift dispersion.

Figure 5 2-D spin exchange/diffusion results obtained on Argonne Premium coal 601 at 25 °C. The pulse sequence used a 90° pulse width of 1.3 μs, and a mixing time of 5 μs. The original data consisted of 64 256-point BR-24 spectra, each obtained with 100 acquisitions. The recycle delay was 3 s. The increment of t1 was one BR-24 cycle, or 108 μs. The contour plot of the pure absorption 2-D spectrum is shown in (d). The (c) and (d) are slices cut along ω2. (a) is the BR-24 spectrum of the coal sample.

Variable Temperature ¹H CRAMPS Experiments on Coal. We carried out ¹H CRAMPS experiments on Argonne premium coals in situ at temperatures from 25 °C to 230 °C. As an example of the variable temperature ¹H CRAMPS spectra of the three
Argonne premium coals 301, 501 and 601, the spectra of coal 301 are shown in Figure 6. Such spectra show that there are no dramatic changes over the 25 - 230 °C temperature range, certainly no expected line narrowing at higher temperature.

From previous studies of this group, dramatic CRAMPS line narrowing can often be achieved by pyridine saturation of coals$^{51-53}$; such line narrowing was not well understood. It was proposed to be mainly due to an enhanced mobility of a substantial number of structural moieties in coal. The enhanced motion will partially average different isotropic chemical shifts that would be "locked in" an untreated coal. Based on theses results, one might have expected similar line narrowing at high temperature. Apparently, this is not the case.

The relationship between the line width of a CRAMPS spectrum and molecular motion is not simple in terms of the efficiency of coherent averaging of dipolar interactions. It was well known that molecular motion with a correlation time close to the cycle time of a multiple pulse sequence will interfere with the coherent averaging of the dipolar interactions$^{54-56}$. Such interference may lead to severe line broadening of a CRAMPS spectrum. The CRAMPS peak will start to get broad as the correlation time of random motion approaches the cycle time of a multiple pulse sequence. The line will get very broad when the correlation time matches the multiple pulse cycle time, and gradually get narrower as the correlation time is made much shorter than the pulse cycle time and the inverse of the strength of static dipolar interactions. In the limiting line-narrowing regime, random averaging due to motion dominates completely over coherent averaging. In the regime in which line narrowing due to random isotropic motion is dominant, the line width can be estimated from the equation, $1/T_2 \approx 3 \Delta^2 \tau_c$, where $\Delta$ is the line width due to static dipolar interactions and $\tau_c$ is the correlation time of the random motion$^{54}$. A typical un-averaged $^1$H NMR line width of coal is on the order of 35 kHz at room temperature. The line width obtained on coal from CMG-48 in this work is about 30 Hz.

Figure 6 $^1$H CRAMPS spectra of premium coal 301 at the temperatures indicated. The BR-24 pulse sequence with a 90° pulse width of 1.2 µs and a cycle time of 108 µs were used to acquire 256 data points, sampled once per cycle. The number of scans was 100. The recycle delays were 5 s. The MAS rates were between 1.6 and 1.8 kHz.
Based on the above equation, random motion with a correlation time on the order of 0.01 μs is needed to get the $^1$H NMR line width of coal from 35 kHz down to the order of 30 Hz. The above equation used here to estimate the correlation time is based on the assumption of isotropic random motion. In relatively rigid solids such as coal, isotropic random motion is not common; most of the random motion that occurs is expected to be anisotropic in nature. This means that the line-narrowing efficiency from random motion could be much lower than that estimated from the above equation.

Random motion in coal could also interfere with the coherent averaging of chemical shift anisotropy by MAS in a CRAMPS experiment. The relationship between the line width and the random motion in this case is qualitatively similar to that for dipolar interactions. However, the time scale is different. The interference will be the most severe when the correlation time matches the inverse of the MAS speed, which was between 0.5 ms and 1 ms in this work.

In summary, at least three averaging processes need to be taken into consideration when one analyzes the CRAMPS line width dependence on random motion. The isotropic chemical shift dispersion in coal may be partially averaged by random motion, e.g., averaging conformational differences. Random motion with a correlation time around 10 to 100 μs could interfere severely with the coherent averaging of dipolar interactions by BR-24. The coherent averaging of chemical shift anisotropy by MAS could be destroyed by random motion with a correlation time on the order of 1 ms.

As seen in the example shown in Figure 6, the line widths of $^1$H CRAMPS spectra of the three coal samples tend to get larger at higher temperature. This result suggests that there is interference of random molecular motion with the coherent averaging of dipolar interactions or/and chemical shift anisotropy at high temperatures. This implies that the fraction of protons experiencing random molecular motion with a correlation time on the order of 10 - 1000 μs is increased as the temperature is increased. Clearly, the fraction of protons undergoing random motion with a correlation time on the order of 0.01 μs or less is not significant even at temperatures up to 230 °C.

The relatively slow motion that is promoted at higher temperatures can also be detected via time-suspension experiments on coal. The CMG-48 spectra of Argonne premium coal 601 obtained at 25 °C, 120 °C and 180 °C are shown in Figure 7. The FWHH obtained at 25 °C is only 30 Hz. It is increased to 60 Hz and 68 Hz at 120 °C and 180 °C, respectively. The line width in a CMG-48 spectrum is mainly due to irreversible processes such as spin lattice relaxation and random motions. Although the theoretical treatment of relaxation under multiple pulse irradiation is very complicated, the line width of CMG-48 should be determined by $T_{1y}$, a decay time constant of magnetization in the toggling frame of the multiple pulses. The $T_{1y}$ value can be estimated from the value of $\Delta v_{\text{FWHH}}$ (FWHH) as $1/(\pi \Delta v_{\text{FWHH}})$ for a Lorentzian line shape, the shape that was observed for all three CMG-48 spectra shown in Figure 7. The $^1$H $T_{1y}$ of premium coal 601 at 25 °C, 120 °C and 180 °C can then be estimated as 11 ms, 5.3 ms and 4.7 ms, respectively. According to the theoretical analysis by Vega et al. and by Dybowski et al., $T_{1y}$ should
be close to the value of $T_{1p}$ in a spin-lock field of $(\gamma T)^{-1}$, where $\tau$ is the length of the short window in the CMG-48 sequence. As $\tau$ was set at 3.0 $\mu$s in this work, $(\gamma T)^{-1}$ can be estimated as 12.5 G, or 53 kHz. This suggests that the line broadening at high temperature is a result of random motion with a correlation time on the order of 18 $\mu$s, estimated from $(\gamma T)^{-1}$ of 53 kHz.

From the line width changes of $^1$H CRAMPS spectra of coal at temperature between 25 °C and 230 °C, we can conclude that slow random motions with correlation times ranging from 10 $\mu$s to 1 ms are promoted in coal at the higher temperatures. However, it is very difficult to get much quantitative information on the molecular dynamics from just these experiments.

To examine explicitly the dependence of molecular motion on the temperature, we carried out various time-domain experiments based on CRAMPS detection at high temperature. The three types of time-domain experiments employed in this study were: the $^1$H-$^1$H dipolar-dephasing experiment, measurement of the $^1$H rotating-frame spin-lattice relaxation time ($T_{1p}$) and $^1$H Zeeman spin-lattice relaxation time ($T_1$, inversion-recovery) measurement. As CRAMPS detection is used in all the time-domain experiments, we can obtain dynamic information on different chemical structures in coal. Appropriate preparation pulses and/or composite pulse were used prior to the multiple-pulse detection cycles to avoid the “pedestal” caused by magnetization spin-locked along the direction of the effective field of the average Hamiltonian of BR-24.

**Variable Temperature Dipolar-Dephasing Experiments.** The $^1$H-$^1$H dipolar-dephasing experiment is very useful for exploring structural-dynamical details of coals. In this experiment, a dephasing period (typically several $\mu$s to ms) in inserted before the multiple pulse sequence. To minimize dephasing effects due to inhomogeneous interactions such as isotropic chemical shifts, a $\pi$ pulse in inserted into the middle of the dephasing period. During this dephasing period, the magnetization of those protons experiencing strong dipolar coupling become dephased and attenuated; the signals of such protons are correspondingly attenuated in the resulting CRAMPS spectrum. Signals from protons that do not participate in strong dipolar couplings are not strongly attenuated.
during the dephasing period and are relatively more prominent in the observed spectrum. Rapid motion of molecules or portions of molecules can reduce the effects of dipolar interactions and therefore lead to the persistence of some signals in a dipolar-dephasing experiment.

To understand better the dipolar dephasing behavior, distinction between coherent and incoherent processes should be clearly made. The secular part of the spin Hamiltonian is responsible for the coherent evolution of spin systems of a rigid solid. In principle, the coherent evolution can be reversed or refocused by pulse sequences or rotations. An incoherent process, usually called relaxation, relies on both secular and nonsecular Hamiltonians. The random modulation of local fields in an incoherent process makes the evolution of the spin system irreversible.

Dipolar dephasing is a coherent process driven by the secular part of homonuclear dipolar Hamiltonians, $H_D$. For a pair of spin-$\frac{1}{2}$ nuclei, the evolution of magnetization in the $xy$ plane ($I_{1x}$ and $I_{2x}$) under the dipolar interaction can be easily derived as,

\[ e^{-iH_D t}(I_{1x} + I_{2x})e^{iH_D t} \rightarrow (I_{1x} + I_{2x}) \cos \left( \frac{3}{2} \omega_D t \right) + 2(I_{1y}I_{2x} + I_{1x}I_{2y}) \sin \left( \frac{3}{2} \omega_D t \right) \]

where \[ H_D = \omega_D (3I_{1z}I_{2z} - \vec{I_1} \cdot \vec{I_2}) \]

and \[ \omega_D = -\frac{\mu_0}{4\pi} \gamma^2 \hbar \frac{1}{2} \frac{3\cos^2 \theta - 1}{r^3} \] (2)

It can be easily seen that such a dipolar dephasing process produces an oscillatory behavior for a pair of spins. In general, similar behavior can usually be seen in a coherent process in small systems with uniform couplings. However, in a complex system, such oscillations are washed out by destructive superposition of many coherent oscillations of various periods, or couplings due to many-body interactions. This produces various dephasing behaviors with time. Gaussian decay is usually seen for dipolar dephasing of strongly coupled protons; Lorentzian (or exponential) decay is common for weaker dipolar interactions.

Although the pulse sequence used for measuring the dipolar dephasing time constant is similar to the one for measuring the spin-spin relaxation time ($T_2$), the real irreversible spin-spin relaxation is usually difficult to detect due to the much faster coherent dipolar dephasing process.

As seen above, high-temperature (up to 230 °C) $^1$H CRAMPS experiments did not result in a dramatic increase in $^1$H CRAMPS resolution for coal. The results are not what we had expected on the basis of the previous studies in which dramatic line narrowing was observed when coal was saturated with pyridine. To examine explicitly the dependence of molecular motion on the temperature, we carried out proton dipolar dephasing experiments at temperatures of 25°C, 120°C and 180°C. As an example to illustrate the variable-temperature dipolar-dephasing spectra obtained on the three
Argonne premium coals, Figure 8 show results for premium coal 301. We can see very clearly from such results that the dephasing rates were reduced significantly for all of the three coals when the sample temperatures were increased. This means, as originally anticipated, that thermal treatment indeed promotes internal motion in coal. The increased mobility of molecules in coals at high temperature reduces the effective dipolar coupling, thus prolonging the dephasing time constants. However, the promoted motion does not lead to CRAMPS line narrowing. This suggests that the thermal treatment may have an effect on the internal molecular motion of coal that is far different from that produced by solvent saturation.

Figure 8 Stack plot of 	extsuperscript{1}H CRAMPS spectra of premium coal 301 obtained in dipolar-dephasing experiments performed at (a) 25 °C, (b) 120 °C, and (c) 180 °C. A 90° pulse width of 1.25 μs and a cycle time of 108 μs were used to obtain the BR-24 spectra with 256 data points. The number of scans was 400. The recycle delay was 3 s. The MAS speed was 1.6 kHz.

To get further quantitative results on dipolar-dephasing dynamics of coals at high temperature, we developed C programs that can automatically or/and interactively deconvolute NMR spectra, and fit the deconvoluted peak intensities to various dipolar dephasing models.

The 	extsuperscript{1}H CRAMPS spectrum of a coal at each dipolar dephasing time was deconvoluted into two peaks using the peak deconvolution computer program. One of the peak corresponds to aliphatic protons (chemical shift 1 - 2 ppm); another corresponds to aromatic proton (chemical shift ~ 6 ppm). Typical spectral deconvolutions of 	extsuperscript{1}H CRAMPS spectra of the three coals were shown in Figure 3. The dipolar dephasing curve can be simulated by a sum of two Gaussian decays, denoted fast and slow, according to the following equation:
\[ M(t) = M_f \exp\left[\frac{t^2}{2T_d^2}\right] + M_s \exp\left[\frac{t^2}{2T_s^2}\right] \]  

As an example of the experimental dipolar-dephasing curves of the three Argonne premium coals at each of three temperatures (25 °C, 120 °C, 180 °C), Figure 9 shows results for premium coal 501 at 120 °C. Such figures also show simulated curves corresponding to the best fit to equation (3).

The dipolar dephasing parameters obtained from the model described above are summarized in Tables 1, 2 and 3 for the three coal samples, Illinois #6 (premium coal 301), Pocahontas #3 (premium coal 501), and Blind Canyon (premium coal 601), respectively.

In most cases for both aliphatic and aromatic protons, the dipolar dephasing can be described by a fast-decay Gaussian component with a time constant around 10 μs, and a slow-decay Gaussian component with a time constant of 40-60 μs. The fast decay component corresponds to more rigid protons, and the slow decay component corresponds to more mobile protons, for which the mobility partially averages proton-proton dipolar interactions. The fact that the two components can be distinguished from each other implies that proton spin diffusion and/or spin exchange between the rigid and mobile domains of coal are not fast compared with the experimental time scale (10 - 100 μs) of the dephasing periods.

As the temperature increases, the fraction of the fast-decay component decreases, and the fraction of slow decay component increases. This means that the promotion of molecular mobility in coal at higher temperature comes from the fact that more motion-restricted molecules are promoted to more mobile states. This suggests that the more rigid molecules in coal are thermally activated at higher temperature to overcome the energy barriers that restrict their motions.

Although the dephasing time-constants, \( T_{dd} = T_s \) (40 - 60 μs) of slow Gaussian components are much larger than those (\( T_{dd} = T_f \)) of fast-decay components, the slow-decay components are still pretty rigid compared with some “soft” solids such as adamantane. The dipolar dephasing time constant \( T_{dd} \) provides a direct measurement of the \(^1\)H NMR line width of coal without multiple pulse decoupling. The correlation time \( \tau_c \) of the random reorientational motion responsible for the reduced line-width can be then estimated. For such random motion in a fluid containing many equivalent dipolar coupled spins, the reduced line width can be quantitatively analyzed based on the spectral density function of random motion under MAS. In the regime where the line is substantially narrowed from its rigid lattice value \( \Delta \), the dependence of \( 1/T_{dd} \) on the correlation time of random motion \( \tau_c \) and magic angle spinning speed \( \omega \), can be expressed as 

\[ \frac{1}{T_{dd}} = \frac{2}{1 + \omega^2 \tau_c^2} + \frac{1}{1 + 4\omega^2 \tau_c^2} \]  

(4)
In the case that \( \omega \) is much smaller than \( 1/\tau_c \), the expression can be simplified as,

\[
\frac{1}{T_{dd}} = 3\Delta^2 \tau_c
\]  

(5)

Table 1  Dipolar dephasing data on Illinois #6 coal (premium coal 301).

<table>
<thead>
<tr>
<th></th>
<th>Fast Gaussian</th>
<th>Slow Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage</td>
<td>( T_f (\mu s) )</td>
</tr>
<tr>
<td>25 °C</td>
<td>Aliphatic 96%</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>Aromatic 90%</td>
<td>17</td>
</tr>
<tr>
<td>120 °C</td>
<td>Aliphatic 79%</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>Aromatic 55%</td>
<td>9.2</td>
</tr>
<tr>
<td>180 °C</td>
<td>Aliphatic 76%</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>Aromatic 52%</td>
<td>9.3</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3%.
b. Estimated standard error for \( T_f \): ±0.7 µs.
c. Estimated standard error for \( T_s \): ±4 µs.

Table 2  Dipolar dephasing data on Pocahontas #3 coal (premium coal 501).

<table>
<thead>
<tr>
<th></th>
<th>Fast Gaussian</th>
<th>Slow Gaussian</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Percentage</td>
<td>( T_f (\mu s) )</td>
</tr>
<tr>
<td>25 °C</td>
<td>Aliphatic 100%</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Aromatic 100%</td>
<td>13</td>
</tr>
<tr>
<td>120 °C</td>
<td>Aliphatic 42%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Aromatic 100%</td>
<td>20</td>
</tr>
<tr>
<td>180 °C</td>
<td>Aliphatic 33%</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Aromatic 75%</td>
<td>9.3</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3%.
b. Estimated standard error for \( T_f \): ±0.8 µs.
c. Estimated standard error for \( T_s \): ±5 µs.
Table 3  Dipolar dephasing data on Blind Canyon coal (premium coal 601).

<table>
<thead>
<tr>
<th></th>
<th>Fast Gaussian</th>
<th>Slow Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentagea</td>
<td>Tc (µs)b</td>
</tr>
<tr>
<td>25 °C</td>
<td>Aliphatic</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>100</td>
</tr>
<tr>
<td>120 °C</td>
<td>Aliphatic</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>40</td>
</tr>
<tr>
<td>180 °C</td>
<td>Aliphatic</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>34</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for Tc: ± 0.7 µs.
c. Estimated standard error for Tc: ± 4 µs.

Based on equation (5), a dipolar dephasing time constant of 40-60 µs corresponds to a random motion with a correlation time of 16 µs, assuming the line width of protons in a rigid lattice is 35 kHz. This is consistent with what we observed in terms of motional interference with line narrowing in CRAMPS. According to equation (3), the dipolar dephasing time constant Tdd is inversely proportional to the correlation time τc for isotropic random motion. The dipolar dephasing time constant is expected to increase with temperature. However, the slow-decay time constants of coal do not change much with temperature up to 180 °C. This suggests that the thermally-promoted motion responsible for slow-decay components is anisotropic in nature, even at a temperature as high as 180 °C. Such anisotropic motion can not average out the dipolar interactions completely.

For high-volatile bituminous (HVB) coals such as Illinois #6 and Blind Canyon coals, the fraction of fast-dephasing components for aliphatic protons is much larger than that for aromatic protons. For low-volatile bituminous (LVB) coals, such as Pocahontas #3 coal, the situation is reversed. The aliphatic components in HVB coals are generally much richer than in LVB coals. The dipolar dephasing results summarized in Tables 1 and 3 suggest that a large fraction (65 - 75%) of the aliphatic structures in HVB coals are either in rigid cross-linked macromolecular networks, or are smaller molecules that are trapped in very tight voids. Those structures are difficult to mobilized even at 180 °C. In contrast, 66% of aliphatic protons in the LVB coal are in a relatively mobile state at 180 °C. These results imply that most of the rigid aliphatic structures in HVB coals may be
converted to aromatic structures during the coalification conversion process from HVB coals to LVB coals.

A large fraction of the aromatic structure in HVB coals (e.g., #301 and #601), can be mobilized at 180 °C. Only 25% of the aromatic protons in a LVB coal, such as Pochahontas #3 (#501), are in a relatively mobile state at 180 °C. This is not surprising, since most of the aromatic structures in a LVB coals are in relatively large aromatic ring systems, which are very rigid and difficult to mobilize.

For aromatic protons in Pocahontas #3 coal, the dipolar dephasing curves are well fitted as a single Gaussian decay at temperatures of 25 °C and 120 °C. The single Gaussian decay time constant is increased from 10 μs to 20 μs as the temperature is increased from 24 °C to 120 °C. At 180 °C, the dephasing curve is better fitted by two Gaussians, with time constants of 9.3 μs and 52 μs. This suggests that the spin diffusion (and/or spin exchange) rates between rigid and mobile domains decrease with increasing temperature, which is consistent with increased mobility of molecules at higher temperature. At 180 °C, the spin diffusion and/or exchange rates are slow enough to make two Gaussian components clearly distinguishable. These results suggest that the aromatic protons in Pocahontas #3 coal are distributed more uniformly, compared to the protons in HVB coals, in densely packed clusters so that spin diffusion and/or exchange between rigid protons and mobile protons is very efficient.

For Pocahontas #3 coal (#501) at 120 °C, two dephasing components can be distinguished for aliphatic protons, while only one component can be detected for aromatic protons. The dephasing time constant (20 μs) of aromatic protons is significantly different from either dephasing constant (10 μs and 52 μs) of the aliphatic protons. This result suggests that the spin diffusion between aromatic and aliphatic protons is not efficient in Pocahontas #3 on the experimental time scale (10 -50 μs). This implies that the aliphatic protons and aromatic protons are not intimately close to each other. This is reasonable, considering the view that most of the aliphatic side chains of aromatic structures are stripped away in the coalification process that leads to a carbon composition of around 91% in the resulting coal.

In conclusion, the ¹H CRAMPS dipolar dephasing experiments provides some detailed information on the molecular dynamics and proton distributions in coals. To get more detailed molecular dynamics information, experiments that can probe the spin diffusion and/or spin exchange rate (such as the Goldman-Shen type and 2D spin exchange experiments) could be helpful. To completely understand the relationship between molecular dynamics and CRAMPS resolution, experiments that combine thermal treatments and solvent saturation would be especially illuminating. These experiments and results are discussed in the following portion of this report.

**Proton Spin-Lattice Relaxation Time in the Laboratory Frame.** Proton spin-lattice relaxation in coal has been investigated quite extensively with ¹H wide-line NMR techniques. Very different relaxation behaviors have been found for various coals.
Both exponential and non-exponential relaxation behaviors were observed for different coals. The presence of moisture and paramagnetic oxygen were found to decrease the relaxation time significantly\textsuperscript{61-64}. Since spin-diffusion in proton rich solids is typically much faster than spin-lattice relaxation, spin diffusion may average out $T_1$ differences of protons in different environments. Information on this kind of behavior can be useful for elucidating heterogeneity of coals. Although the non-exponential relaxation behavior was attributed to the existence of different domains in coals in previous studies\textsuperscript{60,63,65,66}, those experiments were not able to relate the heterogeneities of coals directly to their chemical structures, due to limitations in wide-line $^1$H techniques. The combination of spin-lattice relaxation technique with $^1$H CRAMPS detection should be able to provide much deeper insight into the chemical origin of the heterogeneity of coals. Therefore, we carried out the first variable temperature $^1$H spin-relaxation study on coals with $^1$H CRAMPS detection.

$^1$H NMR spin-lattice relaxation mechanisms in coals were analyzed quantitatively by Wind et al.\textsuperscript{68}. $^1$H spin-lattice relaxation is caused by fluctuating local fields that arise from time-dependent interactions between protons and neighboring spins. It was found that the spin-lattice relaxation in coals was mainly due to two relaxation mechanisms: time-dependent $^1$H-$^1$H dipolar interactions and time-dependent proton-unpaired electron dipolar interactions.

Random molecular motion in coals renders the $^1$H-$^1$H dipolar interactions time-dependent. If proton spin diffusion is fast enough to give a uniform relaxation time in a sample, the spin-lattice relaxation time ($T_1$) is given by\textsuperscript{69,70}

$$\frac{1}{T_1} = f_H A_H \left\{ \frac{\tau_c}{1 + \omega_H^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_H^2 \tau_c^2} \right\},$$

where $f_H$ is the fraction of protons subject to the molecular motions; $A_H$ is a parameter that depends on the strength of the proton-proton interactions and on the specific type motion; $\tau_c$ is the correlation time characterizing the molecular motion, and $\omega_H$ is the proton Larmor frequency. In this case, the Zeeman spin-lattice relaxation time $T_1$ is related to the spectral density of random motion around the $^1$H Larmor frequency $\omega_H$ (187 MHz in this work), and $2\omega_H$ (374 MHz). Thus, $T_1$ is useful for detecting fast motion (i.e., with small correlation time).

There are at least three sources of unpaired electrons in coals: metal ions in the mineral matter content of coal, organic radicals, and paramagnetic oxygen. A simplified model to describe the spin-lattice relaxation of coal due to time-dependent interactions between the protons and the unpaired electrons is given by\textsuperscript{68}

$$\frac{1}{T_1} = A e^{-\Delta},$$

(7)
where $r$ is the distance between the proton and an unpaired electron; and $A_e$ depends on the nature of the time dependence of the proton-electron interaction. Such a time-dependent interaction can result from molecular motion, electron spin-lattice relaxation and electron-electron flip-flops. It was found that electron spin-lattice relaxation (characterized by the time constant, $T_{1e}$) of paramagnetic oxygen was the dominant contributor to proton relaxation based on time-dependent proton-electron interactions\(^5\). And all protons in the vicinity of the paramagnetic centers relax exponentially with a uniform average relaxation rate, since the fluctuating local field from unpaired electrons are much stronger than other interactions. In other words, all protons are inside a so-called “diffusion barrier” around the unpaired electrons; thus electron-proton interactions completely dominate other interactions. In this case, the relaxation rate can be expressed as\(^5\)

$$\frac{1}{T_1} = 4 \left( \frac{h}{2\pi} \frac{h}{2\pi} \right)^2 \frac{N_e}{b} \frac{T_{1e}}{1 + \omega_n^2 T_{1e}^2},$$

where $N_e$ is the concentration of paramagnetic oxygen and $b$ is the radius of the diffusion barrier.

A quantitative assessment of the relaxation mechanism due to paramagnetic oxygen in coal requires the measurement of its electron spin properties, including electron spin-lattice relaxation time ($T_{1e}$), electron spin flip-flop rate, and concentrations. However, direct measurements of these parameters are very difficult, since the E.S.R. line of paramagnetic oxygen is too broad. Nevertheless, it was well established experimentally that paramagnetic oxygen is an effective source of relaxation. It is the dominant relaxation source even for some coal samples that are never exposed to air. Most of the previous studies on this subject tried to avoid oxygen in the sample. But it is unavoidable, especially for lower rank coals, since the paramagnetic oxygen is incorporated into coal structure during the coalification process. It is also difficult to get rid of the paramagnetic oxygen in coal non-destructively, e.g., with evacuation of coal samples at mild temperatures.

Instead of trying to avoid paramagnetic oxygen, we had tried to use paramagnetic oxygen to our advantage in this work. Based on the previous work by Wind et al., the electron spin-lattice relaxation time ($T_{1e}$) is known to be explicitly independent of the rank of coal\(^6\). It is the concentration of paramagnetic oxygen that makes the $^1$H NMR relaxation time rank dependent. In the presence of oxygen, the oxygen distribution and concentration in coal will change with temperature. Such changes should be detectable from the $^1$H spin-relaxation time. As the distribution of oxygen depends on the density and the pore distribution in coal, the distribution of $^1$H NMR spin relaxation times could be used to map the pore structures in coals using paramagnetic oxygen as probe molecules. In the following portions of this report, we will demonstrate that structure heterogeneity in coals could be probed by this technique.
To introduce paramagnetic oxygen into the coal structure, the coal samples used for proton spin-lattice relaxation ($T_1$) measurement were exposed to air for about 4 months after the samples were taken out from sealed bottles and subsequently evacuated (0.01 torr) for 20 hours at 25 °C. The samples were then packed into a spinner, and evacuated very briefly to $10^2$ torr to minimize possible oxidation of samples from excess $O_2$ at high temperature. The MAS rotors containing the samples were then sealed in a glove box with epoxy resin.

Figure 10 Stack plots of $^1$H CRAMPS spectra of premium coal 601 obtained from inversion-recovery $T_1$ measurements performed at (a) 25 °C, (b) 120 °C, and (c) 180 °C. A 90° pulse width of 1.25 μs and a cycle time of 108 μs were used to obtain the BR-24 spectra with 256 data points. The number of scans was 300. The recycle delay was 3 s. The MAS speed was 1.6 kHz.

Figure 10 is presented as an example of the stack plots of $^1$H CRAMPS spectra obtained at 25 °C, 120 °C and 150 °C from inversion-recovery experiments on Argonne premium coals. The peak areas of aliphatic and aromatic protons were obtained from computer peak deconvolution using a home-written peak deconvolution program. The peak area vs. time data were then fit with a sum of individual inversion-recovery expressions as follows,

$$M(t) = \sum M_i(\infty)(1 - 2e^{-t/T_{1i}}),$$

where $T_{1i}$ is the spin-lattice relaxation time of an individual component; $t$ is the inversion-recovery time used in the experiment; and $M(t)$ is the peak area measured at inversion-recovery time $t$. Figure 11 is presented as an example (for coal 301 at 180 °C) of these data analyses, in which experimental data from the premium coals 301, 501, 601 and simulated inversion-recovery curves based on equation (9) are compared. It can be seen from such figures that the simulated curve matches very well with the experimental data.
Tables 4, 5 and 6 present the relaxation parameters obtained from a non-linear least-square fitting program using equation (7).

In general, the relaxation data fitted with equation (9) consist of two exponential decays. Several interesting features of the results will now be discussed.

At room temperature, a very small fraction (<10%) of protons in each of the three coals contribute to the large $T_1$ value (>0.8 s), except for aliphatic protons in premium coal 601. Such slow relaxation components represent protons in very dense and rigid domains that are well isolated from other protons. Paramagnetic oxygen can not easily diffuse into such structures, and $^1$H spin diffusion from fast relaxing protons can not reach these isolated protons either.

![Figure 11](image)

**Figure 11** Experimental data (open circles) from the inversion-recovery $T_1$ measurements of premium coal 301 obtained at 180 °C. The data are fitted with equation (3.9). Dashed curves represent fast and slow relaxation components; solid curves represent the sum of the two relaxation components. (a) Aliphatic protons; (b) Aromatic protons.

<table>
<thead>
<tr>
<th>Table 4 Spin-lattice relaxation times of Illinois #6 coal (301).</th>
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</thead>
<tbody>
<tr>
<td>Slow Component</td>
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<tr>
<td>Percentage$^a$</td>
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<tr>
<td>-----------------</td>
</tr>
<tr>
<td>25 °C</td>
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<td></td>
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<td>120 °C</td>
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<td></td>
</tr>
<tr>
<td>180 °C</td>
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</tbody>
</table>

- a. Estimated standard error for percentage: ±3 %.
- b. Estimated standard error for slow $T_1$: ± 0.03 s.
- c. Estimated standard error for fast $T_1$: ± 0.005 s.
Table 5  Spin-lattice relaxation times of Blind Canyon coal (601)

<table>
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<th></th>
<th>Aromatic</th>
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<td>Percentage</td>
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<td>0.35</td>
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<td>T1 (s)</td>
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<td></td>
<td>T1 (s)</td>
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<tr>
<td>Aromatic</td>
<td></td>
<td>100</td>
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</table>

a. Estimated standard error for percentage: ±4 %.
b. Estimated standard error for slow T1: ± 0.03 s.
c. Estimated standard error for fast T1: ± 0.005 s.

Table 6  Spin-lattice relaxation times of Pocahontas #3 coal (501)

<table>
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<tr>
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<th></th>
</tr>
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<td>T1 (s)</td>
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<td></td>
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<td>Aromatic</td>
<td>Percentage</td>
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<td>0.95</td>
<td>95</td>
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<td>120</td>
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<td></td>
<td>T1 (s)</td>
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<td>Aromatic</td>
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<td>180</td>
<td>Aliphatic</td>
<td>65</td>
<td>0.34</td>
<td>35</td>
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<tr>
<td></td>
<td>T1 (s)</td>
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<td></td>
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<tr>
<td>Aromatic</td>
<td>Percentage</td>
<td>64</td>
<td>0.31</td>
<td>36</td>
</tr>
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</table>

a. Estimated standard error for percentage: ±4 %.
b. Estimated standard error for slow T1: ± 0.04 s.
c. Estimated standard error for fast T1: ± 0.008 s.

At higher temperatures (120 °C and 180 °C), we also observed a slow relaxation component, but with smaller T1 values (0.34 - 0.45 s) and much larger fractions (23% - 60%). Most of these slowly relaxing protons must come from the fast relaxation components at room temperature. The apparent disappearance of the small fraction of very slow relaxation component (T1 > 0.8 s) at the higher temperatures may be due to two reasons. First, paramagnetic oxygen may penetrate into the dense and rigid structures in
coals at higher temperature. High temperature imparts some flexibility to the rigid structures and thus lowers the energy barrier for oxygen to diffuse into them, while the oxygen molecules themselves have increased their thermal energy at higher temperature. The relaxation time of protons in the dense structure can thus be reduced at high temperature as a result of increased concentration of paramagnetic oxygen. Second, a very small fraction of $T_1 > 0.8$ s protons may still exist in the very dense structure at higher temperatures, but they are difficult to observe convincingly in the experimental data because the fraction is too small to ensure a meaningful fit of the data to a three-component model.

As shown in Tables 4, 5 and 6, for each coal the fast relaxation component at room temperature is split into two components at higher temperatures. This can be explained as a result of reduced spin diffusion rates at higher temperatures. There are actually two relevant spin-diffusion processes in this case, proton-proton spin diffusion and electron-electron spin diffusion. Both processes are capable of averaging out the differences between spin-lattice relaxation times of protons that exist in a relatively uniform domain, which is defined as a domain with a relatively uniform spatial distribution of protons and paramagnetic oxygen centers. In such a domain, there are no big spatial gaps between protons and paramagnetic oxygen centers, so that spin diffusion processes can effectively spread over all protons in the domain on the relevant experimental time scale (on the order of $^1H T_1$).

Note that NMR experiments measuring dynamic processes on different time scales correspond to probing spatial structural heterogeneity on different length scales, when effective spin diffusion processes exist. For example, a domain defined by a dipolar dephasing experiment is usually much smaller than the domain defined by spin-lattice relaxation measurement.

We now return to explaining why the fast relaxation components at room temperature are split into two at higher temperatures for each coal. Due to motions promoted at high temperature, the effective dipolar interactions among protons and among unpaired electrons are reduced, thus both proton-proton and electron-electron spin diffusion rates are reduced. In addition, the desorption of paramagnetic oxygen in coal at high temperature will decrease the concentration of paramagnetic oxygen centers. This will also create spatial gaps among the paramagnetic oxygen centers and slow down electron-electron spin diffusion. The net result is that domains with two distinctly different average concentrations of paramagnetic oxygen centers can be detected and distinguished at higher temperature. The fast relaxation components correspond to domains with relatively high concentrations of paramagnetic oxygen; the slow relaxation components correspond to domains with relatively low concentrations of paramagnetic oxygen. It is relatively difficult for paramagnetic oxygen to diffuse into densely packed rigid structures in coals. The void space is also very limited in such structures. So, we propose that the slow relaxation component is due to protons in such densely packed structures.
The expected decrease in the concentration of paramagnetic oxygen in coals at higher temperature is also consistent with the observed changes of relaxation time constant ($T_1^\text{H}$) at higher temperature. At room temperature, the relaxation time of the fast relaxing component is an average of the relaxation times of all protons in that domain. If we assume that the relaxation time constant of each individual proton is still kept the same as the temperature is increased, then the only change considered is the decrease in $^1\text{H}-^1\text{H}$ spin diffusion rate, so that two relaxation time constants can be distinguished at higher temperature. In this case, one of the relaxation time constants will be shorter than the average and the other one will be longer. However, we can see from Tables 4, 5 and 6 that $T_1$ for the fast relaxation components at 180 $^\circ$C is clearly larger than the average $T_1$ at room temperature. Since electron spin-lattice relaxation times for solids are not very temperature dependent, changes in paramagnetic contributions to the proton $T_1$ with temperature should be mainly caused by changes in the concentration of paramagnetic centers, as can be seen from equation (8). The longer proton spin-lattice relaxation time at high temperature can be explained by the reduced concentration of paramagnetic oxygen.

The observed temperature dependence of $^1\text{H}$ $T_1$ in coals also suggests that paramagnetic oxygen is the main source of relaxation. If proton spin-lattice relaxation were mainly due to time-dependent $^1\text{H}-^1\text{H}$ dipolar interactions, the relaxation time would increase with temperature for relatively rigid solids like coal. According to equation (6), the spin-lattice relaxation time reaches a minimum when the correlation time $\tau_c$ is equal to the inverse of proton Larmor frequency $\omega_0$ (here, 187 MHz). For relatively rigid solids like coals, molecular motion is highly restricted even at 180 $^\circ$C, which was confirmed in the dipolar-dephasing study discussed above. The correlation time of random motion should thus be larger than $1/\omega_0$ ($\sim 5 \times 10^{-9}$ seconds), or the random motion would fall into the slow-motion regime of the $T_1$-vs.-$\tau_c$ curve. In this regime, the relaxation time would become smaller at higher temperature, which is not in agreement with the experimental results shown in Tables 4, 5 and 6. This means that time-dependent $^1\text{H}-^1\text{H}$ dipolar interactions due to molecular motion cannot be the dominant spin-lattice relaxation mechanism of coal.

The paramagnetic oxygen relaxation mechanism fits very well with the observed relaxation time dependence on temperature in coals. However, as the temperature increases, the concentration of paramagnetic oxygen in coal is expected to decrease, and the electron-proton relaxation mechanism may be no longer predominant. The $^1\text{H}-^1\text{H}$ dipolar relaxation mechanism is then expected to show its significance at a high enough temperature. For example, the relaxation time constant of the slowly-relaxing aromatic protons in premium coal 301 decreases from 0.34 s to 0.24 s when the temperature is increased from 120 $^\circ$C to 180 $^\circ$C, as shown in Table 4. The decrease of relaxation time at high temperature is probably due to time-dependent $^1\text{H}-^1\text{H}$ dipolar interactions.

The aliphatic protons in coal 601 shows some unique relaxation behaviors. Even at room temperature (25 $^\circ$C), there is large fraction (41 %) of slow relaxation component, with a relaxation time of 0.35 s. Similar behaviors are observed for premium coals 301
and 501 only at 120 °C and 180 °C. This means that there are two aliphatic domains in premium coal 601 that are very well isolated from each other, but not in coals 301 and 501. The phase separation of two aliphatic components can be very clearly seen from the \(^{1}H\) CRAMPS spectra near the null point of an inversion-recovery experiment. The aliphatic portion of the \(^{1}H\) CRAMPS spectra can be well simulated by a superposition of two peaks with the same chemical shift but different line-widths. The slow relaxation component corresponds to a much narrower peak. This is consistent with a relatively uniform and well packed structure.

Although a very large fraction (41%) of aliphatic protons in premium coal 601 undergo spin-lattice relaxation slowly at 25 °C, most of the aromatic protons (93 %) relax very fast, with a \(T_1\) of 0.068 s. This implies that the slow relaxation domain consists mainly of aliphatic structures. The experimental results clearly prove the existence of large aliphatic-rich and aromatic-rich domains in coals. This finding is consistent with the coalification process proposed by Hatcher et al.\(^{71}\). They concluded that most of the aliphatic structures in coal are due to algae or microbial residues, while the aromatics are derived mainly from lignin.

The aromatic protons in premium coal 601 also show an interesting relaxation behavior. Almost all of aromatic protons (96 %) relax fast with a \(T_1\) value that is the same as that of the fast relaxation component of aliphatic protons at 25 °C. At 120 °C and 180 °C, only one relaxation component can be observed for the aromatic protons, and the relaxation time of the aromatics is the same as that of the fast relaxation component of the aliphatic protons within experimental error. This result suggests that the aromatic protons in premium coal 601 are in the same domain as the aliphatic protons with fast relaxation. It also implies that the aromatic protons are inside a relatively open structural domain in which the concentration of paramagnetic oxygen centers is high. This is consistent with the aromatic structures in HVB coals, in which the aromatics are in relatively small aromatic systems with aliphatic substituents\(^{50}\).

In the literature, the fast spin-lattice relaxation component in coal has been tentatively assigned as a molecular phase, which is defined as the mobile (slow-decay) component identified in experiments of the dipolar-dephasing type\(^{52}\). We do not think this assignment is appropriate, since the dipolar-dephasing experiment and spin-lattice relaxation measurement deal with spin dynamics with totally different time and spatial scales. One thing that is in common in both experiments is the spin diffusion of the proton spin system, which averages out distinctly individual behaviors of protons over time and space. The relationship between the dipolar-dephasing experiment and the spin-lattice relaxation experiment is analogous to the relationship between looking at a subject with a magnifier and looking at the subject from a distance. If the sample is homogeneous, a good correspondence between the two observations may be found. However, for a heterogeneous system such as coal, a correspondence between the two experiments can not be established simply.
Spin-Lattice Relaxation Time in the Rotating Frame. The spin-lattice relaxation time in the rotating frame ($T_{1p}$) is sensitive to spectral density of domain motion with a correlation time close to the inverse of strength of spin-lock field ($\omega_1 = \gamma B_z$), which is usually from 30 kHz to 100 kHz in solid state NMR experiments. The $^1$H $T_{1p}$ value of a solid is typically on the order of 1 - 10 ms. $^1$H-$^1$H spin diffusion will average out $T_{1p}$ differences of protons that are intimately dipolar coupled to each other. So, the rotating-frame spin-lattice relaxation time measurement provides dynamical information on the $^1$H spin system on time and spatial scales that are intermediate between that of the dipolar-dephasing experiment and that of the Zeeman spin-lattice relaxation time measurement.

We review here very briefly the theoretical background related to a $^1$H $T_{1p}$ experiment. Under the spin-lock condition with continuous irradiation of the $B_z$ field along the x-axis of the rotating frame, homonuclear dipolar interactions are averaged so, the dipolar interaction is scaled by $-1/2$ from its value in the absence of the spin-lock condition. Spin diffusion still occurs under the spin-lock condition. Because $[I_x, H_{1lx}] = 0$, the initial density matrix ($\rho(0) = I_x$) along the spin-lock field will be invariant to dipolar interactions. Therefore, the magnetization spin-locked along the direction of the RF field will not dephase under dipolar interactions. The decay of the spin-locked magnetization is caused by rotating-frame spin-lattice relaxation, originating from fluctuations of local fields due to random molecular motion. The main relaxation mechanism for $^1$H $T_{1p}$ is time-dependent $^1$H-$^1$H dipolar interactions. If we assume that the random motion is a Gaussian-Markov process with the correlation time $\tau_c$, the $T_{1p}$ due to such “random isotropic modulation” of the dipolar Hamiltonian is given by

$$\left\langle \sum_{j<k} \sum_{\omega_{jk}} (3I_{jk} - \vec{I}_j \cdot \vec{I}_k) \right\rangle = -\frac{1}{2} \sum_{j<k} \sum_{\omega_{jk}} \omega_{jk} (3I_{jk} - \vec{I}_j \cdot \vec{I}_k) = -\frac{1}{2} H_x'' \tag{10}$$

where $\omega_{jk} = (\mu_0 h / 4\pi)(r^3 / r_{jk}^3)(3 \cos^2 \theta_{jk} - 1)$

So, the dipolar interaction is scaled by $-1/2$ from its value in the absence of the spin-lock condition. Spin diffusion still occurs under the spin-lock condition. Because $[I_x, H^x] = 0$, the initial density matrix ($\rho(0) = I_x$) along the spin-lock field will be invariant to dipolar interactions. Therefore, the magnetization spin-locked along the direction of the RF field will not dephase under dipolar interactions. The decay of the spin-locked magnetization is caused by rotating-frame spin-lattice relaxation, originating from fluctuations of local fields due to random molecular motion. The main relaxation mechanism for $^1$H $T_{1p}$ is time-dependent $^1$H-$^1$H dipolar interactions. If we assume that the random motion is a Gaussian-Markov process with the correlation time $\tau_c$, the $T_{1p}$ due to such “random isotropic modulation” of the dipolar Hamiltonian is given by

$$\frac{1}{T_{1p}} = M_2 \left[ \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} + \frac{5}{3} \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} + \frac{2}{3} \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \tag{11}$$

where $\omega_1 = \gamma B_1$, $\omega_0 = \gamma B_0$, and $M_2 = \frac{3}{5} \frac{\gamma^2 h^2}{r^6} I(I + 1)$

$M_2$ is the second momentum due to two spins with the gyromagnetic ratio $\gamma$, separated by the distance $r$. The maximum relaxation rate under isotropic rotation is reached for $\omega_1 \tau_c = 1/2$.

Most $^1$H $T_{1p}$ data on coals were measured indirectly from $^{13}$C CP/MAS experiments, as $T_{1p}$(H) is a very important parameter for setting up and interpreting CP/MAS experiments. The indirect measurement from $^{13}$C CP/MAS also provides resolution of aliphatic and aromatic protons in coals, which is not available in wide-line $^1$H NMR.
experiments. There are also limitations for such indirect ($^{13}$C CP/MAS) measurements of $T_{1p}(^1H)$. Only protons that are strongly dipolar coupled to carbon are detectable via indirect ($^{13}$C) detection, and the quantitation of proton signals is complicated by the cross polarization spin dynamics. Of course, the sensitivity of such indirect measurements is limited by $^{13}$C detection. The rotating-frame spin-lattice measurement based on CRAMPS detection used in this work overcomes these limitation. It provides good quantitation of $^1$H signals with both high resolution and high sensitivity.

Figure 12 shows, as an example (for coal 501 and a spin-lock field of 93 kHz), stack plots of VT $^1$H CRAMPS spectra from $T_{1p}$ measurements on Argonne premium coals 301, 501, and 601 at 25 $^\circ$C, 120 $^\circ$C and 180 $^\circ$C. Each spectrum in the stack plot was deconvoluted into two peaks, corresponding to aliphatic and aromatic protons. The dependence of peak area on spin-lock time were fitted with a sum of individual exponential decays as follows,

$$M(t) = \sum_i M_i(\infty)e^{-t/T_{1pi}}, \quad (12)$$

where $T_{1pi}$ is the spin-lattice relaxation time of individual relaxation components; $t$ is the spin-lock time; and $M(t)$ is the peak area measured at spin-lock time $t$.

![Figure 12 Stack plots of $^1$H CRAMPS spectra of premium coal 501 obtained from $^1$H $T_{1p}$ measurements performed at (a) 25 $^\circ$C, (b) 120 $^\circ$C, and (c) 180 $^\circ$C. The spin-lock field was 93 kHz. A 90° pulse width of 1.25 μs and a cycle time of 108 μs were used to obtain the BR-24 spectra with 256 data points. The number of scans was 200. The recycle delay was 3 s. The MAS speed was 1.6 kHz.](image)
Figure 13 Experimental data (open circles) from $^1$H $T_{1p}$ measurements on premium coal 301 with a spin-lock field of 46 kHz (a,b), and 93 kHz (c,d), at 180 °C. The data were fitted with equation (3.12). Dashed curves represent fast and slow relaxation components; solid curves represent the sum of the two relaxation components. (a), (c): Aliphatic protons. (b), (d): Aromatic protons.

The relaxation parameters obtained from a non-linear least-square fit of experimental data to equation (12) are presented in Tables 7-12. Figure 13 shows an example of these data analyses graphically. The simulated curves, which were calculated from the best fits between experimental data and equation (12), match very well with the experimental data.

Except for premium coal 301 at 25 °C, the relaxation data fit with equation (13) consist of two exponential decays. The fact that two relaxation components can be detected reflects the structural heterogeneity in coal that cannot not be averaged out by spin diffusion on the experimental time scale (1 - 10 ms). Note that the $^1$H-$^1$H spin diffusion is much slower under the spin-lock condition due to the scaling down of the dipolar interaction. That may be why we can clearly observe a two-component experimental decay for premium coals 501 and 601, even at room temperature.

Two spin-lock RF field strengths of 93 kHz and 46 kHz, and three temperatures (25 °C, 120 °C, 180 °C), were used for all three coals in these VT $T_{1p}$ experiments. According to equation (11), $T_{1p}$ will increase as $\omega_{1H}$ increases. However, such increases will be significant only when $\tau_c$ is close to or larger than $1/(2\omega_i)$. For fast random motion with $\tau_c < < (1/2\omega_i)$, the effect of $\omega_i$ cannot be observed.

40
Table 7  Rotating frame spin-lattice relaxation times of Illinois #6 coal (301) measured with a spin-lock field of 46 kHz.

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<th>Fast Component</th>
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<td></td>
<td>Percentage a</td>
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<td>Aromatic</td>
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a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow T₁p: ±0.8 ms.
c. Estimated standard error for fast T₁p: ±0.2 ms.

Table 8  Rotating frame spin-lattice relaxation times of Illinois #6 coal (301) measured with a spin-lock field of 93 kHz.

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a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow T₁p: ±0.8 ms.
c. Estimated standard error for fast T₁p: ±0.2 ms.
Table 9 Rotating frame spin-lattice relaxation times of Blind Canyon coal (601) measured with a spin-lock field of 46 kHz.

<table>
<thead>
<tr>
<th>Aliphatic</th>
<th>Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>120°C</td>
</tr>
<tr>
<td>Percentage</td>
<td>T\text{\textsubscript{IP}} (ms)</td>
</tr>
<tr>
<td>60</td>
<td>8.9</td>
</tr>
<tr>
<td>8.9%</td>
<td>2.7 ms</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow T\text{\textsubscript{IP}}: ±0.8 ms.
c. Estimated standard error for fast T\text{\textsubscript{IP}}: ±0.2 ms.

Table 10 Rotating frame spin-lattice relaxation times of Blind Canyon coal (601) measured with a spin-lock field of 93 kHz.

<table>
<thead>
<tr>
<th>Aliphatic</th>
<th>Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>24°C</td>
<td>120°C</td>
</tr>
<tr>
<td>Percentage</td>
<td>T\text{\textsubscript{IP}} (ms)</td>
</tr>
<tr>
<td>66</td>
<td>12</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow T\text{\textsubscript{IP}}: ±0.8 ms.
c. Estimated standard error for fast T\text{\textsubscript{IP}}: ±0.2 ms.
Table 11 Rotating frame spin-lattice relaxation times of Pocahontas #3 coal (501) measured with a spin-lock field of 46 kHz.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Slow Component</th>
<th>Fast Component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage</td>
<td>$T_{1p}$ (ms)</td>
</tr>
<tr>
<td>24°C Aliphatic</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>24°C Aromatic</td>
<td>17</td>
<td>6.5</td>
</tr>
<tr>
<td>120°C Aliphatic</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>120°C Aromatic</td>
<td>15</td>
<td>7.5</td>
</tr>
<tr>
<td>180°C Aliphatic</td>
<td>19</td>
<td>13</td>
</tr>
<tr>
<td>180°C Aromatic</td>
<td>11</td>
<td>7.6</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow $T_{1p}$: ±0.5 ms.
c. Estimated standard error for fast $T_{1p}$: ±0.1 ms.

Table 12 Rotating frame spin-lattice relaxation times of Pocahontas #3 coal (501) measured with a spin-lock field of 93 kHz.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Slow Component</th>
<th>Fast Component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage</td>
<td>$T_{1p}$ (ms)</td>
</tr>
<tr>
<td>24°C Aliphatic</td>
<td>31</td>
<td>13</td>
</tr>
<tr>
<td>24°C Aromatic</td>
<td>17</td>
<td>9.1</td>
</tr>
<tr>
<td>120°C Aliphatic</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>120°C Aromatic</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>180°C Aliphatic</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>180°C Aromatic</td>
<td>20</td>
<td>7.8</td>
</tr>
</tbody>
</table>

a. Estimated standard error for percentage: ±3 %.
b. Estimated standard error for slow $T_{1p}$: ±0.9 ms.
c. Estimated standard error for fast $T_{1p}$: ±0.2 ms.
A $T_{1p}$ increase with $\omega_1$ can be seen in the fast relaxation components of both aliphatic and aromatic protons in premium coal 501 at 25 $^\circ$C, 120 $^\circ$C and 180 $^\circ$C, as shown in Tables 11 and 12. A similar $T_{1p}$ increase can also be seen for both aliphatic and aromatic protons of premium coal 301 at 25 $^\circ$C. In fact, we can obtain a semi-quantitative estimate of the correlation time $\tau_c$ on the basis of the $T_{1p}$ dependence on $\omega_1$. From equation (11), we obtain a very simple relationship between $T_{1p}$ and $\tau_c$:

$$
\frac{T_{1p}'_{\omega}}{T_{1p}''_{\omega}} = \frac{1 + \omega_1^2 \tau_c^2}{1 + \omega_1^2 \tau_c^2}, \quad \text{when} \quad \omega_0 >> 1/\tau_c \quad \text{and} \quad \omega_0 >> \omega_1
$$

Thus, $\tau_c$ can be directly estimated from the ratio of $T_{1p}$ measured at two different spin-lock fields $\omega_1$ and $\omega_2$. For example, the correlation time of the fast relaxation aliphatic protons in coal 501 at 25 $^\circ$C is estimated as 10 $\mu$s, which is in good agreement with the correlation time estimated from the dipolar-dephasing experiments.

However, we did not always observe an increase in $T_{1p}$ when $\omega_1$ was increased from 46 kHz to 93 kHz. A quick explanation based on the discussion above would be that the random motion is so fast ($\tau_c < < 1/(2\omega_1)$) that the increase in $T_{1p}$ is not detectable from the experimental data. However, that explanation is not very convincing when we examine the $T_{1p}$ data of aromatic protons in premium coal 601 at 25 $^\circ$C, shown in Tables 9 and 10. No significant change of $T_{1p}$ with $\omega_1$ can be seen for the aromatic protons in premium coal 601 at 25 $^\circ$C. According to the above explanation, all of the aromatic protons would have a correlation time $\tau_c < < 5$ $\mu$s, which seems to be too small on the basis of dipolar-dephasing experiments. The $T_{1p}$ dependence on $\omega_1$ is actually complicated by the spin-diffusion process, which averages out, on a time scale of $T_{1p}$ (1 ms - 10 ms), any $T_{1p}$ differences between protons that are strongly dipolar coupled to each other. If spin diffusion is fast and effective, the increase of $T_{1p}$ with $\omega_1$ may give more time for spin diffusion to spread over a larger distance, and result in a redistribution of domains in terms of the $T_{1p}$ behavior of protons. This may lead to a result that a large number of fast relaxation protons are effectively exchanging magnetization with slow relaxation protons via spin diffusion in a larger domain. The average $T_{1p}$ of the large domain with slow relaxation protons may not increase with $\omega_1$, because more fast relaxation protons are involved in the averaging process. Instead, an increase of $T_{1p}$ with $\omega_1$ may actually reflect an increase in the fraction of the slow relaxation component. If spin diffusion is slow, the increase of $T_{1p}$ with $\omega_1$ will not be effectively averaged by spin diffusion processes; thus this increase is still observable in the experimental data.

In summary, when the strength of the spin-lock field increases, one should observe either an increase in $T_{1p}$, or an increase in the fraction of the slow relaxation component, or both. Reexamining all the $T_{1p}$ data in Tables 7-12 in these terms, one can see that the above discussion explains very well the $T_{1p}$ dependence on $\omega_1$. 

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The temperature dependence of $^1H$ $T_{1p}$ in coals is not very simple, since the correlation time of random motion is close to the minimum of the $T_{1p}$-vs.-$\tau_c$ curve\textsuperscript{48}. In such an intermediate motion regime, $T_{1p}$ changes with modest changes in temperature (or $\tau_c$) may not be significant due to the relatively shallow well around the $T_{1p}$ minimum. For fast-relaxation protons in premium coal 501, the $T_{1p}$ value measured with a spin-lock field of 93 kHz decreases consistently with increasing temperature. This indicates that random motion is in the slow motion regime, or $\tau_c < 1/\omega_1 = 5.3 \, \mu s$. For a spin lock field of 46 kHz, we can see that $T_{1p}$ levels off when the temperature is increased from 120 $^\circ$C to 180 $^\circ$C. This implies that the correlation time at 120 $^\circ$C and 180 $^\circ$C is very close to the $T_{1p}$ minimum at $\tau_c \approx 1/\omega_1$, or 11 $\mu$s. This is also in good agreement with the $\tau_c$ value estimated from the $T_{1p}$ dependence on $\omega_1$.

One thing worth mentioning here is that we observed initial transient oscillations in the $^1H$ NMR signals in the $T_{1p}(^1H)$ experiments on all three coal samples at all three temperatures employed in this study. The transient oscillations in the initial spin-lock period can last as long as 200 $\mu$s. The theoretical origin of such transient oscillations was discussed by VanderHart and Garroway\textsuperscript{75}. These initial transients are due to an exchange of energy between the spin-locked rotating frame Zeeman and rotating-frame dipolar reservoirs. For on-resonance irradiation, the oscillations occur at a frequency near $2\omega_1$ and damp out with a time constant on the order of the dipolar dephasing time $T_{dd}$. Our experimental observation is qualitatively in agreement with that theoretical analysis. Such transient oscillations will complicate the cross-polarization dynamics in $^{13}C$ CP/MAS experiments.

In conclusion, $^1H$ rotating-frame spin-lattice relaxation in coals provides us another tool to probe the spin-dynamics and structural heterogeneity in coals. Many structural and dynamical details of coals can be obtained from such studies. This work demonstrates that $T_{1p}$ is useful for studying molecular motion and structure of coal in the temperature range, 25 $^\circ$C to 180 $^\circ$C.

**Variable-temperature $^1H$ CRAMPS Studies of Pyridine Saturated Coal**

**Introduction.** Solvent extraction as a means for studying coal compositions dates from early work in the 1850s\textsuperscript{74,75}, and has become of a major research topic since Bedson discovered that bituminous coals were substantially soluble in hot pyridine in 1902\textsuperscript{76}. A large variety of technical processes for coal conversion, including liquefaction of coal, were also based on interactions between solvents and coals\textsuperscript{77}. The understanding of such interactions at the molecular level is still very limited despite great efforts that have been directed to this area of research\textsuperscript{77}.

Both liquid-state and solid-state NMR techniques have played a very important role in studying coal structures by solvent swelling and extraction\textsuperscript{78,79}. As coal is partially soluble in various organic solvents, some information about coal structure has been obtained from liquid-state $^1H$ and $^{13}C$ NMR experiments. There are two problems with
such studies based on liquid-state NMR techniques. First, it is uncertain how well the structural information derived from the liquid extract of a coal corresponds to the actual structure of the whole, solid coal. Second, the structure of the insoluble residue of coal extraction can not be determined from liquid-state NMR techniques. The development of high-resolution solid-state $^1$H and $^{13}$C NMR techniques from the late 1970s to the early 1980s have made it possible to extract structural information directly from untreated solid coal samples. Both $^{13}$C CP/MAS and $^1$H CRAMPS techniques have been used to study untreated coals and solvent extraction products of coal.

It has been found that significant differences exist between the structures of an untreated coal and that of the solvent-extract of the coal. Some solvents (e.g., pyridine) were found to be very effective in increasing the mobility of coal constituents. Such increases of mobility leads to an enhancement of spectral resolution in both $^{13}$C and $^1$H solid-state NMR spectra of coal.

Previous studies in this group have found that pyridine saturation can dramatically increase the apparent spectral resolution of $^1$H CRAMPS spectra of some types of coals at room temperature. The exact mechanism of the resolution enhancement was not determined. Dipolar-dephasing experiments based on $^1$H CRAMPS detection were used to confirm the fact that molecular mobility is enhanced significantly in pyridine-saturated coals. The mobilized structure in pyridine-saturated coal was assigned as the molecular phase, which is the relatively mobile structure determined from experiments of the dipolar-dephasing type on both untreated coals and pyridine-saturated coals. However, significant differences in chemical structure (e.g., aromaticity) between the mobile component of untreated coal and solvent-saturated coal were reported in $^{13}$C CP/MAS experiments and $^1$H CRAMPS experiments. The mobile component in untreated coal contains more aromatic hydrogen, and the situation is just reversed in pyridine-saturated coal. A $^1$H CRAMPS study of pyridine-saturated Polish coal shows similar aromaticity in both mobile and rigid phases. The discrepancy among different experiments has been around for years. A reconciliation of the discrepancy should be very helpful for us to understand solvent-coal interactions at the molecular level.

We presented above results of a systematic $^1$H CRAMPS study of untreated coals at temperatures between 25 $^\circ$C and 230 $^\circ$C. In contrast to the dramatic resolution enhancement observed from pyridine saturated coal at room temperature, we did not observe such resolution enhancement by simply heating the coal up to 230 $^\circ$C, although we confirmed the fact that there is a significant increase of molecular mobility at high temperatures via various CRAMPS-based time-domain experiments. Our results suggest that the thermally induced molecular motion is very different from the motion enhanced by solvent saturation. Variable-temperature time-domain $^1$H CRAMPS experiments on pyridine saturated coal are needed to unveil the nature of the molecular motion that is enhanced by pyridine saturation. Such a study will also help us to understand the mechanism of $^1$H CRAMPS spectral resolution enhancement induced by solvent swelling.
We here present experimental results of a variable-temperature (VT) $^1$H CRAMPS study of pyridine-saturated coal and the pyridine extraction residue of coal. Dipolar-dephasing experiments, which were carried out on untreated coal samples, as discussed above, were also applied to the corresponding pyridine-saturated coal and its extraction residue. These studies provide many new insights into the molecular dynamical and structural changes induced in coal by thermal treatment and solvent saturation.

The molecular/macromolecular (M/M) structural model of coal$^3$ will be discussed on the basis of our new results. The nature of the molecular phase and macromolecular phase in coal and the relationships between the M/M structural model and molecular mobility experimentally detected by NMR will be reexamined. We have developed a coherent view of the molecular structure and dynamics of coal based on the new experimental results. Many discrepancies in the literature on these issues are well resolved by this view, and the resolution enhancement due to solvent-saturation is also satisfactorily explained.

Most of these studies concentrate on Argonne premium coal 601, which is a high-volatile bituminous (HVB) coal and is substantially soluble in hot pyridine. Comparative studies on the low-volatile bituminous (LVB) coal, Pocahontas #3 (premium coal 501), which is not very soluble in pyridine, were also carried out.

The original coal samples were dried at 10$^2$ torr at room temperature for 20 hours. The coal samples were saturated with perdeuterated pyridine-d$_5$ (Cambridge Isotope Laboratory, 99.94% $^2$H) with a weight ratio of 1:2 (one part coal : 2 parts pyridine). The sample was sealed in a home-made glass MAS rotor with epoxy resin. The sealed glass spinner with the pyridine-saturated coal sample was put in an oven at 80 °C for one week to allow the establishment of equilibrium between pyridine and coal.

Coal extraction was carried out for 21 days with refluxing pyridine-d$_5$ (~ 95 °C) in a soxhlet extractor under a nitrogen atmosphere. The residue was dried in a vacuum oven (0.1 torr) at 80 °C for 3 days, after which no further weight change was detected.

$^1$H CRAMPS Experiments. Dipolar-dephasing experiments based on $^1$H CRAMPS detection were used to study the molecular dynamics and structural heterogeneity of pyridine-saturated coals. Although dipolar-dephasing experiments based on $^1$H CRAMPS detection were used extensively in previous studies on coal in this group$^{12-14}$, those earlier studies were all carried out at room temperature. Furthermore, in the work summarized here, the pulse sequence was improved by inserting appropriate composite pulse(s) prior to multiple-pulse trains, with proper phase cycling. The composite pulse(s) and properly phase-cycled preparation pulse(s) were used to minimize base-line distortions of $^1$H CRAMPS spectra caused by magnetization that is spin-locked to the effective field of the average Hamiltonian of the multiple-pulse sequence employed (BR-24). Without these improvements, reliably quantitative analysis of time-domain experimental data is difficult.
**Data Analysis.** Although the resolution of $^1$H CRAMPS spectra of pyridine-saturated coals is dramatically enhanced relative to untreated coals for some HVB coals, the $^1$H CRAMPS spectra still consists of severely overlapped peaks due to the distribution of chemical structures. Reliable peak deconvolution is required for quantitation of different chemical structures in pyridine-saturated coals. Manual adjustment of spectral parameters for individual peaks in peak deconvolution was used in previous work; this approach was tedious, time-consuming, and not very reliable. A computer program for automatic peak deconvolution was developed in this work to ensure reliable and efficient quantitation based on spectral deconvolution. Many powerful features not available in commercial NMR data processing packages have been incorporated into the deconvolution program.

In a time domain experiment, a series of $^1$H CRAMPS spectra is acquired with a certain time parameter varied systematically. The S/N of each spectrum in the series will change as the time parameter is varied. For example, the S/N of a $^1$H CRAMPS spectrum in a dipolar-dephasing experiment will decrease with an increase of the dephasing time. The accuracy of peak deconvolution for a relatively broad peak is usually more sensitive to slight baseline distortions or misphasing of $^1$H CRAMPS spectra than for a narrow peak. This problem is very serious for spectra with relatively low signal-to-noise ratios (S/N), such as the $^1$H CRAMPS spectra obtained after long dipolar-dephasing times. To ensure reliable deconvolution of a series of $^1$H CRAMPS spectra acquired in a time-domain experiment, the spectra with good S/N are deconvoluted first, with all the peak parameters optimized by the computer deconvolution program. Some of the optimized parameters, such as peak shape, full width at half height (FWHH) and peak position are then averaged and used as fixed values for peak deconvolution of the spectra with low S/N. This procedure works very well for quantitative analysis of time-domain data.

Another computer program was also developed in this work for fitting different models that describe the time-evolution of NMR signal in time-domain experiments. Multiple-component relaxation for a single peak in the NMR spectrum of coal are common. This program directly supports models with any number of relaxation components, and is limited only by the amount of computer memory.

Both the peak deconvolution program and the model-fitting program are based on a non-linear least-squares optimization routine using the Leveberg-Marquardt algorithm. User-friendly graphical interfaces are implemented in both programs.

**Chemical Functionality in Premium Coals 601 and 501.** VT $^1$H CRAMPS study of pyridine-saturated coals were carried out on premium coals 601 (HVB) and 501 (LVB). As the boiling point of pyridine is 115 °C, the highest temperature we used in these experiments was 90 °C. Figure 14 shows $^1$H CRAMPS spectra of pyridine-saturated premium coals 601, along with the $^1$H CRAMPS spectra of the untreated coals. Dramatic resolution enhancement can be seen in the $^1$H CRAMPS spectra of the C$_5$D$_3$N-saturated coal. The spectral change for C$_5$D$_3$N-saturated premium coal 501 is significant (not
shown here), but not as dramatic as that for premium coal 601. These observations are in agreement with the work of Jurkiewicz et al.\textsuperscript{14}.

When the temperature is increased from 25 °C to 90 °C, there are no dramatic changes in the \textsuperscript{1}H CRAMPS spectra of C$_2$D$_3$N-saturated coals. For C$_3$D$_5$N-saturated premium coal 601, the \textsuperscript{1}H CRAMPS spectrum obtained at 60 °C has better spectral resolution than the spectra obtained at 25 °C and 90 °C. For C$_2$D$_3$N-saturated premium coal 501, the fine structure in the \textsuperscript{1}H CRAMPS spectra is seen most distinctly at 25 °C. These small spectral resolution changes that occur with temperature variation are probably due to small changes in the spectral densities of random motion with correlation times around the cycle-time of the multiple-pulse sequence (10 - 100 μs), which may interfere with the coherent averaging of dipolar interactions by the multiple-pulse sequence\textsuperscript{88,89}.

From a comparison of the pyridine saturation effects shown in Figure 14 with the thermal effects displayed earlier, it is clear that pyridine saturation induces molecular dynamical and structural changes in coal that can not be achieved by thermal treatment up to 230 °C. Dipolar-dephasing experiments were used to study these changes induced by pyridine saturation.

The determination of chemical structure and functionality is one of the most difficult challenges in coal science. For bituminous coals, \textsuperscript{13}C CP/MAS and \textsuperscript{1}H CRAMPS techniques can usually resolve only two broad peaks, corresponding to aliphatic and aromatic structures in coal\textsuperscript{80}. The enhanced spectral resolution of coal by pyridine-saturation make it possible to elucidate additional structural details.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.jpg}
\caption{\textsuperscript{1}H CRAMPS spectra of C$_2$D$_3$N-saturated premium coal 601 obtained at (b) 25 °C, (c) 60 °C, and (d) 90 °C. For comparison, the \textsuperscript{1}H CRAMPS spectrum of the untreated coal at 25 °C is shown in (a). The BR-24 pulse sequence was used with a cycle time of 108 μs and a 90° pulse width of 1.25 μs in the experiments. Each spectrum was acquired with 200 scans and a 3 s recycle delay. The MAS speed was between 1.5 and 1.8 kHz.}
\end{figure}
Figure 15 (a) $^1$H CRAMPS spectrum of C$_2$D$_3$N-saturated premium coal 601 obtained at 25 °C. (b) Spectrum simulated by computer peak deconvolution. In the simulated spectrum, the dashed lines represent individual peaks from the deconvolution, and the solid line represents the sum of all the deconvoluted peaks.

Figure 15 shows the experimental $^1$H CRAMPS spectrum of premium coal 601 and the spectrum simulated by computer deconvolution. The following peaks and shoulders can be identified via deconvolution: 1.0 ± 0.1 ppm, 1.7 ± 0.2 ppm, 3.4 ± 0.9 ppm, 6.9 ± 0.3 ppm, and 8.4 ± 0.6 ppm. The standard error of the position and area of the 3.4 ppm peak are larger than those of other peaks, because there are severe overlaps of aliphatic and aromatic peaks in this region, and only a shoulder is seen at about 3.4 ppm in the experimental $^1$H CRAMPS spectrum. To get a reasonably good fit in the spectrum simulated by peak deconvolution, a broad band at 11.5 ± 1.5 ppm must be included. The position and area of this broad band cannot be determined as accurately as those of other peaks due to inherent uncertainties about the nature of the baseline of typical $^1$H CRAMPS spectra. The fraction of each type of protons are listed in Table 14.

Table 14 The relative concentrations (%) of the various types of protons in C$_2$D$_3$N-saturated premium coal 601.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>1.0</th>
<th>1.7</th>
<th>3.4</th>
<th>6.9</th>
<th>8.4</th>
<th>11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>6.5</td>
<td>35</td>
<td>20</td>
<td>19</td>
<td>15</td>
<td>3.8</td>
</tr>
<tr>
<td>FWHH (ppm)</td>
<td>0.8</td>
<td>2.5</td>
<td>3.4</td>
<td>1.9</td>
<td>2.3</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The 1.0 ± 0.1 ppm chemical shift is characteristic of CH$_3$ groups on aliphatic chains or attached at a position γ or further away from an aromatic ring. This assignment is also confirmed by the dipolar-dephasing experiments, which we will discuss later.
The largest fraction of protons (35\%) corresponds to a chemical shift of $1.7 \pm 0.2$ ppm. This chemical shift can be attributed to two possible structures: alicyclic CH$_2$ and CH$_2$ in a position $\beta$ to an aromatic ring or in tetralin-like structures$^8$. As the FWHH of this peak is 2.5 ppm, we cannot exclude the existence of a small fraction of other chemical functionalities with chemical shifts different from, yet still close to, 1.7 ppm. For example, a methyl (CH$_3$) group that is attached to an aromatic ring in the $\beta$ position will have a chemical shift around 1.4 ppm; methines other than those $\alpha$ to an aromatic ring will have chemical shifts from 1.6 to 2.0 ppm$^8$.$^9$. These functional groups were identified in the solvent extract of coal$^{90}$.$^9$.1.

The aliphatic peak at $3.4 \pm 0.9$ ppm contains about 19\% of the protons in the C$_2$D$_2$N-saturated coal 601. The chemical shift of this peak matches well with methylene protons of aliphatic ethers (R-CH$_2$-O-). The oxygen content of premium coal 601 is about 11\% by weight. The molar fraction of oxygen is only 5\%. According to various molecular models of coal structure, oxygen exists in coal mainly as hydroxyl groups and carbonyl (C=O) groups. So, it is unlikely that 19\% of the protons are all in aliphatic ether structures. In addition, the peak at 3.4 ppm is broad, with a FWHH of 3.4 ppm, and this peak position is not determined as accurately as those of other aliphatic peaks. Chemical structures with chemical shifts between 2.0 ppm and 5.0 ppm could also contribute to this peak. Such structures include CH$_2$ groups of acenaphthenes and indenes (3.0 - 3.3 ppm), CH group $\alpha$ to an aromatic ring (2.0 - 3.3 ppm), and CH$_2$ groups $\alpha$ to two aromatic rings (3.3 - 4.7 ppm)$^9$.

The peak at $6.9 \pm 0.3$ ppm can be attributed to protons attached to monoaromatic rings, rather than condensed-ring systems such as naphthalene, anthracene or pyrene. The peak at $8.4 \pm 0.6$ ppm can be assigned to protons in sterically hindered aromatic structures$^{90}$, to phenolic OH protons, to protons at positions $\alpha$ to nitrogen in a aromatic (pyridine-type) ring, and to protons in benzothiophene-type structures$^{92}$. The fractions of these two peaks are similar in C$_2$D$_2$N-saturated premium coal 601, as can be seen in Table 14. The total percentage of aromatic protons is 34\%.

The broad band around $11.5 \pm 1.5$ ppm contains only 4\% of the total proton population. As this band is broad and low in intensity, the

![Figure 16](image-url)
peak position and area calculated from spectral deconvolution are very sensitive to variations (distortions) in the baseline of \textsuperscript{1}H CRAMPS spectra. The chemical shift of this peak corresponds to protons in carboxyl groups, or hydroxyl protons in hydroxypyridine-like structures\textsuperscript{81}.

A similar deconvolution on the \textsuperscript{1}H CRAMPS spectrum of C\textsubscript{2}D\textsubscript{3}N-saturated premium coal 501 is difficult due to limited spectral resolution. However, we found that the dipolar-dephasing experiment is very helpful for assigning fine structures that are dominated by broad peaks due to protons in rigid structures. Figure 16b shows the \textsuperscript{1}H CRAMPS spectrum of C\textsubscript{2}D\textsubscript{3}N-saturated premium coal 501 obtained with a dipolar-dephasing time of 184.6 \textmu s. All of the sharp features of fine structure in the un-dephased \textsuperscript{1}H CRAMPS spectrum (Figure 16a) are preserved in the dipolar-dephased spectrum. As we will discuss later, the sharpest features of the fine structure in the \textsuperscript{1}H CRAMPS spectra of C\textsubscript{2}D\textsubscript{3}N-saturated coals are largely due to protons in mobile moieties that show Lorentzian dipolar-dephasing behavior with long dephasing time constants (0.2 --\textendash 10 ms). The total \textsuperscript{1}H CRAMPS spectrum of a pyridine-saturated coal can be considered as a superposition of a spectrum of "mobile" protons and a spectrum of "rigid" protons. The former generate a much higher spectral resolution, while the later render a resolution that is comparable to that of the \textsuperscript{1}H CRAMPS spectrum of the untreated coal. As can be seen from Figure 16c, the difference spectrum, obtained by subtraction of the \textsuperscript{1}H CRAMPS spectrum of C\textsubscript{2}D\textsubscript{3}N-saturated premium coal 501 obtained without a dipolar-dephasing period from the spectrum obtained with a dipolar-dephasing time of 184.6 \textmu s, looks very much like the \textsuperscript{1}H CRAMPS spectrum of the untreated coal without pyridine saturation. All the fine structure disappeared in the difference spectrum, except for small humps around 4.7 ppm due to incomplete cancellation of the 4.7 ppm peak in the difference spectrum. As can be seen from the deconvolutions shown in Figures 17a and 17b, the difference spectrum can be well fitted with two broad peaks, just as in the deconvolution of the \textsuperscript{1}H CRAMPS spectrum of the untreated premium coal 501.

Six peaks can easily be identified in the deconvolution of the \textsuperscript{1}H CRAMPS spectrum of C\textsubscript{2}D\textsubscript{3}N-saturated premium coal 501 obtained with a dipolar-dephasing period of 184.6
μs (Figure 17c,d). The chemical shifts of the six peaks are at 1.0 ± 0.1 ppm, 2.0 ± 0.1 ppm, 3.7 ± 0.1 ppm, 4.8 ± 0.1 ppm, 7.0 ± 0.3 ppm, and 8.6 ± 0.2 ppm, respectively. The relative fractions and FWHHs of the six peaks are listed in Table 15. We can see that the chemical shifts of these peaks are close to those of the C₃D₅N-saturated premium coal 601, except for the peak at 4.8 ppm. The peak assignments given above for coal 601 for spectral contributions at 1.0, 2.0, 3.7, 7.0 and 8.6 ppm should still apply to the ¹H CRAMPS spectrum of C₃D₅N-saturated premium coal 501. The narrow peak at 4.8 ppm may be due to water, which could be released from the very tight internal voids of coal when the coal structure is swollen by pyridine.

Table 15 Relative concentrations (%) of the various types of protons in the ¹H CRAMPS spectrum of C₃D₅N-saturated premium coal 501 obtained with a dipolar-dephasing time of 184.6 μs.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>1.0</th>
<th>2.0</th>
<th>3.7</th>
<th>4.8</th>
<th>7.0</th>
<th>8.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>23</td>
<td>5.3</td>
<td>35</td>
<td>15</td>
<td>19</td>
<td>2.5</td>
</tr>
<tr>
<td>FWHH (ppm)</td>
<td>1.1</td>
<td>0.6</td>
<td>1.9</td>
<td>0.5</td>
<td>1.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Chemical Functionality in the C₃D₅N-Saturated Extraction Residue of Premium Coal 601. To understand better the relationship between molecular mobility and pyridine extractability of coal, we separated the extraction residue of premium coal 601 after 21-day soxhlet extraction of the original coal with refluxing (95 °C) pyridine. The extraction residue was then dried (80 °C, 0.1 torr) for ¹H CRAMPS studies.

The ¹H CRAMPS spectrum of the dried residue is shown in Figure 18a. By comparing the spectrum with that of original coal (shown in Figure 14a), one can see that the relative intensity of the aliphatic peak is lower for the extraction residue. This suggests that aliphatic protons are preferentially extracted by pyridine. This is in agreement with both liquid-sample and solid-sample NMR studies on pyridine extracts, which proved that the aliphatic component is preferentially populated in pyridine extract.

Figures 18b - 18d show the VT ¹H CRAMPS spectra of the pyridine saturated residue. These spectra are similar to those of pyridine-saturated original (untreated) coal. One additional peak at about 4.9 ppm, with an intensity that is less than 1% of the total intensity, can be clearly seen in the ¹H CRAMPS spectra of pyridine-saturated residue (Figure 14b-d). This peak is assigned as water. To trace the origin of this peak, we checked the ¹H NMR spectrum of the C₃D₅N used for preparing this sample; we found a small peak at 4.9 ppm in the C₃D₅N, which could contribute part of the 4.9 ppm peak observed for the C₃D₅N-saturated residue. We then used a dry C₃D₅N sample (from a freshly opened ampoule of another batch of C₃D₅N purchased from Cambridge Isotopes Laboratory), for which the NMR spectrum is very clean at 4.9 ppm, to prepare another
sample of the C,D,N-saturated residue. After the extraction residue was evacuated at 10^3 torr for 48 hours at 110 °C, the dry pyridine was added to the evacuated dry residue and then sealed into the MAS rotor with epoxy resin in a glove box. We repeated the previous ¹H CRAMPS experiments, and found that the 4.9 ppm peak was still visible with about 1/3 of the intensity observed previously. The result suggests that water in this sample was released from the dried extraction residue after the structure of the residue was swollen by pyridine.

There are at least two reasons why we did not observe this water peak before the pyridine was added (Figure 18a). First, the water molecules in the dried residue can be strongly bonded to the macromolecular structure of coal via hydrogen bonding, or can be intercalated into very small voids of the macromolecular matrix of coal. Water molecules in such rigid environments would give a relatively broad peak. Second, the total water content is less than 1%. Thus, the water peak in the ¹H spectra of dried residue could be very weak and broad. Therefore, it is difficult to detect the water peak form the ¹H spectra of dried residue. When pyridine is added to the residue, the crosslinks due to hydrogen bonding can be effectively broken by pyridine molecules. The water molecules can thus be detached from the macromolecular structure due to breakage of hydrogen bonding. They can also be released from very small voids because of significant swelling of the residue structure caused by pyridine saturation. Both mechanisms would significantly mobilize the residual water molecules in the dried extraction residue of coal, thus producing a sharp ¹H NMR peak of water molecules. Although the relative area of the water peak is still very low, the intensity of the water peak can be significantly increased because of the dramatic reduction of the peak width. That is why we can recognize the water peak easily in the ¹H NMR spectra of pyridine saturated extraction residue of coal.

Figure 18 ¹H CRAMPS spectra of C,D,N-saturated extraction residue of premium coal 601 obtained at (b) 25 °C, (c) 60 °C, and (d) 90 °C. For comparison, the ¹H CRAMPS spectrum of the dried residue is shown in (a). BR-24 pulse sequence was used with a cycle time of 108 µs and a 90° pulse width of 1.2-1.3 µs. Each spectrum was acquired with 250 scans and a 3 s recycle delay. The MAS speed was between 1.5 and 1.8 kHz.
Figure 19 (a) $^1$H CRAMPS spectra of C$_2$D$_3$N-saturated extraction residue of premium coal 601 obtained at 25 °C. (b) Simulated spectrum from computer peak deconvolution. In simulated spectra, dashed lines represent individual peaks from the deconvolution; the solid line represents the sum of all the deconvoluted peaks.

Figure 19 shows the experimental $^1$H CRAMPS spectrum of the C$_2$D$_3$N-saturated residue of the pyridine extraction of coal 601, and the simulated spectrum obtained by computer deconvolution. The chemical shifts, relative intensities (%) and FWHHs of the deconvoluted peaks are listed in Table 16.

Table 16 Relative concentrations (%) and FWHH of various types of protons in the C$_2$D$_3$N-saturated pyridine extraction residue of premium coal 601.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>1.0</th>
<th>1.7</th>
<th>4.7</th>
<th>6.8</th>
<th>8.3</th>
<th>11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>4.6</td>
<td>48</td>
<td>0.9</td>
<td>34</td>
<td>5.1</td>
<td>7.1</td>
</tr>
<tr>
<td>FWHH (ppm)</td>
<td>0.8</td>
<td>3.7</td>
<td>0.4</td>
<td>2.9</td>
<td>2.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Several important differences between the original (untreated) premium coal 601 and its pyridine extraction residue can be seen from Tables 14 and 16:

1. The 3.4 ppm contribution in the $^1$H CRAMPS spectrum of the C$_2$D$_3$N-saturated residue can not be identified as a separate aliphatic peak. Instead, the spectral region between 1.2 and 4.5 ppm is better fitted with a single peak at 1.7 ppm with a FWHH of 3.7 ppm, which is much larger that the FWHH (2.5 ppm) of the 1.7 ppm peak in the $^1$H CRAMPS spectrum of the C$_2$D$_3$N-saturated original coal. Based on dipolar-dephasing results presented later, the aliphatic component in the residue is more rigid than that of the original coal. Pyridine saturation can not mobilize the aliphatic structure in the residue as effectively as that in the original coal. That explains why a single broader peak between 1.2 and 4.5 ppm is observed in $^1$H CRAMPS spectrum...
of the C₅D₅N-saturated residue. It is also possible that some of protons with a chemical shift close to 3.5 ppm are preferentially extracted by pyridine.

(2) As shown in Tables 14 and 17, the fraction of aliphatic protons in the residue is lower than that in the original coal; the fraction of aromatic protons in the residue is higher than that in the original coal. This is in agreement with the well-established result that aliphatic structures are preferentially extracted

(3) The intensity ratios of methyl protons (1.0 ppm) to non-methyl aliphatic protons (1.7 and 3.4 ppm) in the original coal and its residue are 0.13 and 0.080, respectively. This difference in the ratios suggests that structures containing methyl groups are preferentially extracted by pyridine. This implies that methyl groups in coal are mainly distributed in relatively small molecules, that can be easily extracted by pyridine. This view is consistent with the general trend that the average molecular weight in coal increases with C/H ratio

'H-'H Dipolar-Dephasing Studies of Pyridine-Saturated Coal 601. Earlier we showed that molecular mobility in coal is significantly promoted by thermal treatment. In contrast to the dramatic resolution enhancement of 'H CRAMPS spectra of coal by pyridine-saturation at room temperature, we did not observe such enhancement with thermal activation up to 230 °C. These results suggest that thermal treatment and solvent saturation have quite different effects on the molecular dynamics of coal. 'H-'H dipolar-dephasing experiments were carried out on pyridine-saturated coals to explore the molecular dynamical and structural changes induced by pyridine saturation.

Figure 20 illustrates stack plots of 'H VT CRAMPS spectra of C₅D₅N-saturated premium coal 601 obtained at (a) 25 °C and (b) 90 °C. The BR-24 pulse sequence was used with a cycle time of 108 μs and a 90° pulse width of 1.2-1.3 μs. Each spectrum was acquired with 200 scans and a 3 s recycle delay. The MAS speed was between 1.5 and 1.8 kHz.
premium coal 601 at 180 °C. It is therefore clear that pyridine saturation can dramatically promote molecular motion even at room temperature while thermal treatment is much less effective at even 180 °C.

To quantify the dipolar-dephasing behavior of the C\textsubscript{3}D\textsubscript{3}N-saturated coal, computer peak deconvolutions, similar to what was described above, were employed to obtain the areas of deconvoluted peaks in the spectra shown in Figure 20. Typical spectral deconvolution of the \textsuperscript{1}H CRAMPS spectrum of the C\textsubscript{3}D\textsubscript{3}N-saturated premium coal 601 is shown in Figure 15. As spectral resolution between the peak at 1.7 ppm and the one at 2.5 ppm was not good enough to assure reliable deconvolution of these two peaks over the whole range of dephasing periods, we combined the areas of these two peaks together to model the dipolar-dephasing behavior. As these two peaks represents non-methyl aliphatic protons, we will use the term “non-methyl protons” for later discussion. For the same reason, we combined the areas of the 6.9 and 8.4 ppm peaks as the area for aromatic protons. The peak at 1.0 ppm represents protons in methyl groups, and is analyzed separately from non-methyl protons. As the very weak and broad peaks at 11.5 ppm are too sensitive to variations/distortions in the baseline of \textsuperscript{1}H CRAMPS spectra, we did not include this peak in the quantitative analysis.

Both Gaussian and Lorentzian decay components were used to model the dipolar-dephasing behavior of C\textsubscript{3}D\textsubscript{3}N-saturated premium coal 601. A general equation for describing the dipolar-dephasing curve is as follows:

\[ M(t) = M_{GF}(0)e^{-t^2/(2T_{GF}^2)} + M_{GS}(0)e^{-t^2/(2T_{GS}^2)} + M_{LF}(0)e^{-t/T_{LF}} + M_{LS}(0)e^{-t/T_{LS}}, \]

where \( M_{GF}(0) \) and \( M_{GS}(0) \) are the initial amplitudes of the fast and slow Gaussian decays, respectively; \( M_{LF}(0) \) and \( M_{LS}(0) \) are the initial amplitudes of fast and slow Lorentzian decay components, respectively; \( T_{GF}, T_{GS}, T_{LF}, \) and \( T_{LS} \) represent corresponding dipolar-dephasing time constants. The fraction of each dephasing component can be calculated from its initial amplitude as:

\[ f_i = \frac{M_i(0)}{M_{GF}(0) + M_{GS}(0) + M_{LF}(0) + M_{LS}(0)}, \]

where \( i = GF, GS, LF, LS \)

Non-linear least-squares analysis, based on equation (14), was used to determine how many dephasing components should be included in the model that fits best the dipolar-dephasing curves of methyl protons, non-methyl protons and aromatic protons. The dipolar-dephasing time constants were then calculated from the best fit of the model to the dipolar-dephasing curve for each type of protons. The results from the graphical/numerical data analysis are listed in Table 17.
Table 17  Dipolar-dephasing parameters of the various types of protons in C₅D₅N-saturated premium coal 601.\(^{a,b}\).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>25</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methyl</td>
<td>Nonmethyl</td>
<td>Aromatic</td>
<td>Methyl</td>
<td>Nonmethyl</td>
<td>Aromatic</td>
<td>Methyl</td>
<td>Nonmethyl</td>
<td>Aromatic</td>
</tr>
<tr>
<td>f₉F (%)(^a)</td>
<td>-</td>
<td>63</td>
<td>55</td>
<td>-</td>
<td>34</td>
<td>38</td>
<td>-</td>
<td>0.012</td>
<td>0.021</td>
</tr>
<tr>
<td>T₉F (ms)(^b)</td>
<td>10</td>
<td>0.011</td>
<td>0.020</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
<td>0.032</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>f₉G (%)(^a)</td>
<td>11</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>T₉G (ms)(^b)</td>
<td>0.031</td>
<td>0.081</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f₉L (%)(^a)</td>
<td>41</td>
<td>11</td>
<td>33</td>
<td>27</td>
<td>34</td>
<td>49</td>
<td>0.18</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>T₉L (ms)(^b)</td>
<td>0.25</td>
<td>0.24</td>
<td>0.17</td>
<td>0.18</td>
<td>0.13</td>
<td>-</td>
<td>10</td>
<td>9.3</td>
<td>11</td>
</tr>
<tr>
<td>f₉S (%)(^a)</td>
<td>48</td>
<td>15</td>
<td>13</td>
<td>73</td>
<td>26</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T₉S (ms)(^b)</td>
<td>9.9</td>
<td>8.6</td>
<td>4.3</td>
<td>10</td>
<td>9.3</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) The fractions (%) of the four dephasing components are denoted as f₉F, f₉G, f₉L, and f₉S.
b) T₉F, T₉G, T₉L, and T₉S denote the dipolar dephasing time constants of fast Gaussian, slow Gaussian, fast Lorentzian and slow Lorentzian dephasing components, respectively.

A methyl group has a very low energy barrier for internal rotation around its C₃ axis. As a methyl group is often a terminating group of long aliphatic chains, it can also easily rotate relative to the rest of molecules. As one might have expected, most of the methyl protons (89%) belong to the Lorentzian dephasing components at 25 °C. The remaining 11% of the methyl protons, which show slow Gaussian dephasing behavior at 25 °C, were all converted to mobile Lorentzian decay components at 90 °C. This suggests that the energy barriers that restrict rotation of the methyl protons are not much higher than kT at room temperature (i.e., 0.6 kcal/mole).

The dipolar-dephasing curve of non-methyl aliphatic protons (not shown) consists of contributions from all four types of dephasing components in equation (14). Time constants of the Gaussian dephasing components in the C₅D₅N-saturated coal are very close to those of aliphatic protons in untreated premium coals (c.f. Table 2). Most of the non-methyl aliphatic protons show Gaussian dephasing behaviors at 25 °C. This means that most non-methyl protons are distributed among very rigid structures, which can not be easily mobilized by pyridine saturation. When the temperature is increased to 90 °C, a large fraction of the Gaussian decay components at 25 °C are thermally activated to show fast or slow Lorentzian dephasing behaviors. The fractions of fast and slow Lorentzian dephasing components are increased by 23% and 11%, respectively, at 90 °C. The time constants of Lorentzian dephasing components of non-methyl protons are very close to those of methyl protons at both 25 °C and 90 °C. This suggests that mobile methyl and non-methyl aliphatic protons may exist in the same domain and that \(^1\)H-\(^1\)H spin-diffusion effectively averages out differences of dephasing time constants on a time scale of 0.1 to 10 ms. The existence of a large aliphatic-rich domain in premium coal 601 was demonstrated by the spin-lattice relaxation measurements described above.
The dipolar-dephasing curve of aromatic protons C,D,N-saturated coal 601 (not shown) consists of three components: fast Gaussian, fast Lorentzian and slow Lorentzian. A single Gaussian dephasing component, with a dephasing time constant of 16 ps, was observed for the original (untreated) premium coal 601, as shown in Table 2. We can still identify one Gaussian dephasing component for rigid protons in the C,D,N-saturated coal, although the dephasing constant is a little larger (20 μs) than that in the original coal (16 μs). This means that some of the rigid aromatic structures in the C,D,N-saturated coal are essentially unperturbed by the addition of pyridine. However, a large fraction (45 – 60%) of the aromatic protons in the untreated coal are mobilized by pyridine saturation to show either fast or slow Lorentzian dephasing behaviors. When the temperature is increased from 25 °C to 90 °C, the dephasing time constant of the slow Lorentzian component of aromatic protons is significantly prolonged, from 4.3 to 11.0 ms, but the fraction of this component is essentially unchanged. The rigid Gaussian dephasing aromatic protons are apparently converted (partially) only to the fast Lorentzian dephasing component at 90 °C. This behavior will be discussed later on the mechanism of enhancement of molecular mobility by pyridine saturation.

Mechanism for Promoted Molecular Motion in C,D,N-Saturated Coal. As shown in Table 17, large fractions of protons in C,D,N-saturated premium coal 601 show Lorentzian dephasing behavior with dephasing time constants from 0.13 to 11 ms, even at 25 °C. However, the protons in the original (untreated) coal show only Gaussian dephasing behavior, with time constants smaller than 0.07 ms at temperatures up to 180 °C. The presence of very mobile Lorentzian dipolar-dephasing components in the C,D,N-saturated coal shows that pyridine-saturation is much more effective in promoting molecular motion than is thermal treatment. This result correlates well with the changes of macroscopic properties of coal with solvent-saturation or thermal treatment. For example, the uniaxial optical anisotropy of raw bituminous coal disappeared within a few seconds when the coal sample was immersed in pyridine at room temperature; but the anisotropy is not destroyed thermally until the temperature reaches around 350 °C. From the thermodynamics point of view, Brenner concluded, based on his study on the optical anisotropy of solvent-swollen coal, that pyridine-swollen coal behaves like a cross-linked rubber, while untreated coal behaves like a macromolecular glassy plastic. In fact, the Lorentzian dephasing time constants obtained in this study for C,D,N-saturated coals are much smaller than those expected for small molecules in liquid phases, but comparable with typical values for the mobile, amorphous phase of cross-linked semicrystalline polymers above the glass-rubber transition temperatures. Our results, obtained from direct detection of molecular dynamics, support Brenner’s thermodynamic view of solvent-swollen coal.

For all three types of protons (aromatic, non-methyl aliphatic, and methyl), both fast and slow Lorentzian dephasing components are identified in the dipolar-dephasing experiments. The dephasing time constants of fast Lorentzian components are between 0.13 and 0.25 ms; the time constants for fast Lorentzian dephasing components range from 4 to 11 ms. Compared with Gaussian dephasing time components, both Lorentzian dephasing components decay much slower than either of the Gaussian dephasing
components. The Lorentzian dephasing behavior is a characteristic of structures with substantial rotational mobility\textsuperscript{43}.

The fast Lorentzian dephasing component has a much more restricted rotational mobility than the slow Lorentzian dephasing component, as the dephasing time constant of the fast Lorentzian dephasing constant is an order of magnitude smaller than that of the slow component. According to equation (5), a typical dipolar-dephasing time of 10 ms for the slow Lorentzian dephasing components corresponds to an isotropic random molecular motion with a correlation time on the order of 0.03 $\mu$s, assuming the line width of protons in a rigid lattice is 35 kHz. So, the slow Lorentzian dephasing component corresponds to protons in structures with very high rotational mobility. Such structures could conceivably be assigned to small molecules, and to very flexible long side chains on the macromolecular network of coal. The fast Lorentzian dephasing component could also be assigned to protons in small molecules and side chains of macromolecular structures; however, for fast Lorentzian dephasing components, the rotational mobility of small molecules and side chains are limited to a certain extent by their environments, such as relatively tight-fitting voids around the substantially mobile structures. Another possible contributor to the fast Lorentzian dephasing component is from protons in macromolecular chain segments that undergo fast segmental reorientation. The presence of such segmental chain motion was confirmed by rapid reappearance of the optical anisotropy with pressures exerted on the pyridine-saturated coal\textsuperscript{43}.

The two Gaussian dephasing components found in C\textsubscript{5}D\textsubscript{5}N-saturated coal are comparable with the two Gaussian dephasing components observed in the original coal. The fast Gaussian dephasing component with a dephasing time constant of 10 - 20 $\mu$s corresponds to protons in the rigid lattice of coal structure. The slow Gaussian dephasing component with a dephasing time constant of 30 - 80 $\mu$s represents protons in structures with very limited anisotropic rotational mobility. In the literature\textsuperscript{3,12-14,94}, the fast Gaussian dephasing component was assigned as protons in the rigid macromolecular structure of coal. However, this may not be entirely appropriate, based on our results presented in Table 17. We can see that about half of the fast Gaussian dephasing component of non-methyl protons was converted to either slow or fast dephasing Lorentzian components with the moderate temperature increase from 25 °C to 90 °C. This means that the energy barrier that retains only about half of the population of the fast Gaussian dephasing protons in the rigid lattice at 25 °C is not much higher than kT at room temperature. Therefore, the view that all the protons that contribute to the fast Gaussian dephasing population are located in the rigid macromolecular structures is not convincing. Comparison of the change of fraction of fast Gaussian dephasing from the untreated coal to the C\textsubscript{5}D\textsubscript{5}N-saturated coal also leads to the same conclusion: that protons constituting the fast Gaussian dephasing characteristic are not entirely located in the rigid macromolecular structure. In fact, as seen by comparing results obtained at 25 °C and 90 °C in Table 17, at least half of such protons in the original coal can be converted by pyridine saturation to very mobile states with Lorentzian dephasing characteristics. This leads us to conclude that a substantial fraction of the fast Gaussian dephasing components in the original coal corresponds to protons in small molecules and long side chains of the
macromolecular structure. The mobility of the small molecules and the side chains are severely restricted by very tight-fitting voids around these relatively mobile structures in the original coal. Thus, in the absence of pyridine treatment, protons in these structures show rigid lattice behavior, just like protons in the rigid macromolecular structures in the original coal.

The rigid macromolecular structure in the original (untreated) coal is stabilized by intra- and inter-chain cross-links. Secondary interactions, such as hydrogen bonds and electrostatic bonds in charge-transfer complexes, play a very important role in stabilizing coal structure. Green studied bituminous coals whose hydroxyl groups had been acetylated. He concluded that there are about three times as many hydrogen bonding cross-links as covalent cross-links in the untreated coal samples studied. In exhaustively soxhlet-extracted coal samples, the cross-link density is less than half of the density in the unextracted coals.

Based on our results, the dramatically enhanced molecular mobility in coal brought about by pyridine saturation can be understood in terms of the following solvent/coal interaction mechanism. Pyridine molecules can effectively penetrate into the macromolecular network of the untreated coal by disrupting most of the hydrogen bonds and electrostatic bonds that cross-link and stabilize the macromolecular structure of coal. This causes significant swelling or expansion of the macromolecular network of coal. Small molecules and long side chains that are tightly confined in small voids in the coal structure are released and become a major component of the very mobile phase (slowly dephasing Lorentzian component) in pyridine-saturated coal. It is also possible that some small molecules are "attached" to the macromolecular structure of coal through hydrogen bonds or electrostatic interactions; these molecules can be detached from the macromolecular structure by pyridine. When the temperature is increased from 25 °C to 90 °C, the kinetic energy and mobility of pyridine molecules are significantly increased. So, pyridine molecules break more secondary interactions; thus more trapped small molecules are released at higher temperature and the void space is further enlarged. That is why the fraction of the very mobile phase in the pyridine saturated premium coal is significantly increased at higher temperature.

The key to understanding the enhanced mobility brought about by pyridine saturation is the expansion of void spaces in pyridine-swollen coals. It was reported that the average pore volume could increase twofold after pyridine saturation of bituminous coals. The increase in void space has several kinds of impact on the molecular mobility of coal. First, the increase of void space can dramatically lower the energy barrier that restricts the rotational mobility of small molecules and long side chains originally trapped in tight voids; the increased void space will substantially reduce steric hindrance of rotational motion. Enlarged void space also lowers intermolecular interactions between small molecules and the macromolecular matrix, as Van der Waals interactions are strongly distance dependent. The increased rotational mobility will effectively average out both intramolecular and intermolecular 1H-1H magnetic dipolar interactions. Second, the larger void space permits more isotropic motion of small molecules and side chains. This...
is also required for effective averaging of $^1$H-$^1$H dipolar couplings. Third, a larger void space means a longer average distance between protons in small molecules and protons in the rigid macromolecular matrix around the molecules. As the strength of $^1$H-$^1$H dipolar interactions is also strongly distance-dependent, the increased distance can effectively lower dipolar couplings between protons in small molecules and protons in the surrounding macromolecular matrix.

We think that it is the dramatically increased void space that leads to a dramatic increase in molecular mobility observed in pyridine-saturated coal. This new insight explains satisfactorily why much lower molecular mobility is induced by thermal treatments than by pyridine saturation. The thermal energy at temperatures up to 230 °C is not large enough to break either hydrogen bonding “bridges” or covalent bonding cross-links in macromolecular structures of coal. The macromolecular structure and void spaces are essentially unchanged when the temperature is increased from 25 °C to 230 °C. Thus, the energy barrier that restricts the motion of small molecules and side chains trapped in tight voids are essentially unchanged at temperatures up to 230 °C. When the temperature is increased, the fraction of small molecules and side chains that are able to overcome the energy barrier increases according to the Boltzman distribution. That explains why the fraction of the slow Gaussian dephasing component increases as the temperature is increased. However, these thermally induced motions are very restricted and anisotropic in nature, as the very tight void spaces in the untreated coal structure prohibit isotropic rapid rotational motion. That is why we do not observe a mobile Lorentzian dephasing behavior at temperatures as high as 180 °C. As we will see later, the proposed new model also explains well the different dipolar dephasing behaviors between the higher rank LVB coal and the lower rank HVB coal.

It is interesting to see how our measures of molecular mobility correlate with the measured size distribution of void spaces in pyridine saturated coal. Spears et al. studied changes in pore structures of premium coals using an electron paramagnetic resonance (EPR) spin probe method. Using nitroxide radicals of different sizes to determine the pore size distribution in solvent-swollen coals, they found that the shape of the pore in coals is cylindrical and a significant pore elongation occurred with pyridine saturation, even at room temperature. They used nitrooxide radicals with various skeletal chain lengths to investigate the size distribution of such cylindrical pores. The pore size distribution of pyridine-swollen lower rank coals, such as premium coal 301 and 601, exhibit clearly a bimodal size distribution. One maximum was found for a spin probe skeletal chain length of 11 carbon atoms, while another maximum was found for a chain length of 15 atoms at 25 °C. When the temperature was increased to 60 °C, the pore size distribution still showed a bimodal distribution, with one maximum unchanged at a chain length of 11 atoms and another maximum shifted to a chain length of 24 atoms. Their results correlate well with our finding of two Lorentzian dephasing components. The slow Lorentzian dephasing component could correspond to small molecules and side-chains in large pores created by pyridine swelling. It is possible that the fast Lorentzian dephasing component corresponds to small molecules and side chains in smaller pores that are larger than the voids in the original coal, but not large enough to allow a more
isotropic rotational motion. The further enlargement of large pores at higher temperatures is in agreement with the slight increase in the time constants of the slow Lorentzian dephasing component (Table 17).

There is actually a slight decrease in the dephasing time constants of the fast Lorentzian components when the temperature is increased from 25 °C to 90 °C, but the fractions of both slow and fast Lorentzian dephasing components increase with increasing temperature. These two observations may be explained as manifestations of the enlargement of existing pores and the creation of new pores at higher temperature. Enlargement of the small pores associated with the fast Lorentzian dephasing component will lead to an increase of the fraction of slow Lorentzian dephasing components. The creation of new, small pores will increase the fraction of fast Lorentzian components. Pores that can be created only at higher temperature are more likely in a rigid environment with a significant population of covalent cross-links, which can not be broken by pyridine. It is conceivable that such pores are smaller in size or less flexible than pores that are created in an environment that is rich in hydrogen bonding. This could be the reason why a smaller dephasing time constant is observed at higher temperature for the fast Lorentzian dephasing component.

We mentioned above that the fraction of the slow Lorentzian dephasing aromatic component is unchanged, but its time constant is increased, when the temperature is increased from 25 °C to 90 °C. The change in time constant is understandable on the basis of the above discussion. Aromatic structures are less flexible and perhaps typically larger than aliphatic structures in bituminous coals. Isotropic motion of aromatic structures requires a much larger free space. This explains why we observe a pronounced increase in the time constant for aromatic protons with slow the Lorentzian dephasing characteristic, but only a slight increase in the time constant for aliphatic protons at high temperature. The unchanged fraction of the slow Lorentzian dephasing aromatic component with increase of temperature from 25 °C to 90 °C could be due to difficulties associated with further enlargement of small pores created at 25 °C by pyridine saturation. Another possible explanation for the unchanged fraction of slow Lorentzian dephasing aromatic component is that the fast Lorentzian dephasing component of aromatic protons is mainly associated with segmental motion of mobile chains of the macromolecular structure. Such motion is not directly related to the sizes of pores.

Dipolar-dephasing behavior of Pyridine-Saturated Premium Coal 501. The high rank coal Pocahontas #3 (premium coal 501) has a much lower pyridine extractability than coal 601 discussed above. It is therefore interesting to compare the molecular mobility of premium coal 501 with that of premium coal 601 under pyridine saturation.

Figure 21 illustrates the stack plots of 1H CRAMPS spectra of C6D6N-saturated premium coal 501 obtained in dipolar-dephasing experiments at 25 °C and 90 °C. One can see that a small, but significant, fraction of the 1H NMR signal persists up to 6 ms, after a fast initial decay of the signal. In the dipolar-dephasing experiments on the original (untreated) premium coal 501, we did not get a detectable 1H NMR signal with a
dephasing time of 180 μs, even at 180 °C. This proves that a small but significant fraction of protons are effectively mobilized by pyridine saturation in coal 501. This is similar to what we observed from pyridine saturated premium coal 601. However, the fraction of mobilizable protons in C₅D₅N-saturated premium coal 501 is much smaller than that in premium coal 601. This is qualitatively in agreement with the fact that pyridine extractability of premium coal 501 is much lower than that of premium coal 601.

¹H CRAMPS spectra obtained with dipolar-dephasing times longer than 150 μs on C₅D₅N-saturated premium coal 501 show very high resolution of individual chemical functionalities in the mobile components, although spectral resolution of the ¹H CRAMPS spectra obtained with a short dephasing period is very poor. Significant spectral changes are observed in the aliphatic region of the dipolar dephased spectrum of C₅D₅N-saturated coal 501 when the temperature was increased from 25 °C to 90 °C. It appears as if the sharp mobile proton peak due to methyl groups has either disappeared or is severely broadened at 90 °C. Maybe some kind of broadening due to chemical exchange is responsible for the observed spectral change.

Quantitation of the dipolar-dephasing behavior of C₅D₅N-saturated premium coal 501 is very challenging because of very poor spectral resolution. As we discussed above, the ¹H CRAMPS spectrum of C₅D₅N-saturated premium coal 501 can be considered to be a superposition of a spectrum of mobile protons and a spectrum of rigid protons. The spectrum due to rigid protons can be obtained from the difference spectrum derived by subtraction of ¹H CRAMPS spectra obtained with a very short dipolar-dephasing period from one obtained with a dipolar dephasing time of 184.6 μs. In the ¹H CRAMPS spectrum obtained with a dipolar dephasing time of 184.6 μs, almost all the Gaussian dephasing components due to rigid protons have decayed away, while the signals due to mobile protons are hardly affected. This strategy was successfully used for deconvoluting ¹H CRAMPS spectra obtained with short dipolar-dephasing periods. A typical spectrum of rigid protons obtained from the subtraction is shown in Figure 16. Representative
spectral deconvolutions of the difference spectra and spectra of mobile protons are shown in Figure 17. As only two peaks can be resolved in the $^1$H CRAMPS spectra of rigid protons, we used the total areas of aliphatic components and the total areas of aromatic components to analyze the dipolar-dephasing data over the entire dephasing period. The resulting dipolar-dephasing curves of aliphatic and aromatic protons (not shown here) were analyzed using the model described in equation (14). The results from such graphical/numerical data analysis are presented in Table 18.

Table 18 Dipolar-dephasing time constants of aliphatic and aromatic protons in C$_5$D$_3$N-saturated premium coal 501$^{a,b}$.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>25</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic</td>
<td>Aromatic</td>
</tr>
<tr>
<td>$f_{GF}$ (%)$^a$</td>
<td>67</td>
<td>96</td>
</tr>
<tr>
<td>$T_{GF}$ (ms)$^b$</td>
<td>0.0091</td>
<td>0.013</td>
</tr>
<tr>
<td>$f_{GS}$ (%)$^a$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$T_{GS}$ (ms)$^b$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$f_{LF}$ (%)$^a$</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>$T_{LF}$ (ms)$^b$</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>$f_{LS}$ (%)$^a$</td>
<td>14</td>
<td>4.3</td>
</tr>
<tr>
<td>$T_{LS}$ (ms)$^b$</td>
<td>12</td>
<td>5.9</td>
</tr>
</tbody>
</table>

a) The fractions (%) of the four dephasing components are denoted as $f_{GF}$, $f_{GS}$, $f_{LF}$, and $f_{LS}$.
b) $T_{GF}$, $T_{GS}$, $T_{LF}$, and $T_{LS}$ denote the dipolar dephasing time constants of fast Gaussian, slow Gaussian, fast Lorentzian, and slow Lorentzian dephasing components, respectively.

The dipolar-dephasing curve of aromatic protons in pyridine-saturated coal 501 consists of only two dephasing components, a fast Gaussian and a slow Lorentzian, at both temperatures used in this study. The time constant for the Gaussian dephasing component in the C$_5$D$_3$N-saturated coal at both temperatures is the same within experimental errors as that measured for the original coal at 25 °C. This means that the rigid aromatic structures are essentially preserved under pyridine saturation. Only a very small fraction (4 - 5%) of the aromatic protons show slow Lorentzian dephasing behavior in the pyridine-saturated coal 501. The absence of other dephasing components with intermediate rotational mobility suggests that the aromatic structures are very rigid, with a high degree of covalent cross links, which can not be broken by pyridine. This is in agreement with the expected structure of a high rank LVB coal. When the temperature is increased from 25 °C to 90 °C, no significant changes in either the dephasing time constants or the fractions of the two dephasing components are observed. This further confirms the view that pyridine is not effective in mobilizing the aromatic structures in premium coal 501.
The aliphatic protons in C,D,N-saturated premium coal 501 show very interesting behaviors. At 25 °C, the dephasing curve of aliphatic protons consists of three types of dephasing components: fast Gaussian, slow Lorentzian and fast Lorentzian. In contrast to the very small changes discussed above for the aromatic structures, a significant fraction (32%) of the aliphatic protons are mobilized to show Lorentzian dephasing behavior at 25 °C when the coal is saturated with C,D,N. This implies that a significant fraction of the cross-links or “bridges” that constrain aliphatic structures in the untreated coal are due to hydrogen bonds. At 90 °C, the dephasing curve of aliphatic protons in pyridine-saturated coal 501 still consists of 3 types of dephasing components. However, the fast Lorentzian dephasing component observed at 25 °C has disappeared, and a slow Gaussian dephasing component was observed at 90 °C. It would appear that the fast Lorentzian dephasing component has changed back to a less mobile state at higher temperature; we don’t have a reasonable explanation for this observation at this stage. Further studies on more coal samples with similar ranks are needed to understand this observation.

Resolution Enhancement by Solvent Saturation. We have seen that spectral resolution enhancement of 1H CRAMPS spectra of coal can be realized by pyridine saturation. A comparison between room temperature 1H CRAMPS spectra of untreated and C,D,N-saturated samples for all 8 Argonne premium coals can be found in a paper by Jurkiewicz et al. The extent of resolution enhancement depends very much on the structure of an individual coal. In general, HVB and MVB coals show more dramatic resolution enhancement than coals of other ranks. The origin of such difference was not clearly understood in previous work.

The change in spectral resolution with variation of the dipolar-dephasing time really gives us a hint on this problem. For 1H CRAMPS spectra of C,D,N-saturated premium coal 501 and 601, the following observations were established:

(1) The spectral resolution of 1H CRAMPS spectra obtained with dipolar dephasing increases with the dipolar-dephasing time until it reaches about 180 μs. 1H CRAMPS spectra obtained with a dipolar-dephasing time of 180 μs show very good spectral resolution, irrespective of the resolution of 1H CRAMPS spectra obtained without a dephasing period. With a dephasing time longer than 180 μs, no appreciable change of spectral resolution can be observed beyond that achieved with a 180 μs dephasing period.

(2) All of the fine structure (such as identifiable sharp peaks and shoulders) in the 1H CRAMPS spectrum obtained without a dipolar dephasing period are preserved in the 1H CRAMPS spectra obtained with a dipolar dephasing period longer than 180 μs. In fact, these fine structure features are much easier to recognize in 1H CRAMPS spectra obtained with dipolar-dephasing periods longer than 180 μs, because of much better resolution.

(3) Almost all the fine structures seen in the 1H CRAMPS spectrum of a coal disappears in the difference spectrum obtained by subtracting the 1H CRAMPS spectrum obtained
with a dipolar-dephasing period of 180 μs from the \(^1\)H CRAMPS spectrum obtained without a dephasing period. The spectral resolution of the difference spectrum is comparable to that obtained on the untreated coal. Only two broad peaks, due to aliphatic and aromatic protons, are clearly recognizable from the difference spectrum.

The spectrum obtained with a dephasing period of 180 μs represents the spectrum of mobile protons with Lorentzian dephasing characteristics. Thus, the difference spectrum represents the spectrum of rigid protons in C\(_2\)D\(_3\)N-saturated coals. The \(^1\)H CRAMPS spectrum of C\(_2\)D\(_3\)N-saturated coal obtained without a dipolar-dephasing period can be considered as a superposition of a spectrum of rigid protons and a spectrum of mobile protons. This clean separation of the \(^1\)H CRAMPS spectrum into two distinct component types is understandable on the basis of results from \(^1\)H spin-exchange experiments. From the spin-exchange/diffusion experiments discussed later, we have proven that there is no observable spin exchange and/or spin diffusion between the rigid protons with Gaussian dephasing characteristics and the mobile protons with Lorentzian dephasing characteristics.

Based on these observations, we can conclude that the enhanced resolution of the \(^1\)H CRAMPS spectrum of a C\(_2\)D\(_3\)N-saturated coal has its origin in the high resolution \(^1\)H CRAMPS spectrum of the mobile protons showing Lorentzian dephasing characteristics. As we see below, this conclusion explains satisfactorily differences in the \(^1\)H CRAMPS resolution observed previously among C\(_2\)D\(_3\)N-saturated coals of various ranks.

In HVB coals, pyridine can effectively break the hydrogen bonding bridges that stabilize the macromolecular structures. The resulting severe swelling of coal structure converts a substantial portion of the proton containing moieties into very mobile states with Lorentzian dephasing characteristics. As the fraction of Lorentzian dephasing component is large, the overall \(^1\)H CRAMPS spectral resolution of a C\(_2\)D\(_3\)N-saturated HVB coal appears much higher than that of the corresponding untreated coal. In a high rank coal, such as a LVB coal, the bridging density from hydrogen bonding is very low. Therefore, pyridine can not effectively swell the macromolecular structure of a high rank coal, and only a very small fraction (~10%) of protons show Lorentzian dephasing behavior. The \(^1\)H CRAMPS spectrum of a C\(_2\)D\(_3\)N-saturated high rank coal is thus a superposition of a large, relatively low-resolution signal and a small, high-resolution signal. The overall resolution will not be much improved from that of the untreated coal.

Variable-Temperature \(^1\)H CRAMPS Study of the Pyridine Extraction Residue of Coal. The molecular/macromolecular (M/M) model of coal has been a subject of frequent debate in the literature\(^5\). Although the M/M model is widely accepted as a concept, the detailed nature of the molecular and macromolecular phases is still not fully understood. One of the best pieces of evidence supporting the M/M model at a molecular level is from solid-state \(^1\)H NMR studies of original and C\(_2\)D\(_3\)N-saturated coal samples. However, a direct correspondence between molecular mobility and the molecular phase has not been firmly established. There are many controversial issues among the results obtained using different NMR techniques. The existence of a molecular phase is directly
supported by solvent extraction studies of coals\textsuperscript{16}. Establishing a correspondence between the extractable fraction of coal and molecular mobility determined from NMR studies would be a major step in understanding the nature of the molecular and macromolecular phases in coal. Although there are many discussions and debates on this issue\textsuperscript{16,17}, it has not been settled.

In the study described here, we have seen that both untreated coal and C\textsubscript{5}D\textsubscript{3}N-saturated coal show very complicated molecular dynamics, which depends strongly on both the structure and the temperature of coal. Most previous NMR studies on solvent extraction were performed only at room temperature. However, solvent extraction is usually carried out near the solvent boiling point. It is not surprising to see many discrepancies generated from previous studies in the literature.

We here present comparative variable-temperature (VT) \textsuperscript{1}H CRAMPS studies on the C\textsubscript{5}D\textsubscript{3}N-extraction residue of premium coal 601. This study should improve our understanding of the M/M model and the relationship between molecular mobility and the M/M model.

**Variable-Temperature \textsuperscript{1}H CRAMPS Studies on Dried C\textsubscript{5}D\textsubscript{3}N-Extraction Residue.** According to the M/M model, the C\textsubscript{5}D\textsubscript{3}N-extraction residue would mainly consist of the macromolecular phase of coal. Comparative studies on the original coal and its extraction residue using VT dipolar-dephasing experiments will provide information on the molecular dynamics of both the macromolecular phase and the molecular phase in coal.

Figure 22 Stack plots of \textsuperscript{1}H VT CRAMPS spectra of the dried C\textsubscript{5}D\textsubscript{3}N-extraction residue of premium coal 601 obtained at (a) 25 °C, (b) 120 °C and (c) 180 °C. The BR-24 pulse sequence was used with a cycle time of 108 μs and a 90° pulse width of 1.2-1.3 μs. Each spectrum was acquired with 200 scans and a 3 s recycle delay. The MAS speed was between 1.5 and 1.8 kHz.
Experimental VT dipolar-dephasing $^1$H CRAMPS results on the original premium coal 601 were presented and discussed above. Figure 22 shows stack plots of $^1$H CRAMPS spectra of the dried C,D,N-extraction residue of premium coal 601 obtained from dipolar-dephasing experiments at temperatures of 25 °C, 120 °C and 180 °C. Similar to what we observed on the original coal, we do not see dramatic resolution changes in the $^1$H CRAMPS spectra of the dry residue at temperatures up to 180 °C. We can see that the dephasing rates are reduced at higher temperature. The dephasing rates of the dry residue appear to be higher than those of the original coal at 120 °C and 180 °C. This observation is qualitatively in agreement with the view that most of the rigid macromolecular structures are left in the extraction residue of coal. However, in both cases, there are no detectable signals left in spectra obtained with a dephasing time longer than 150 μs.

To extract dipolar-dephasing constants from the dipolar-dephasing experiments, the $^1$H CRAMPS spectrum of the dry residue obtained at each dipolar dephasing time was deconvoluted into aliphatic and aromatic peaks. Areas of the aliphatic and aromatic components were then used to construct experimental dipolar-dephasing curves. Each dipolar-dephasing curve can be simulated by a sum of two Gaussian decays, as described in equation (3). The dipolar-dephasing constants and fractions of both dephasing components obtained from the data analyses are summarized in Table 19.

Table 19 Dipolar-dephasing constants and fractions of fast and slow Gaussian dephasing components in the dried C,D,N-extraction residue of premium coal 601.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Aliphatic</th>
<th>Aromatic</th>
<th>Aliphatic</th>
<th>Aromatic</th>
<th>Aliphatic</th>
<th>Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>94</td>
<td>10</td>
<td>6</td>
<td>46</td>
<td>94</td>
<td>10</td>
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<td>120</td>
<td>89</td>
<td>10</td>
<td>11</td>
<td>73</td>
<td>89</td>
<td>10</td>
</tr>
<tr>
<td>180</td>
<td>80</td>
<td>11</td>
<td>20</td>
<td>76</td>
<td>77</td>
<td>13</td>
</tr>
</tbody>
</table>

The dependence of molecular mobility on the temperature in the C,D,N-extraction residue is qualitatively similar to that seen above for the original coal. As the temperature is increased, the fraction of the fast dephasing component decreases, and the fraction of
the slow dephasing component increases. This suggests that rigid structures in the residue are thermally activated at higher temperature and change to more mobile states. Comparing Table 3 with Table 19, one can clearly see that the increase in the fraction of slow dephasing components in the residue is much less than that in the original coal at 120 °C and 180 °C. This effect is much more pronounced for aromatic protons. For aromatic protons in the residue, the fraction of slow dephasing component is increased from 0% to 23% when the temperature is increased from 25 °C to 180 °C. Under the same conditions, the fraction of the slow dephasing component of aromatic protons in the original coal is increased from 0% to 66%. This may suggest that most of the mobile aromatic protons in the original coal are extracted by pyridine, while mobile aliphatic protons can not be extracted as easy as mobile aromatic protons. However, this interpretation may not be appropriate, since significant structural changes in the macromolecular phase of coal can be expected as a result of pyridine saturation.

Dephasing time constants of the fast decay component are mainly in the 9 - 16 μs range for both the original coal and the extraction residue at all three temperatures. The time constants of the slow decay component of the residue are 46 - 76 μs, a little bit larger than those of the original coal. However, the fractions of the fast decay component in the residue are much higher than those of the original coal for the higher temperatures (120 °C and 180 °C). This is in qualitative agreement with the view that most of the mobile components in the original coal are extracted by pyridine. As we will see in the discussion below, this kind of simple interpretation may not be entirely correct. We will see that the dipolar dephasing behavior of the residue may be better explained by structural changes in the entire coal (not just removal of mobile species) as a result of pyridine extraction.

One can assume that the inter-chain distances and void spaces in coals are dramatically increased with pyridine saturation. According to this view, after removal of small trapped molecules and pyridine from the large void space generated by drying under vacuum, a new structure is formed in the dried residue. In the dried residue, macromolecular chains and aromatic rings of the macromolecular network may get closer to each other after the collapse of the large void space formed during swelling. In particular, aromatic structures may get closer and better aligned, after the removal of small molecules between them. In fact, the dipolar-dephasing behavior of the aromatic component of the extraction residue of coal 601 is very similar to that of the untreated high rank LVB coal 501.

As discussed above, small molecules can be buried in small, very tight voids of coal and show very rigid behavior like that of the rigid macromolecular structures. However, with pyridine saturation, some of small molecules that are buried in small voids can be released and gain substantial rotational mobilities. Thus, molecular dynamics information obtained from NMR studies on the original (untreated) coal or the dried extraction residue can not be directly used to correlate the pyridine extractable components with components that show different molecular mobilities. We should emphasize this point here, because many confusions in the literature have arisen from a lack of awareness of this point.
Tekely et al. studied the $^1$H dipolar-dephasing behavior of untreated coal indirectly through $^{13}$C CP/MAS detection at room temperature$^{34,85}$. They concluded that the mobile component in untreated coal contains relatively more aromatic hydrogen than does the immobile component. This result was discussed in several papers as an example that seems to contradict the chemical composition of the solvent extract$^{34,98}$. The results of Tekely et al. were believed to be due to the inappropriate use of indirect detection of proton behaviors through the $^{13}$C CP/MAS experiment$^{98}$. However, as we have just discussed, the simple truth is that the relatively mobile protons detected in the untreated coal can not be directly related to the pyridine extractable component in coal. Although indirect detection via $^{13}$C CP/MAS may underestimate the amount of mobile protons to a certain extent, this does not mean that the conclusions drawn by Tekely et al. are not entirely appropriate. Our $^1$H dipolar-dephasing results, based on direct $^1$H CRAMPS detection, clearly show that the relative fractions of aliphatic and aromatic protons in mobile components of an untreated coal depend on both the structure and temperature of the coal sample. For untreated HVB coals, the fractions of aromatic protons in mobile components are higher at 180 °C than that of mobile aliphatic protons. For untreated LVB coal, the fraction of aromatic protons in mobile components is lower than that of mobile aliphatic protons for temperatures up to 180 °C. There is no simple correlation between molecular mobility in an untreated coal and the pyridine extractable components of the coal.

To make more direct comparison of pyridine extractable components and molecular mobility, we discuss next VT $^1$H CRAMPS results obtained on the pyridine saturated residue of premium coal 601.

C$_{3}$D$_{5}$N-Saturated Extraction Residue of Premium Coal 601. The chemical functionality obtained from $^1$H VT CRAMPS spectra of the C$_{3}$D$_{5}$N-saturated residue of premium coal 601 was discussed earlier. All the types of protons that can be identified from the $^1$H CRAMPS spectrum of the C$_{3}$D$_{5}$N-saturated coal are present in the $^1$H CRAMPS spectrum of the C$_{3}$D$_{5}$N-saturated residue. However, the relative fraction of each type of protons is changed by pyridine extraction. The fraction of aliphatic protons in the residue is lower than that in the original coal. This is in agreement with the well established view that small aliphatic molecules are preferentially transferred to the extract$^6$.

Figure 23 presents stack plots of $^1$H CRAMPS spectra of C$_{3}$D$_{5}$N-saturated residue obtained from dipolar-dephasing experiments at 25 °C and 90 °C. One can clearly see that there are still significant quantities of very mobile components left in the extraction residue of coal 601. This means that not all of the mobile protons are extractable from the original coal. Comparing Figures 23 and 20, we can see that the aliphatic proton magnetization in the C$_{3}$D$_{5}$N-saturated residue dephases much faster than that in the C$_{3}$D$_{5}$N-saturated coal. This suggests that pronounced molecular dynamical changes occur in the aliphatic structure of residue as a result of extraction.
The dipolar-dephasing data were processed using a procedure similar to that described above. As the overall resolution of \(^1\)H CRAMPS spectra of the C\(_5\)D\(_5\)N-saturated residue is lower than that of the C\(_5\)D\(_3\)N-saturated original coal, a reliable deconvolution between the methyl peak (1.0 ppm) and the non-methyl aliphatic component (1.7 ppm) can not be realized over the whole dephasing period. Therefore, we combined the peak areas of these two peaks into the area for aliphatic protons, and on this basis the quantitative analysis of the dipolar-dephasing behavior was performed in terms of aliphatic protons and aromatic protons in the C\(_5\)D\(_5\)N-saturated residue. An example of the peak deconvolution of \(^1\)H CRAMPS spectrum of the C\(_5\)D\(_5\)N-saturated residue is shown in Figure 19. The experimental dipolar-dephasing curves (not shown here) for aliphatic and aromatic protons were fitted with a model described in equation (14). The dipolar-dephasing time constant and the fraction of each dephasing component obtained from the data analysis are summarized in Table 20.

The dipolar-dephasing curves for aliphatic protons in the C\(_5\)D\(_5\)N-saturated extraction residue of premium coal 601 consist of four components: fast Gaussian, slow Gaussian, fast Lorentzian, and slow Lorentzian. There are still 16\% of mobile Lorentzian dephasing aliphatic components left in the extraction residue at 25 °C. This clearly demonstrates that not all of the very mobile components with Lorentzian proton dephasing characteristic can be completely extracted. However, the fractions of fast and slow dephasing Lorentzian components in the C\(_5\)D\(_5\)N-saturated residue are dramatically decreased as a result of pyridine extraction. At 90 °C, \(f_{LF}\) and \(f_{LS}\) of the aliphatic protons in the C\(_5\)D\(_3\)N-saturated coal 601 are 33\% and 34\%, respectively. At the same temperature, these two fractions in the C\(_5\)D\(_3\)N-saturated residue are reduced to 13\% and 7\%, respectively. Clearly, the slow Lorentzian dephasing component is preferentially extracted because of its high mobility. When the temperature is increased from 25 °C to 90 °C, about 8\% of the fast Gaussian component of aliphatic protons change to more mobile states in the C\(_5\)D\(_3\)N-saturated residue. With the same temperature increase, 29\% of the fast Gaussian component change to Lorentzian dephasing components in the C\(_5\)D\(_3\)N-saturated coal. This means that the aliphatic structures left in the C\(_5\)D\(_3\)N-saturated residue are more rigid than those in the C\(_5\)D\(_3\)N-saturated original coal 601. The fractional
change of the fast Gaussian dephasing component with change in temperature suggests that a significant fraction of the small molecules present in coal are buried in a rigid macromolecular matrix, and they can be released with an increase of temperature. As most such small molecules are transferred to the extract during extraction, there is a much smaller amount of small molecules left in the rigid macromolecular matrix of the residue than was present in the original coal. This explains why a much smaller fractional change of the fast Gaussian component of aliphatic protons is observed with an increase in temperature in the C5D3N-saturated residue than is the case in the C5D3N-saturated original coal.

Table 20 Dipolar-dephasing time constants and fractions of various types of protons in the C5D3N-saturated extraction residue of premium coal 601.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>25</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic</td>
<td>Aromatic</td>
</tr>
<tr>
<td></td>
<td>fGF (%)</td>
<td>fGS (%)</td>
</tr>
<tr>
<td>TGF (ms)</td>
<td>63</td>
<td>22</td>
</tr>
<tr>
<td>TGS (ms)</td>
<td>0.011</td>
<td>0.019</td>
</tr>
<tr>
<td>TLF (ms)</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>TLS (ms)</td>
<td>0.020</td>
<td>0.012</td>
</tr>
</tbody>
</table>

a) The fractions (%) of the four dephasing components are denoted as fGF, fGS, fLF, and fLS.
b) TGF, TGS, TLF, and TLS denote the dipolar dephasing time constants of fast Gaussian, slow Gaussian, fast Lorentzian and slow Lorentzian dephasing components, respectively.

Just as in the case for aromatic protons in the C5D3N-saturated coal, the dipolar-dephasing curves of aromatic protons in the C5D3N-saturated residue can be modeled with three dephasing components: fast Gaussian, fast Lorentzian and slow Lorentzian. At 90 °C, the fractions of these three dephasing components in the C5D3N-saturated residue are close to those in the C5D3N-saturated coal. As expected, the fLS value of aromatic protons in the C5D3N-saturated residue is lower than fLS of the C5D3N-saturated coal. But this difference is much less pronounced than that for aliphatic protons. This suggests that the aromatic structures are not changed as significantly as aliphatic structures by pyridine extraction. In particular, the fLF value measured in the extraction residue at 90 °C is essentially unchanged by pyridine extraction. This suggests that the fast Lorentzian dephasing component of aromatic protons is essentially non-extractable. This component may be due to aromatic structures in macromolecular chains that undergo mobile segmental motion. It is also possible that this component corresponds to aromatic...
structures in flexible side chains that are attached to the macromolecular network through single covalent bonds. We see later that the former possibility is more plausible.

**Correspondence between Extractable Components and Molecular Mobilities.** As the ratio of aliphatic to aromatic protons in the pyridine extraction residue is much lower than in the untreated coal, a comparison of the fractional changes of different components based on the total number of protons of each major type (aliphatic and aromatic) in the sample should be informative. The relative fractions of each component listed in Tables 17 and 20 were converted to fractions relative to the total number of aliphatic and aromatic protons in the original coal and in the residue, respectively. Tables 21 and 22 list all the converted fractions of the various components in the C₅D₅N-saturated coal and C₅D₅N-saturated residue.

Table 21 Fraction (%) of various types of protons in the C₅D₅N-saturated premium coal 601. $F_{GF}$, $F_{GS}$, $F_{LF}$, and $F_{LS}$ are fractions of fast Gaussian, slow Gaussian, fast Lorentzian and slow Lorentzian dephasing components, respectively, relative to the total number of protons in premium coal 601.

<table>
<thead>
<tr>
<th></th>
<th>$F_{GF}$ (%)</th>
<th>$F_{GS}$ (%)</th>
<th>$F_{LF}$ (%)</th>
<th>$F_{LS}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>Aliphatic</td>
<td>38</td>
<td>7.7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>16</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>90°C</td>
<td>Aliphatic</td>
<td>20</td>
<td>3.6</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>11</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 22 Fraction (%) of various types of protons in the C₅D₅N-saturated residue of premium coal 601. $F_{GF}$, $F_{GS}$, $F_{LF}$, and $F_{LS}$ are fractions of fast Gaussian, slow Gaussian, fast Lorentzian and slow Lorentzian dephasing components, respectively, relative to the total number of protons in the residue (100%).

<table>
<thead>
<tr>
<th></th>
<th>$F_{GF}$ (%)</th>
<th>$F_{GS}$ (%)</th>
<th>$F_{LF}$ (%)</th>
<th>$F_{LS}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>Aliphatic</td>
<td>31</td>
<td>11</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>35</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>90°C</td>
<td>Aliphatic</td>
<td>27</td>
<td>12</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>25</td>
<td>-</td>
<td>24</td>
</tr>
</tbody>
</table>
In order to compare the number of protons of each component between Tables 21 and 22, we need to set a common base. The fractions in Table 22 can be scaled down according to the extraction yield, using the total number of protons in the original coal as a common base (100%). Nishioka studied the pyridine extraction yield of premium coals of various ranks. The pyridine extraction yields of extract for HVB coals were determined to be from 37 - 44 wt % on the dried ash free (daf) basis. As we employed the same extraction procedure as Nishioka did, we chose a value of 40% for the extraction yield to generate the figures in Table 23, which lists the fractions of each component in C,D,N-saturated residue on the basis of the total number of protons in the original coal.

Table 23 Fractions (%) of various types of protons in the C,D,N-saturated residue on the basis of total number of protons in the original coal (100%), as scaled by the extraction yield of 40%.

<table>
<thead>
<tr>
<th></th>
<th>F_{GF} (%)</th>
<th>F_{GS} (%)</th>
<th>F_{LF} (%)</th>
<th>F_{LS} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>Aliphatic</td>
<td>19</td>
<td>6.6</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>21</td>
<td></td>
<td>7.8</td>
</tr>
<tr>
<td>90°C</td>
<td>Aliphatic</td>
<td>16</td>
<td>7.2</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>15</td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>

A correlation between molecular mobility and extractable components can be established directly by comparing Tables 21 and 23. As 90 °C is very close to the soxhlet extraction temperature that we used (~ 95 °C), fractional changes of the various categories of protons at 90 °C should be more meaningful than at some other temperatures. Considering the experimental errors involved in the fractions and uncertainties in the extraction yield, we will not emphasize small changes in fractions in the following discussion.

Fast Gaussian dephasing components in coals correspond to very rigid structures that lack substantial molecular motion. The slow Gaussian dephasing component is due to rather rigid structures with very limited anisotropic motion. Previously, the Gaussian dephasing components have always been assigned in the literature as protons in the rigid macromolecular phase of coal and have been regarded as unextractable components. The results presented in Tables 21 and 23 clearly show that this interpretation is not entirely correct.

In the C,D,N-saturated premium coal 601, 46% of the protons are aliphatic protons with Gaussian dephasing characteristics at 25 °C. After pyridine extraction, only 30% of the original aliphatic protons remain in the residue. This clearly proves that a significant
fraction of the protons that show Gaussian behavior at 25 °C are extracted. This further confirms our conclusion that a significant quantity of small molecules are buried in tight voids of the macromolecular matrix of the untreated coal. When the temperature of a pyridine-saturated coal is increased from 25 °C to 90 °C, the small voids in the rigid macromolecular matrix can be enlarged by thermally more energetic pyridine molecules. This leads to a further release of small molecules that had been trapped in the rigid macromolecular structures at 25 °C. A pronounced increase of the fraction of Lorentzian components in the C₅D₅N-saturated premium coal 601 at 90 °C can be seen in Table 7.

One can also see from Tables 7 and 9 that the number of protons showing Gaussian dephasing behaviors in the C₅D₅N-saturated coal at 90 °C is close to that in the C₅D₅N-saturated residue at 90 °C. Considering the fact that 90 °C is close to the extraction temperature used in this work, this result suggests that almost all of the small molecules that can be mobilized by pyridine under extraction conditions are already mobilized in the C₅D₅N-saturated coal at 90°C. It is well known that the pyridine extraction process is very slow and that refluxing with frequently refreshed solvent is needed to achieve high yields. Based on the above results, it seems that mobilization of small molecules is not a rate determining step in the extraction. The extraction rate seems to be mainly determined by molecular diffusion from enlarged pores to the liquid phase. The number and weight averages of molecular weight of the pyridine extract of HVB coals were determined to be on the order of 600 and 1600, respectively, using size exclusion chromatography. So, the average sizes of extracted molecules are much larger than that of pyridine molecules. Pyridine could easily diffuse into rigid structures, break hydrogen bonds around small molecules, and create large pores inside the rigid macromolecular matrix. However, the mobilized molecules may not be able to diffuse out as easy as pyridine diffuses in. Therefore, the extractability of coal depends not only on the sizes of pores but also on the connectivity of pores created by pyridine swelling. As the dipolar-dephasing time constant reflects mainly the rotational mobility of a molecule, the dephasing constant will depend mainly on the size of the pore in which the molecule is located, and is not very sensitive to the connectivity of pores. Connectivity could be a factor that contributes to unextractable Lorentzian components.

As can be seen from Tables 21 and 23, most of the slow Lorentzian components, for both aliphatic and aromatic protons, are extracted by pyridine. This implies that large pores tend to have good pore connectivity in the C₅D₅N-saturated coal. Based on the above discussion, the extractability of slow Lorentzian components suggests that there exist large domains in premium coal 601 that are relatively rich in hydrogen bonding bridges.

Most of the aliphatic protons in the C₅D₅N-saturated premium coal 601 with fast Lorentzian dephasing characteristics are also extracted by pyridine, but to a smaller extent than those with slow Lorentzian dephasing characteristics. However, the fast Lorentzian dephasing component of aromatic protons is not effectively extracted. We think that this component is likely due to mobile chains of the aromatic structures with segmental motion. This conclusion is based on the fact that the extraction residue can still
be effectively swollen by pyridine, yielding a material with rubber-like behavior, suggesting that the macromolecular chain segments are still very mobile. As shown in Table 22, the fraction of the fast Lorentzian dephasing aromatic component is much higher than that of other Lorentzian dephasing components (fast or slow Lorentzian aliphatic components). Segmental motion of the mobile macromolecular chains is most probably manifested in dipolar-dephasing experiments as aromatic protons with fast Lorentzian dephasing components. As discussed above, this assignment is also consistent with the fact that the fast Lorentzian dephasing component of aromatic protons in the C₃D₃N-saturated coal can not be further converted to slow Lorentzian components when the temperature is increased from 25 °C to 90 °C.

In contrast to premium coal 601, there is no identifiable fast Lorentzian dephasing component in C₃D₃N-saturated premium coal 501. This difference between the coals is related to structural differences between HVB and LVB coals. The macromolecular structure of a HVB coal is believed to consist of relatively small aromatic units connected by flexible aliphatic cross-links. Hydrogen bonding bridges will further stabilized the macromolecular network and make it rather rigid. When the hydrogen bonding bridges are broken by pyridine, the aromatic structure in the macromolecular chain could gain substantial segmental mobility in HVB coals. In LVB coals such as 501, the aromatic units are much larger, and connected by shorter and less flexible cross-links; this makes the aromatic structure much more rigid, so it can not be effectively mobilized by pyridine.

In summary, VT ¹H CRAMPS studies are very powerful for elucidating dynamical and structural details of pyridine/coal interactions. With comparative studies on a C₃D₃N-saturated coal and its extract, a correlation between pyridine extractable component and molecular mobility can be established. The following conclusions can be drawn from this study:

(1) Molecular mobilities determined for an untreated coal or a dried extraction residue can not be directly related to either the solvent-extractable components of the coal or the molecular/macromolecular phases in coal.

(2) Molecular mobility in coal depends very strongly on temperature. Without systematic variable temperature studies, correlation between molecular mobility and extractable components can not be correctly established by NMR. NMR experiments performed at the extraction temperature provide a more direct correlation between molecular mobility and extractable components than do comparisons of room-temperature results.

(3) Gaussian dephasing components (dephasing time constants: 10 - 80 μs) determined from ¹H NMR measurements on a C₃D₃N-saturated coal could be partially due to small molecules buried in tight voids of the macromolecular matrix. Such small molecules can be extracted by pyridine.
(4) Most of the component corresponding to aliphatic protons with Lorentzian dephasing characteristics (dephasing time constants: 0.13 - 10 ms) in C$_2$D$_3$N-saturated premium coal 601 at 90 °C can be extracted by pyridine. The component corresponding to aromatic protons showing fast Lorentzian dephasing behavior (time constants: 0.2 - 0.3 ms) is largely unextractable. This dephasing component may correspond to aromatic structures in macromolecular chains that undergo segmental motion.

**The M/M Model of Coal and Molecular Mobility.** Our variable temperature studies on both untreated coal and C$_2$D$_3$N-saturated coal support the basic idea of the M/M model. However, the relationships between the M/M model and molecular dynamics is much more complicated than expected.

A significant fraction of the very rigid component is always detected in our $^1$H CRAMPS experiments on coal, no matter whether the coal sample is under thermal treatment or pyridine-saturation. The existence of this rigid component could conceivably be attributed to the existence of a highly cross-linked macromolecular structure. However, this rigid component is not equivalent to the macromolecular component in coal. In this work, we have, for the first time, proposed and proven that small molecules can be buried in tight voids of the macromolecular matrix of coal and show dynamical behavior that is similar to that of rigid molecules, even when the coal is saturated with pyridine. Our work also suggests that the macromolecular network of coal can undergo mobile segmental motion with pyridine saturation, and thus show Lorentzian dephasing behavior with dephasing time constants as long as 0.3 ms.

The molecular phase in coal shows even more complicated dynamical behavior than exhibited by the macromolecular phase. Our work demonstrates that extractable small molecules in coal can, in principle, exhibit any kind of molecular dynamical behavior, depending on the structure and surrounding matrix of the molecule and the sample temperature.

A problem that has been discussed many times in the literature is whether the mobile components in coal detected by NMR overestimate the fraction of a molecular phase in coal. However, our results show that there is no simple one-to-one correspondence between the molecular phase and molecular dynamics. Without a systematic variable-temperature study of coal under a variety of conditions, a definite answer can not be obtained. And, it is unlikely that there will be a universal answer for coals of different ranks and origins. As small molecules can be buried in tight voids of the macromolecular matrix of coal, some of these molecules may not be mobilized without breaking covalent bonds of the macromolecular structure. Once the covalent bonds are broken, there will be a very small chance of distinguishing the small molecules that are buried inside the coal matrix of an untreated sample from small molecules that are formed by the breakdown of the macromolecular network. In this regard, the conceptual molecular phase may never be completely detected experimentally. However, the M/M model is
still very useful as a working hypothesis for stimulating further studies on the complex structure of coal.

\(^1\)H-\(^1\)H spin exchange in coal

**Introduction.** The spatial structural heterogeneity of coal can be probed indirectly by these time-domain experiments because of the existence of efficient \(^1\)H-\(^1\)H spin-diffusion in coals. However, the kinds of indirect studies of the \(^1\)H-\(^1\)H spin-diffusion process presented above usually provide only qualitative information on structural heterogeneity. The direct study of the \(^1\)H-\(^1\)H spin-diffusion process can provide further details on the structural heterogeneity of coal.

Both 1D and 2D \(^1\)H-\(^1\)H spin-exchange experiments have been successfully used to investigate the heterogeneity of polymers on the spatial scale from 10 to 2000 Å. These techniques have been proven to be very powerful tools for estimation of domain sizes in polymer blends. However, there have been very few publications devoted to the direct study of \(^1\)H-\(^1\)H spin-exchange processes in coal. This is perhaps partly due to the fact that the chemical structures of coal are much more complicated and heterogeneous than those of synthetic polymers.

Tekely et al. used a modified Goldman-Shen pulse sequence with indirect \(^{13}\)C CP/MAS detection to study spin-diffusion between rigid and mobile protons in an untreated French coal sample. This study showed some potential for utilizing \(^1\)H-\(^1\)H spin-diffusion information in coal studies, although the simple 1D spin-exchange experiment employed did not give conclusive results on the complicated spin-diffusion process in coal. The indirect \(^{13}\)CP/MAS detection used in their study is also a questionable feature. Although a short contact time of 100 \(\mu\)s was used in their study, we have shown in this work that significant \(^1\)H-\(^1\)H spin-diffusion occurs within 100 \(\mu\)s in untreated coal samples, possibly scrambling the information detected via \(^{13}\)C NMR.

Barton et al. applied experiments of the type used by Edzes and Samulski with \(^1\)H wide line detection to \(C_3D_2N\)-imbibed bituminous coal samples. They used a dipolar-dephasing time of 60 \(\mu\)s to select relatively mobile proton species in \(C_3D_2N\)-saturated coal and concluded that mobile protons can rapidly spin-exchange with rigid protons within 10 ms. According to the dipolar-dephasing studies on \(C_3D_2N\)-saturated coal described above, up to four distinctively different dipolar-dephasing constants can be identified for protons in \(C_3D_2N\)-saturated coal. Although a dipolar-dephasing time of 60 \(\mu\)s can eliminate almost all of the fast Gaussian dephasing component, a significant fraction of quite rigid protons that show slow Gaussian dephasing behavior are still retained in the signal. The spin-exchange process observed by Barton et al. may result only from exchange among relatively rigid proton species.

Spin-exchange measurements among protons of different chemical functionalities would be very useful for studying chemical structural heterogeneity in coal. \(^1\)H wide line
detection is certainly unable to supply such valuable information. Knowledge of the spin-exchange processes in coal has been very limited. Expanding our knowledge in this area should provide valuable insights into the structural heterogeneity of coal. Therefore, we carried out the first 1D and 2D $^1\text{H}^-\text{H}$ spin-exchange studies of coals based on $^1\text{H}$ CRAMPS detection. In this study, we designed and implemented a new 2D spin-exchange pulse sequence, which is able to probe complicated spin-exchange pathways among protons with different mobilities and chemical shifts.

$^1\text{H}^-\text{H}$ Spin-Exchange Process. Both $^1\text{H}^-\text{H}$ spin-diffusion and $^1\text{H}^-\text{H}$ chemical exchange can be probed by a $^1\text{H}^-\text{H}$ spin-exchange experiment. We use the term “spin-exchange” here to represent both the effects of $^1\text{H}^-\text{H}$ spin-diffusion and chemical exchange. Although both processes can facilitate $^1\text{H}^-\text{H}$ magnetization transfer, the underline physical processes are totally different. Chemical exchange occurs between pairs of labile protons that are close together and are able to exchange their chemical environments (chemical shifts) via a chemical reaction or a conformation change. Efficient long-distance chemical exchange is also possible through a network of hydrogen bonding. In an untreated (original) coal, $^1\text{H}^-\text{H}$ chemical exchange is unlikely to be a significant contributor to $^1\text{H}^-\text{H}$ spin-exchange process. In pyridine-saturated coals, chemical exchange could be significant, but is unlikely to be the dominant process of spin-exchange. The rate of chemical exchange would usually increase by thermal activation, but spin-diffusion would usually slow down at high temperature due to enhanced efficiency in the averaging of dipolar-couplings. Variable temperature experiments should in principle be able to separate effects of spin-exchange from spin-diffusion.

Spin diffusion is expected to be the dominant $^1\text{H}^-\text{H}$ spin exchange mechanism in rigid, proton-rich solids, like coals. In the following discussion, we focus on the spin diffusion process. Contrary to what is suggested by the term “diffusion”, spin-diffusion can be a coherent, reversible process. It is driven by the homonuclear dipolar Hamiltonian$^{110,113,114}$. For a pair of spin $\frac{1}{2}$ nuclei, the secular term of the homonuclear dipolar Hamiltonian reads

$$H_D = \omega_D (3I_x I_x - \vec{I}_1 \cdot \vec{I}_2),$$

where

$$\omega_D = -\frac{\mu_0}{4\pi} \gamma^2 \hbar \frac{1}{2} \frac{3\cos^2 \theta - 1}{r^3}$$

If we express $H_D$ in terms of raising and lowering operators, we get:

$$H_D = \omega_D \left[ 2I_x I_x - \frac{1}{2} (I_1^+ I_2^- + I_1^- I_2^+) \right]$$

The term $(I_1^+ I_2^- + I_1^- I_2^+)$ is usually called the flip-flop term. The flip-flop transition of two dipolar-coupled spins is an energy-conserving process. Considering the case in which only one of two spins is initially polarized, or the initial density operator is given by $\rho(0)$
the time evolution of \( \rho(0) \) under \( H_0 \) is governed by the propagator \( \exp(-iH_0t) \). As \((I_{iz} I_{2z})\) and \((I_{iz} I_{2z}^* + I_{iz} I_{2z}^+ )\) commute, we can simplify the propagator as follows:

\[
\exp(-iH_0t) = \exp\left[ -i\frac{\omega_D}{2} (I_{iz} I_{2z}^* + I_{iz} I_{2z}^+)\right] \exp\left[ -i\omega_D (2I_{iz} I_{2z})t \right].
\]

Since \( \exp(-i\omega_D 2I_{iz} I_{2z}t) \) commutes with \( I_{iz} \), the evolution of \( \rho(0) \) will be affected only by the flip-flop term. The following expression for the evolution of \( \rho(0) \) can thus be derived:\(^\text{12}\)

\[
\exp(-iH_0t)I_{iz} \exp(iH_0t) \rightarrow I_{iz} \left\{ \frac{1}{2} (1 + \cos \omega_D t) + I_{2z} \frac{1}{2} (1 - \cos \omega_D t) \right\} + \left( I_{1y} I_{2x} - I_{1x} I_{2y} \right) \sin \omega_D t
\]

This means that homonuclear polarization transfer \( I_{iz} \rightarrow I_{2z} \) is realized via energy-conserving flip-flop processes.

Spin systems with spatially inhomogeneous \( z \) magnetization will evolve under the total dipolar Hamiltonian to minimize the \( z \) magnetization gradient through successive spin flip-flops. This coherent process is called spin-diffusion. From equation (19), one sees that the transfer of \( z \) magnetization via spin flip-flops produces oscillations in a two-spin system. For spin system with large number of spins, the complicated coupling network cancels the oscillations and produce a diffusive behavior.\(^\text{10}\)

**Spin-Diffusion Equation.** For a large network of dipolar coupled spins, the effect of successive energy-conserving spin flip-flops can be described by a diffusion equation. For a radial spin diffusion process with an isotropic diffusion coefficient \( D \), the diffusion equation reads:\(^\text{15,116}\)

\[
\frac{\partial m(r,t)}{\partial t} = D \frac{\partial^2 m(r,t)}{\partial r^2}
\]

where \( m(r,t) \) represents magnetization at the radial position \( r \) and at the arbitrary moment of time \( t \). If the diffusion process is spherical starting from a point source at \( r = 0 \), the solution of equation (5.5) is:\(^\text{115}\)

\[
m(r,t) = \frac{m_0}{8\pi D \frac{r^2}{4Dt}} \exp(-r^2/4Dt)
\]

where \( m_0 \) is the total magnetization.

The mean square distance \(<r^2>\) that the magnetization has moved from the point source during the time \( t \) can be calculated from equation (5.6) as:\(^\text{116}\)
which permits us to use spin diffusion measurements to estimate finite domain sizes.

Of course, the spherical diffusion model is a simplified model of a real system. A more realistic model would include various morphologies, dimensionalities, and a distribution of diffusion time constants in the system. Many efforts have been devoted to develop various spin diffusion models for polymer systems. As the structure of coal is much more complicated and heterogeneous than that of a synthetic polymer, at this stage, the information available is not enough for one to decide what kind of model is suitable for describing the spin diffusion process in coal quantitatively. Extensive experimental and theoretical work is needed to clarify this issue. Although the spherical diffusion model is simple, it does predict important spin-diffusion features which are in good agreement with much more sophisticated models. In this report, this model is used for semi-quantitative estimation of structural heterogeneity in coal.

Spin-Diffusion Coefficients. In order to obtain information on domain size and morphology of a heterogeneous system, spin-diffusion coefficients must first be evaluated. If the morphology of a heterogeneous system is well defined, the spin-diffusion coefficient can be directly determined experimentally from spin-diffusion experiments on the system. So far, there have been no direct experimental determinations of spin-diffusion coefficients on any coal samples.

Fortunately, spin-diffusion coefficients can be estimated indirectly from other experimental parameters. For a powder sample, the spin-diffusion coefficient $D$ can be expressed in terms of local dipolar field as

$$ D = \sqrt{\frac{\pi}{60}} \langle d^2 \rangle B_L $$

where $\langle d^2 \rangle$ is the mean square distance between the nearest spins and $B_L$ is the local magnetic field strength, due to local perturbations, expressed in the laboratory frame. If $B_L$ is completely determined only by the contribution from dipolar interactions, $B_L$ can be estimated as

$$ B_L^2 = \frac{5}{3} M_2 $$

where $M_2$ is the second moment of the NMR absorption line for a powder sample in a high magnetic field.

The second moment can be estimated directly from the dipolar-dephasing constant $T_{dd}$. For a Gaussian line shape,
\[ M_2 = \frac{1}{T_{dd}^2} \]

For a Lorentzian line shape, the integral diverges. However, truncation of the integral to the range \(-\alpha < \omega < \alpha\), where \(\alpha\) is a cut-off frequency, can give a pseudo-second moment:

\[ M_2 = \frac{2\alpha}{\pi T_{dd}} = \frac{\beta}{\pi T_{dd}^2}, \]

where \(\beta\) is defined as \(\beta = 2\alpha T_{dd}\), which is a ratio of the frequency cut-off range \(2\alpha\) over \(1/T_{dd}\). As a Lorentzian peak intensity drops below 1% of its maximum value when \(\beta > 10\), we use \(\beta = 10\) to estimate the \(M_2\) value of a Lorentzian line. Diffusion coefficients for Gaussian and Lorentzian dephasing components can thus be estimated from dipolar-dephasing time constants via the following equations:

\[ D_G = \frac{\sqrt{\pi} \langle d^2 \rangle}{6 T_{dd}} \]

and

\[ D_L = \frac{\sqrt{\beta} \langle d^2 \rangle}{6 T_{dd}}. \]

As the exact molecular structure of coal is unknown, it is impossible to accurately estimate \(\langle d^2 \rangle\). However, a semi-quantitative estimation of \(\langle d^2 \rangle\) can be made from the known proton density of coal. Taking a typical value of hydrogen content of 5 wt% (dmmf: dry mineral matter free) and a density of 1.2 g/cm³, a dmmf hydrogen volume percentage of about 6% (dmmf, cm³) in coal is obtained. \(\sqrt{\langle d^2 \rangle}\) can then be estimated as about 3 Å, assuming a cubic lattice of protons.

For the fast Gaussian dipolar-dephasing components in coal, a typical dephasing time constant is 10 μs. The spin-diffusion coefficient can then be estimated as \(2.7 \times 10^{-11}\) cm²/s. For the slow Gaussian dephasing component with a dephasing time constant of 50 μs, the spin diffusion coefficient is about \(5.3 \times 10^{-12}\) cm²/s according to Equation (27). In many organic polymer systems, \(D\) is on the order of \(10^{-11}\) to \(10^{-12}\) cm²/s. For example, \(D\) for a diblock copolymer of poly(styrene) and poly(methylmethacrylate) was determined to be \(8 \times 10^{-12}\) cm²/s; for polyethylene, \(D = 6.2 \times 10^{-12}\) cm²/s. So, the estimated spin-diffusion coefficients for coal is at least of the right order of magnitude. The inter-proton distance of 3 Å estimated above may be overestimated to some extent for rigid fast Gaussian dephasing components in coal, which could lead to an overestimation of the spin-diffusion coefficient for the fast Gaussian dephasing components.
Indirect Detection of Spin-Diffusion Process via Time-Domain Experiments. We demonstrated that various time-domain experiments can provide detailed information on structural and dynamical heterogeneity of coal over a broad range of spatial dimensions. The spatial information obtained from those time-domain experiments relies on the $^1\text{H}-^1\text{H}$ spin-diffusion process in coal. As the proton density in coal is high and the $^1\text{H}-^1\text{H}$ dipolar interactions are strong, $^1\text{H}-^1\text{H}$ spin-diffusion in coal is fast. Such fast spin-diffusion processes tend to average out differences between dynamical behaviors of individual domains.

For a simple two-domain system, there are two limiting possibilities: the dynamical process of the system behaves as a single homogeneous system or as a physical mixture of two independent systems. In the first case, one can assume that the domains are small enough for spin-diffusion to average out the differences between the two domains. In the latter case, the domains are too large for spin-diffusion to equalize the individual dynamical behaviors. If we assume that the intrinsic time constants of a certain dynamical process (e.g., spin-lattice relaxation, or dipolar dephasing) for domains A and B are $T_A$ and $T_B$, the time constant of the system ($T_s$) that is effectively averaged by spin-diffusion would be

$$\frac{1}{T_s} = \frac{p_A}{T_A} + \frac{p_B}{T_B}$$

(29)

where $p_A$ and $p_B$ are the relative fraction of protons in domains A and B, respectively.

If the domain sizes A and B are very large or spin-diffusion is very slow compared to $T_A$ and $T_B$, the system will behave just like a mixture of two independent systems, and two separate time constants $T_A$ and $T_B$ are needed to describe the dynamical behavior of the system.

In the intermediate case in which the spin-diffusion rate is close to $1/T_A$ or $1/T_B$, the dynamical behavior of the two-domain system must still be described as two components, but the time constants of the two components are no longer the intrinsic time constants of the two separate domains ($T_A$ and $T_B$). The spin-diffusion rate can be extracted quantitatively in this case from deviations of the two time constants relative to their intrinsic values ($T_A$ and $T_B$ values without spin diffusion between A and B).\textsuperscript{122}

In any case, one can estimate the limit of the domain size $L_D$ from the time constant $T_s$ of a certain dynamical process in a specific domain as\textsuperscript{116}:

$$L_D = \sqrt{\langle r^2 \rangle} = \sqrt{6DT_s}$$

(30)

If the domain sizes are bigger than $L_D$, two different time constants $T_A$ and $T_B$ would be observed for the two domains. If the domain sizes are smaller than $L_D$, only one time constant, $T_s$, which is the average value of $T_A$ and $T_B$, given in equation (29), would be observed.
For untreated coals, the $^1\text{H}-^1\text{H}$ dipolar dephasing time constant is on the order of 10 - 70 μs (see above). If we use a spin-diffusion constant of $10 \times 10^{12}$ cm$^2$/s, a value that is typical of rigid organic solids, and a $T_{sd}$ of 30 μs, we can estimate $L_D$ as 4 Å. This means that dipolar-dephasing experiments can probe local structural heterogeneity of the system over only very short distances. Only domains that are intimately mixed on a molecule level will show a single dephasing time constant.

The rotating-frame $^1\text{H}$ spin-lattice relaxation time in untreated coals have been determined to be on the order of 1 - 15 ms. As we have discussed above, the dipolar interaction strength is scaled by $\frac{1}{2}$ under a spin-lock condition. The spin-diffusion coefficient should correspondingly be scaled by $\frac{1}{2}$. Using $D = 5 \times 10^{12}$ cm$^2$/s and $T_{1p} = 10$ ms, we obtain $L_D(T_{1p}) \approx 55$ Å. In most cases, we have identified two $T_{1p}$ components in untreated coals. This suggests, according to equation (30), that structural heterogeneity in coal also exists on a length scale of 50 Å.

The Zeeman spin-lattice relaxation time of an untreated coal is on the order of 60 ms to 300 ms. The limiting domain size $L_D$ can be estimated from equation 5.15, using $D = 10 \times 10^{12}$ cm$^2$/s and $T_1 = 200$ ms, as $L_D(T_1) \approx 350$ Å. We have also found that two relaxation components are needed to describe the proton spin-lattice relaxation of most coal samples. This implies that very large domains exist in coal.

The time-domain experiments outlined above clearly show that coal is an extremely heterogeneous material with structural heterogeneity over a broad spatial dimension from 4 Å to 350 Å.

1D Spin Exchange Experiment Based on CRAMPS. The general one-dimensional spin-exchange pulse sequence consists of three time periods: selection, mixing, and a detection period. In the selection period, a gradient of spin temperature is created by utilization of different spectral and/or dynamical properties of different phases or domains of a system. For systems with well resolved chemical shifts from different phases, various chemical-shift selection schemes can be applied to select magnetization with certain chemical shift(s), thus creating a magnetization gradient between the phase(s) with the selected chemical shift(s) and the phase(s) with chemical shift(s) that are different from the selected value. In the presence of strong dipolar couplings, chemical shift selection can not be realized by simply irradiating a with long, soft pulse.

The DANTE pulse sequence is widely used for selective excitation in solid-state NMR$^{123-125}$. However, to achieve selective excitation in a $^1\text{H}$ CRAMPS experiment, there is the added complication of combining DANTE-type pulse trains with the line-narrowing multiple-pulse sequences of CRAMPS. This combination has been implemented for the MREV-8 pulse sequence by alternating lengthened and shortened final pulses in the MREV-8 cycle$^{126}$. If there are only a couple of resolved chemical shifts in a $^1\text{H}$ CRAMPS spectrum, a simplified scheme, termed the ‘chemical-shift filter’, which is based on chemical-shift differences, has been used for studying simple polymer blends$^{106,127}$. As
the $^1$H CRAMPS resolution of bituminous coals is too poor to assure reliable chemical-shift selection, we did not use the chemical-shift selection approach in this work.

A commonly used strategy for creating a magnetization gradient relies on the heterogeneity of molecular motion in a system. It includes selection schemes based on differences in the dipolar dephasing constant $T_{dd}$, the rotating-frame spin-lattice relaxation time $T_1$, or the effective relaxation time ($T_{1D}$) under multiple-pulse irradiation. We have shown in earlier parts of the report that coal is an extremely heterogeneous material at the molecular level. Different behaviors in molecular dynamics have been observed for aliphatic protons and aromatic protons. Even for the same type of protons (either aliphatic or aromatic protons), distinctly different dipolar-dephasing constants $T_{dd}$, spin-lattice relaxation time $T_1$ and $T_{1p}$ have also been found in each individual coal sample. For example, four different dipolar-dephasing constants, spreading over four orders of magnitude, have been determined for aliphatic protons in pyridine-saturated premium coal 601 (see above). This extremely large motional heterogeneity in coal provides many possible schemes for magnetization selection.

In this work, we focused mainly on the selection scheme based on dipolar-dephasing constants, for the following reasons. First, coal components with different dipolar-dephasing constants in coal are related to molecular/macromolecular phases in coal, which we have discussed above. Measurements of spin exchange among components with different dipolar-dephasing constants should therefore provide details of coal structure in terms of the M/M model. Second, dipolar-dephasing constants are less affected by spin exchange than are spin-lattice relaxation times $T_1$ and $T_{1p}$, since dipolar-dephasing is much faster than spin-lattice relaxation processes in rigid solids, like coal. Thus, dipolar-dephasing constants reflect dynamical behaviors of individual small domains in coal. For an extremely heterogeneous system like coal, interpretations based on dipolar-dephasing processes should be more straightforward and simpler than those based on other relaxation processes.

The pulse sequence used in this work is an extension of the famous Goldman-Shen sequence. With a dipolar dephasing period right after the first $\pi/2$ pulse, the Goldman-Shen experiment exploits the dipolar-dephasing time differences between rigid and mobile proton species to select magnetization of mobile species. The magnetization of mobile protons is then placed along the z direction by the second $\pi/2$ pulse. Spin exchange between rigid proton components and mobile proton components proceeds during the mixing period. The NMR signal is detected after the third $\pi/2$ pulse. Diffusion of magnetization from the mobile protons to the rigid protons is monitored with variable mixing period, and a diffusion constant can thus be determined.

The Goldman-Shen experiment was originally used for static samples, using the wide-line $^1$H NMR detection technique. In this work, we implemented $^1$H CRAMPS detection in the basic Goldman-Shen experiment. Although magic-angle spinning, an integral part of the CRAMPS technique, can slow down the spin-diffusion process, the spin-diffusion rate in rigid proton-rich solids should not be much affected by the modest
MAS spinning speeds (around 1.6 kHz) used for $^1$H CRAMPS detection$^{107}$. This point is supported by dipolar-dephasing studies described above. The dipolar-dephasing time constants obtained by $^1$H CRAMPS detection in this work are very close to those measured by the $^1$H wide-line technique on static samples$^4$. This demonstrates that the modest MAS speed used in $^1$H CRAMPS detection does not significantly lower the dipolar interaction strength, which determines spin diffusion rates.

A modified Goldman-Shen experiment, with $^1$H CRAMPS detection and a refocusing $\pi$ pulse in the middle of dephasing period, has been used to study proton spin-exchange in silica gel and geminating seeds$^{128,129}$. $^1$H CRAMPS detection provides high resolution $^1$H NMR spectra of solids. This makes it possible to detect spin-exchange among proton species with different chemical shifts. The CRAMPS/Goldman-Shen approach has been improved in this work in two main respects. First, proper composite pulses are inserted prior to the $^1$H CRAMPS detection period to maximize the detected signal intensity and minimize the spectral distortions caused by magnetization that is spin-locked along the effective field of a multiple pulse sequence; this is accomplished by aligning the magnetization perpendicular to the direction of the effective field prior to the multiple pulse cycles via the composite pulses. Second, a phase cycling procedure was implemented in order to: (i) eliminate baseline distortion caused by the residual magnetization that is still spin-locked along the effective field of a multiple-pulse sequence, (ii) compensate for spectral distortions caused by small misadjustment of pulse-widths and phases, (iii) reduce the distortion caused by multiple quantum coherence$^{101,130}$, and (iv) reduce the effect of spin-lattice relaxation during the mixing time$^{131}$.

**A New 2D Spin-Exchange Experiment.** As discussed above, we observed that proton spin-exchange in coals occurs on a time scale similar to that of $^1$H dipolar-dephasing processes. Such spin-exchange and spin diffusion processes may be used to probe microscopic spatial heterogeneity due to either molecular mobility or chemical heterogeneity in coals. The one-dimensional spin-exchange experiments discussed above are very useful for monitoring the spin-exchange process among protons with different mobilities. However, spin-exchange among protons with different chemical shifts occurs at the same time as the exchange among protons of different mobilities in heterogeneous systems such as coal. As the spin-exchange pathways in coals are very complicated, a simple 1D spin-exchange experiment may not be suitable for probing the whole spin-exchange process.

The liquid-state two-dimensional (2D) exchange experiment (NOESY) is well known for its ability to monitor the complete exchange pathways of species with different chemical shifts$^{130}$. An extension of the 2D exchange experiment to $^1$H spin-exchange in rigid solids was made by Caravatti et al.$^{103}$ Proton 2D spin diffusion experiments based on the MREV-8 line-narrowing sequence have been used successfully to study the miscibility and morphology of polymer blends$^{103}$. This technique is very useful for identifying spin exchange pathways among spins with different chemical shifts. However, in coals, protons with quite different mobilities can have very similar chemical shifts, which are unresolved in $^1$H CRAMPS spectra, as we have demonstrated in our dipolar-
dephasing experiments described above. Spin exchange processes among spins with overlapping chemical shifts but different mobilities cannot be investigated directly using the previously reported “standard” 2D spin exchange/diffusion experiments.

To address this problem, we designed a new 2D spin exchange pulse sequence, which is able to probe the spin exchange pathways among spins with different chemical shifts and/or different mobilities. With the introduction of a dipolar-dephasing period in the preparation period, the new pulse sequence selects relatively mobile protons, discriminating against protons in rigid, proton-rich environments. Thus, gradients of Zeeman spin order among protons of different mobilities, and possibly different chemical shifts, are established prior to the evolution and mixing periods. To encode chemical shift information into the t₁ dimension (evolution period), multiple-pulse cycles must be employed during that period. The multiple pulse train is also required during the evolution period for suppression of ¹H−¹H spin diffusion. During the mixing period, spins encoded in terms of both molecular mobility and chemical shift are allowed to transfer their Zeeman orders to other spins. ¹H CRAMPS detection provides chemical shift resolution in the second dimension of the resulting 2D exchange spectrum. With this new pulse sequence, spin exchange between rigid and mobile protons with unresolved chemical shifts can be detected from the broadening of peaks along the ω₂ axes of 2D exchange spectra; and spin exchange between protons with resolved chemical shifts can be readily identified from cross peaks.

To obtain the best CRAMPS resolution possible, we used BR-24 as the basis for the new 2D spin-exchange pulse sequence. To minimize baseline distortion and "pedestals" due to magnetization spin-locked along the direction of the effective field of the average Hamiltonian, composite pulses (α,β) are used in the pulse sequence to align magnetization perpendicular to this direction prior to the BR-24 cycles. Right after the evolution period, composite pulses (β,φ) are also inserted before the mixing period to return the magnetization from the toggling frame back to the xy plane of the rotating frame and bring the y component of magnetization to the direction of \( B₀ (z) \). This composite pulse \( β,φ \) can be considered to be equivalent to \( β,α,π/2,α \) with \( φ = π/2 - α \). As the effective field of the average Hamiltonian of BR-24 is along the axis of \( (eₓ - eᵧ + eₚ)/\sqrt{3} \) in the rotating frame (where \( eₓ, eᵧ \) and \( eₚ \) are unit vectors in this frame), the composite pulse used in this pulse sequence is just one of many possible composite pulses that could be used to serve the same purpose. This approach can also be implemented using only single channel detection. A phase cycling procedure has also been implemented for the same purposes as those discussed for 1D spin-exchange experiments.

For the best spectral resolution in a 2D experiment, the pure-absorption mode 2D spectrum is desired. For the pulse sequence with single channel detection, pure absorption 2D exchange spectra can easily be realized by setting the carrier frequency outside the spectral range and performing a real Fourier transformation with respect to \( t₁ \). If quadrature detection in both dimensions is desired, which is unnecessary in most cases, the TPPI scheme can be easily adapted to the new pulse sequence to obtain pure absorption mode 2D spectra.
An appropriate dipolar-dephasing period was used in both 1D and 2D spin-exchange experiments to select components in coal with different mobilities. To select the slow Gaussian dephasing component from the fast dephasing component in untreated coal samples, a dipolar-dephasing period of 30 µs was used. As shown above, the dipolar-dephasing time constant of the fast Gaussian dephasing component is about 10 µs, while the dephasing time constant of the slow Gaussian dephasing component ranges from 30 to 70 µs. A dipolar-dephasing period of 30 µs achieves a 99% suppression of signals from the fast Gaussian dephasing component, and retains 40% - 93% of signals from the slow Gaussian dephasing component. For experiments on C,D,N-saturated coal samples, a dipolar dephasing period of 200 µs was used to select signals from Lorentzian dephasing components (dephasing time constants: 0.13 - 11 ms) and suppress signals from Gaussian dephasing components (dephasing time constants: 9 - 80 µs).

In the 2D spin-exchange experiments based on the new pulse, the increment of the evolution period (t_e) is the period of one BR-24 cycle, or 108 µs. Depending on the sample, either 64 or 128 increments were used in the evolution period, and 128 to 512 data points were acquired in the BR-24 detection period. We used single-channel detection with a carrier frequency on one side of the whole spectral region in all the experiments. The signal was averaged with 200 to 500 scans. The MAS rate was set as 1.6 ± 0.1 kHz. The recycle delay was 2 to 5 seconds. A complete 2D data set was processed according to standard procedures. To obtain pure absorption-mode 2D spectra, the time-domain data set was transformed to frequency domains by double real Fourier transformation.

Spin Exchange in Premium Coal 601. Figure 24 shows a stack plot of the 'H CRAMPS spectra obtained in a 1D spin-exchange experiment on the untreated premium coal 601 at 25 °C. A dipolar-dephasing period of 30 µs was used to select the relatively mobile slow Gaussian dephasing component. According to the dipolar-dephasing time constants measured at 25 °C (Table 3), 5% of the signals from aliphatic protons and 13% of the signals from aromatic protons are retained after the dipolar-dephasing period. Comparing the 'H CRAMPS spectrum with a dipolar-dephasing period of 30 µs and a mixing period of 0.1 µs (virtually no mixing period) with the original 'H CRAMPS spectrum (Figure 24a), one can see a slight shift of the maximum of the aliphatic peak to higher shielding and a significant loss of signal intensity in the spectral region between 2 and 5 ppm. The change of peak shape in the aliphatic region suggests that non-methyl aliphatic protons dominate the rigid fast Gaussian dephasing component of aliphatic protons. As only one Gaussian dephasing component was identified for aromatic protons at 25 °C, the change of peak shape in the aromatic region during the 30 µs dipolar dephasing period is much less pronounced.
As shown in Figure 24, as a result of spin exchange that occurs during sufficiently long mixing times (e.g., >2 ms), the above-mentioned signal depletion in the region between 2 and 5 ppm recovers and the shape of the original $^1$H CRAMPS spectrum returns. From the observed changes in peak shapes, one can clearly see that spin-exchange begins to show its significance at a mixing time of 50 $\mu$s, and essentially reaches an uniform spin temperature at a dephasing time of 2 ms. No significant additional change of peak shapes was observed with a dephasing time larger than 2 ms. We observe a slight decrease of total integrated spectral intensity (around 10%) with a dephasing time of 10 ms. This is due to the effect of spin-lattice relaxation during the mixing period. An intensity decrease of about 10% is expected at a mixing time of 10 ms based on the measured spin-lattice relaxation time at 25 $^\circ$C (Table 5). For untreated coal samples, spin exchange should be due mainly to spin diffusion, and chemical exchange is unlikely to be main mechanism of spin-exchange. The experimental 1D spin-exchange results clearly show that $^1$H-$^1$H spin diffusion is very efficient in coal. Spin-diffusion in coal is significant on a time scale less than 100 $\mu$s. This is in agreement with the VT dipolar-dephasing studies on coal discussed above.

Comparing Figure 24a with Figures 24f and 24g, one can see that the peak shape of the standard $^1$H CRAMPS spectrum (Fig. 24a) is not exactly the same as the spin-exchange spectra (Fig. 24f and 24g) obtained with sufficiently long mixing times. The intensity ratio of aliphatic to aromatic peaks in the standard $^1$H CRAMPS spectrum is larger than those in spin-exchange spectra obtained with long mixing times of 2 ms and 10 ms. A mixing time of 10 ms corresponds to a spin diffusion distance of about 80 Å, according to equation (30), assuming a typical diffusion coefficient of $D = 5 \times 10^{-12}$ cm$^2$/s. If all the aliphatic structural units and aromatic structural units in coal are smaller than 80 Å, and they are randomly distributed in coal, the peak shape of the spin-exchange
spectra obtained with a sufficiently long mixing time ($\geq 10$ ms) should be the same as the standard CRAMPS spectra of coal. The fact that we observed a difference in peak shapes implies that there exist large aliphatic-rich or/and aromatic-rich domains (larger than at least 80 Å) in premium coal 601. This is consistent with the spin-lattice relaxation ($T_1$) studies on premium coal 601, in which we concluded that aliphatic-rich domains larger than 350 Å exist in premium coal 601.

Aromatic protons can not effectively transfer their magnetization to the aliphatic protons in large aliphatic-rich domains. As 13% of the signals from aromatic protons and only 5% of the signals from aliphatic protons are retained after the dipolar-dephasing period of 30 μs in the spin-exchange experiment, the intensity ratio of aliphatic to aromatic peaks in the spin-exchange spectra, even when obtained with a sufficiently long mixing period, would still be lower than that in the standard spectrum due to the existence of large aliphatic-rich domains. This is exactly what we observed in these spin-exchange experiments on premium coal 601. As we did not observe further significant changes of the peak shape of spin-exchange spectra obtained with mixing times longer than 2 ms, the aromatic units in the premium coal 601 must be surrounded by aliphatic structures with dimensions less than about 35 Å, which is the effective spin-diffusion distance corresponding to a mixing period of 2 ms. This result suggests that the aromatic structural units in premium coal 601 are not large. This finding is in agreement with the average aromatic cluster size derived from a $^{13}$C CP/MAS study of HVB coals by Solum et al.$^{13}$

If the spin-exchange pathway is well defined, the spin-exchange rate can in principle be extracted from a 1D spin-exchange experiment. However, spin-exchange pathways are very complicated in coal. From Figure 24, we can see that the magnetization from both mobile aliphatic and mobile aromatic protons are transferred to that of rigid non-methyl aliphatic protons. Quantifying such diffusion processes is difficult from a 1D spin-exchange experiment.

The detection of spin-exchange in a 1D spin-exchange experiment relies on changes in the shape and relative intensity of each peak. Spin-exchange processes among spins with overlapping chemical shifts but different mobilities can not be directly detected in a 1D spin-exchange experiment. As we discussed above, a standard 2D spin-exchange experiment can not identify such exchange processes either. In order to elucidate the complete spin-exchange pathways among protons with different chemical shifts and/or different mobilities, we designed a new 2D spin-exchange pulse. VT 2D spin-exchange experiments based on the new pulse sequence are discussed below.

Figure 25 presents contour plots of 2D spin-exchange spectra of premium coal 601 obtained at 25 °C with mixing periods of 0.1 μs, 50 μs, 500 μs and 5 ms. From Figure 25b (50 μs mixing time), one can clearly see a spread of spectral density along the $\omega_2$ axis of the 2D exchange spectrum, and no appreciable cross peaks between aliphatic and aromatic protons. This suggests that spin-exchange among protons within either aliphatic structures or aromatic structures occurs very fast on the order of 50 μs. Assuming a typical diffusion coefficient of $D = 5 \times 10^{-12}$ cm$^2$/s, the spin diffusion distance
corresponding to a 50 µs spin diffusion period can be estimated as 5 - 6 Å, according to equation (30). Thus, the 50 µs spin-exchange result suggests that an aliphatic (aromatic) proton in coal is surrounded most probably by other aliphatic (aromatic) protons within a sphere with a radius of 5 - 6 Å. The distribution of protons in coal can thus be visualized as a mixture of small clusters of aliphatic protons and small clusters of aromatic protons. This postulate can explain well the different dipolar-dephasing behaviors, between aliphatic and aromatic protons. If these small aliphatic and aromatic proton clusters are distributed uniformly in the coal structure, one would not be able to observe large aliphatic-rich or aromatic-rich domains in coals. However, from spin-lattice relaxation (T₁) studies on premium coal 601 presented earlier, we concluded that large aliphatic-rich domains (on the order of 300 Å) exist in coal. Thus, the distribution of these small aliphatic and aromatic proton clusters is not uniform within the coal structure.

Figure 25 Contour plots of the pure absorption 2D ¹H-¹H spin-exchange spectra of premium coal 601 obtained at 25 °C with mixing times of (a) 0.1 µs, (b) 50 µs, (c) 500 µs, and (d) 5 ms. The pulse sequence used a dephasing period of 30 µs. The increment of the evolution period was one BR-24 cycle, or 108 µs. The original data consisted of 64 256-point BR-24 spectra, each acquired with 400 scans and a 3 s recycle delay. The BR-24 pulse sequence was used with a cycle time of 108 µs and a 90° pulse width of 1.2 - 1.3 µs. The MAS speed was 1.6 kHz.
With a mixing time of 500 μs (Figure 25c), cross peak intensity between aliphatic and aromatic protons is clearly seen, and aromatic and aliphatic diagonal peaks are severely broadened along both ω₂ and ω₁ axes. This means that extensive spin-exchange among protons with different chemical shifts and mobilities occurs within 500 μs. According to equation (30), the spin-diffusion distance corresponding to a mixing time of 500 μs is estimated as about 17 Å. This suggests that a significant fraction of the aliphatic protons are located within a distance of 17 Å from aromatic protons.

As shown in the 2D spin-exchange spectra obtained from mixing times of 500 μs and 5 ms (Figures 25c and 25d), cross peak intensity between aliphatic protons and aromatic protons has continued to grow, because spin diffusion spreads over longer distances with increasing mixing time. A 5 ms mixing period corresponds to an effective spin-diffusion distance on the order of 55 Å. The 500 μs and 5 ms results suggest that aliphatic protons and aromatic protons separated by a distance more than 17 Å can exchange Zeeman order with a mixing period of 5 ms.

Some of the detailed spectral features of 2D exchange spectra are shown more clearly in slices cut parallel to either the ω₁ axis or the ω₂ axis. For example, the relative intensity of the lower-right cross peak between the aliphatic and aromatic protons can be compared with the intensity of the diagonal aliphatic peak in the slice cut parallel to the ω₁ axis; the relative intensity of the same cross peak to that of the aromatic diagonal peak can be seen in the slice cut parallel to the ω₂ axis. Figures 26a–d show slices cut parallel to the ω₁ axis at a chemical shift of 1.0 ppm. This set of slices illustrates intensity changes of the diagonal aliphatic peak and its cross peak in the aromatic region. There is some small residual spectral intensity in the aromatic region for slices corresponding to a mixing time of 0.1 μs (Figure 26a). This is certainly not a cross peak, and is due to the tail of the broad aromatic peak. When the mixing time is changed from 0.1 μs to 50 μs, the intensity of the aliphatic peak decreases appreciably due to broadening of the aliphatic peak along the ω₂-direction; there is no significant change of intensity in the aromatic region. This is consistent with the analysis based on 2D contour plots. Within a mixing period of 50 μs, spin exchange is limited within small aliphatic or aromatic domains, and there is no significant spin exchange between aliphatic protons and aromatic protons. With longer mixing periods (500 μs and 5 ms), spin diffusion between aliphatic and aromatic protons becomes significant. This is reflected in Figures 26c and 26d as a continual decrease of the diagonal aliphatic peak and a growth of the cross peak in the aromatic region as the mixing time is increased.

Figures 26e–h illustrate slices cut along the ω₂ axis at a chemical shift of 6.9 ppm. There is some small residual spectral intensity in the aliphatic region in the ¹H CRAMPS spectrum obtained with a mixing time of 0.1 μs (Figure 26e). This is due to the tail of the broad aliphatic peak. With a mixing time of 50 μs, we can see the broadening of the diagonal aromatic peak at 6.7 ppm. As the mixing time is increased to 500 μs, the intensity of the cross peak at 1.0 ppm increases at the expense of the diagonal aromatic peak. The ¹H CRAMPS spectrum (Figure 26h) obtained with a mixing time of 5 ms is
close to the “normal” $^1$H CRAMPS spectrum of coal. This suggests that spin-exchange is close to complete.

![Figure 26](image)

**Figure 26** Slices cut from the 2D $^1$H-$^1$H spin-exchange spectra of premium coal 601 shown in Figure 25. Slices cut along $\omega_1$ at 1.0 ppm are shown in (a), (b), (c) and (d). Slices cut along $\omega_2$ at 6.9 ppm are shown in (e), (f), (g) and (h). The corresponding mixing times used in the experiments are labeled by the side of each slice.

The dipolar-dephasing experiments discussed earlier in this report suggest that the proton spin-exchange process is slowed down at higher temperature. A 2D spin-exchange experiment performed at high temperature should provide direct evidence on this assumption. Figure 27 shows contour plots of 2D spin-exchange spectra of premium coal 601 obtained at 180 °C, with a dipolar-dephasing period of 30 μs.

Based on the dipolar-dephasing constants measured at 180 °C, we can estimate that 37% of the signals from aromatic protons survive after the dephasing period (30 μs). Much higher fractions of proton signals are retained at 180 °C, because fractions of the slow Gaussian dephasing component are dramatically increased due to thermal activation. The fraction of aromatic signals remaining after 30 μs of dipolar dephasing is close to that of aliphatic protons at 180 °C, while the fraction of aromatic signals preserved is about 2.5 times that of aliphatic signals at 25 °C. This difference is clearly reflected in Figures 25 and 27. The relative intensity of the aliphatic peak is much higher at 180 °C than that at 25 °C.

The dependence of the 2D spin-exchange spectra on mixing time at 180 °C is similar to that at 25 °C. The spatial distribution of protons in coal derived from the above analysis of 2D spin-exchange spectra of coal at 25 °C are confirmed by the results obtained at 180 °C. As a result of a mixing time of 50 μs, expansion of the diagonal peak along $\omega_2$ is much less pronounced than what we observed in the corresponding spectra.
obtained at 25 °C. This means that a higher temperature can retard the magnetization
transfer from slow Gaussian dephasing components of aliphatic or aromatic protons to
fast Gaussian dephasing components of the same structural type of protons. This explains
why we can always identify two distinctively different dipolar-dephasing components at
180 °C, while sometimes only one dephasing component may be identified at 25 °C, as
discussed above. Comparing the 2D spectrum acquired with a mixing time of 500 μs at
180 °C (Figure 27c) with that obtained at 25 °C (Figure 25c), we can see that the rate of
spin-exchange between aliphatic and aromatic protons is also decreased at 180 °C. The
2D spectrum obtained with a mixing time of 5 ms at 180 °C (Figure 27d) is very similar
to that obtained at 25 °C (Figure 25d). These results suggest that spin exchange among
protons is almost complete within 5 ms at 180 °C, although the spin-exchange rate is
significantly lower at 180 °C than at 25 °C.

Figure 27  Contour plots of the pure absorption 2D ¹H-¹H spin-exchange spectra of premium coal
601 obtained at 180 °C with mixing times of (a) 0.1 μs, (b) 50 μs, (c) 500 μs, and (d) 5 ms. The
pulse sequence used a dephasing period of 30 μs. The increment of the evolution period was one
BR-24 cycle, or 108 μs. The original data consisted of 64 256-point BR-24 spectra, each acquired
with 400 scans and a 3 s recycle delay. The BR-24 pulse sequence was used with a cycle time of
108 μs and a 90° pulse width of 1.2 - 1.3 μs. The MAS speed was 1.6 kHz.
These features seen in the 2D contour plots are also clear in slices cut along the $\omega_1$ and $\omega_2$ axes of the 2D spin-exchange spectra. Figures 28a-d show slices cut parallel to the $\omega_1$ axis at a chemical shift of 1.0 ppm. The decrease of peak intensity at 1.0 ppm in the slice with increasing mixing time reflects the intensity decrease of the diagonal aliphatic peak in the 2D spectrum, due to its spreading along the $\omega_2$ direction or transferring of magnetization to cross peaks with the aromatic peak. Comparing Figure 28b with Figure 26b, it is very clear that spin-exchange within small aliphatic domains is not appreciable with a mixing time less than 50 $\mu$s at 180 $^\circ$C, but is significant at 25 $^\circ$C. Growth of the cross peak in the aromatic region is also slower at 180 $^\circ$C than at 25 $^\circ$C, as can be seen by comparing Figures 28c and 25c.

![Diagram](image)

**Figure 28** Slices cut from the 2D $^1$H-$^1$H spin-exchange spectra of premium coal 601 shown in Figure 27. Slices cut along $\omega_1$ at 1.0 ppm are shown in (a), (b), (c) and (d). Slices cut along $\omega_2$ at 6.9 ppm are shown in (e), (f), (g) and (h). The corresponding mixing times used in the experiments are labeled by the side of each slice.

Figures 28e-h show slices cut along the $\omega_2$ axis at a chemical shift of 6.9 ppm. We can see that the slice (Figure 28f) corresponding to a mixing time of 50 $\mu$s is not dramatically different from that corresponding to a mixing time of 0.1 $\mu$s. Again, this implies that highly efficient aliphatic-aromatic spin exchange does not occur at 180 $^\circ$C within 50 $\mu$s. The growth of cross peaks in the aliphatic region and spreading of the diagonal aromatic peak along the $\omega_2$ axis are clearly seen in the slices obtained with mixing times of 500 $\mu$s and 5 ms. The slice corresponding to a mixing time of 5 ms looks very close to the "normal" $^1$H CRAMPS spectrum of premium coal 601. This again suggests that spin-exchange is close to complete within 5 ms at 180 $^\circ$C.

As seen in the discussion above, the new 2D exchange experiment provides many structural and dynamical details of coal, which are not available from other techniques. Various spin-exchange pathways can be differentiated and identified from such studies.
The spin-exchange process can be easily monitored semi-quantitatively from the 2D spin-exchange spectral change versus mixing time.

Spin Exchange in Premium Coal 501. The same type of 1D and 2D spin-exchange experiments were also carried out on premium coal 501. Figures analogous to Figures 24 - 28 are not shown here, in order to save space.

At 25 °C, there is only one Gaussian dipolar-dephasing component for either the aliphatic or aromatic protons of coal 501. Based on the dipolar-dephasing constants measured at 25 °C, one can estimate that 6% of the signals from aliphatic protons and 10% of the signals from aromatic protons are retained after the 30 μs dipolar-dephasing period. The aliphatic region of the 1H CRAMPS spectrum obtained with a short mixing period should show a depletion of signal intensity relative to the aromatic region. A significant change in the spectral line shape can be seen with a mixing time as short as 20 μs, and the shape of the original 1H CRAMPS spectrum returns with a mixing time of 10 ms. This suggests that 1H-1H spin diffusion in premium coal 501 is also very efficient. Similar features can be seen in 1H CRAMPS spectra obtained in a 1D spin-exchange experiment at 180 °C.

From the 2D contour plot of 2D spin-exchange spectra of premium coal 501 obtained at 25 °C with a 30 μs dephasing period and mixing periods of 50 μs, one can clearly see that within a mixing time of 50 μs spin exchange occurs mainly among protons with similar chemical shifts. As the mixing time is increased to 500 μs, various spin-exchange pathways among protons with different chemical shifts and mobilities can be identified. At a mixing time of 5 ms, the spectral density spreads out over the 2D spectrum due to further spin-diffusion among various types of protons. Such a spin diffusion pattern may suggest a uniformly random distribution of aliphatic structures and aromatic structures.

1H-1H Spin Exchange in C,D,N-Saturated Coal. In an earlier portion of this report, we showed that pyridine-saturation can dramatically change the structure and molecular mobility of coal. In addition to Gaussian dipolar-dephasing component(s) with dipolar-dephasing time constants less than 90 μs, two Lorentzian dipolar-dephasing components with dephasing time constants from 0.13 to 11 ms were identified in C,D,N-saturated coal.

The dipolar-dephasing experiments presented above strongly suggest that a significant fraction of the Lorentzian dephasing components correspond to protons in small molecules that undergo rapid rotational motion in large pores created by cleavage of hydrogen bonding bridges in the macromolecular network. A study of spin-diffusion between mobile Lorentzian components and rigid Gaussian dephasing components should provide more direct information on the spatial distribution of protons with different mobilities. It would also be interesting to see if there is any significant spin exchange among mobile protons with different chemical shifts, which are well resolved in 1H CRAMPS spectra of mobile protons showing Lorentzian dephasing behaviors. Such spin-exchange processes would be mainly contributed from intramolecular dipolar couplings.
among protons in different structural moieties, because Lorentzian dephasing components are very mobile. The degree of substitution of aromatic rings could then be estimated from the ratio of the intensity of the cross peak between aliphatic and aromatic peaks to the intensity of the diagonal aromatic peak.

Spin Exchange Between Lorentzian Dephasing Components and Gaussian Dephasing Components in C₂D₃N-Saturated Coal. As large difference of dephasing time constants exists between Lorentzian and Gaussian dipolar-dephasing components, a dipolar-dephasing period can be used to select the mobile Lorentzian dephasing component in a spin-exchange experiment. In this work, a dipolar-dephasing period of 200 µs was used in all the spin-exchange experiments.

Figure 29 shows a stack plot of ¹H CRAMPS spectra of C₂D₃N-saturated premium coal 601 obtained in 1D spin-exchange experiments at 25 °C with mixing times from 0.1 µs to 100 ms. If there is significant spin-exchange between Lorentzian and Gaussian dephasing components, the resolution of highly resolved ¹H CRAMPS spectra of mobile protons would degrade as the mixing time increases. With a sufficiently long mixing period, the original ¹H CRAMPS spectrum of C₂D₃N-saturated coal (Figure 29a) should be at least partially restored. However, Figure 29 clearly shows that there is no significant change in the shape and relative intensity of each peak in the ¹H CRAMPS spectrum obtained with a mixing time up to 100 ms. This proves that there is no significant spin-exchange between the Lorentzian dephasing components and the Gaussian dephasing components within 100 ms. A decrease in the total integrated intensity of the ¹H CRAMPS spectrum obtained with a mixing time of 100 ms (Figure 29f) can be seen. This is due to the effect of spin-lattice relaxation (T₁) during the mixing period. In fact, the ¹H spin-lattice relaxation time places a limit on the largest mixing time possible for a spin-exchange experiment.

Figure 29 ¹H CRAMPS spectra of C₂D₃N-saturated premium coal 601 obtained at 25 °C in a 1D spin-exchange experiment. The mixing times were set as (b) 0.1 µs, (c) 0.1 ms, (d) 1 ms, (e) 10 ms, and (f) 100 ms. The dipolar dephasing period was 200 µs. The BR-24 pulse sequence was used with a cycle time of 108 µs and a 90° pulse width of 1.2 - 1.3 µs. Each spectrum was acquired with 500 scans and 3 s recycle delay. The MAS speed was 1.6 kHz. For comparison, a standard ¹H CRAMPS spectrum of the same sample obtained at 25 °C is shown in (a).
Analogous results (stack plots of $^1$H CRAMPS spectra) of C$_2$D$_3$N-saturated premium coal 501 were obtained in 1D spin-exchange experiments with mixing times from 0.1 $\mu$s to 100 ms at temperatures of 25 °C and 90 °C (not shown here). There is also no significant change of shape and relative intensity of each peak in $^1$H CRAMPS spectra obtained either at 25 °C or 90 °C, as the mixing time is varied up to 100 ms. This demonstrates again that there is no significant spin-exchange between protons with Lorentzian dephasing characteristic and protons showing Gaussian dephasing behavior in C$_2$D$_3$N-saturated coal.

The above results can be used to estimate a lower limit on the size of domains ($L_L$) of Lorentzian dephasing components. As the spin-diffusion between Lorentzian and Gaussian dephasing components is not significant with mixing time $\tau_m$ at least up to 100 ms, $L_L$ must be larger than the effective spin-diffusion distance of protons showing Lorentzian dephasing behavior, or:

$$L_L > \sqrt{6D_L \tau_m}$$

(31)

where $\tau_m = 100$ ms, and $D_L$ is the spin-diffusion coefficient of a Lorentzian dephasing component. For Lorentzian dephasing components, $D_L$ can be estimated from the dephasing constants $T_{dd}$ according to equation (28). Plugging equation (28) into expression (31), we have

$$\frac{L_L}{\sqrt{\langle d^2 \rangle}} > \sqrt{\beta} \sqrt{\frac{\tau_m}{T_{dd}}}$$

(32)

where $\langle d^2 \rangle$ is the mean square distance between the nearest protons in Lorentzian dephasing components.

As we don’t know the exact molecular structure of Lorentzian dephasing components, an estimation on $\langle d^2 \rangle$ is difficult. Nevertheless, the ratio $L_L/\sqrt{\langle d^2 \rangle}$ can give us an idea how far mobile protons are away from rigid protons in the macromolecular structure of coal in terms of $\sqrt{\langle d^2 \rangle}$. For fast Lorentzian dephasing components, we can estimate $L_L/\sqrt{\langle d^2 \rangle}$ to be greater than 40, using $T_{dd} = 0.2$ ms and $\beta = 10$. For slow Lorentzian dephasing components, $L_L/\sqrt{\langle d^2 \rangle}$ is estimated to be greater than 6, using $T_{dd} = 10$ ms and $\beta = 10$. As the $\tau_m$ used in this experiment is limited by $T_1$, underestimation of $L_L/\sqrt{\langle d^2 \rangle}$ should be much more severe for slow dephasing Lorentzian components than that for fast Lorentzian dephasing components. From dipolar-dephasing experiments, we know that slow Lorentzian dephasing components should be located in larger pores than are fast Lorentzian dephasing components. Therefore, the ratio, $L_L/\sqrt{\langle d^2 \rangle}$, for slow Lorentzian dephasing components should be at least as large as that for fast dephasing components.
As discussed above, a rough estimation of $<d^2>$ is about 3 Å. That gives a minimum domain size of Lorentzian dephasing components of at least 120 Å. The number average molecular weight of extractable small molecules in coal has been reported to be about 600. This means that the average number of carbons in a small molecule is around 40 - 50. That gives us a picture of small molecules packed in large pores of macromolecular matrix. This kind of rough estimation is compatible with our view of the structural and dynamical changes in coal induced by pyridine saturation.

Spin Exchange among Mobile Protons with Lorentzian Dephasing Characteristics. We just showed that there is no appreciable $^1$H-$^1$H spin-exchange between Lorentzian dephasing components and Gaussian dephasing components within 100 ms in C$_3$D$_3$N-saturated coals. The study of spin exchange processes among mobile protons of Lorentzian dephasing components is thus simplified, since exchange pathways between Lorentzian dephasing components and Gaussian components are excluded. As the $^1$H CRAMPS spectra of mobile protons show several well resolved peaks, the newly designed 2D spin-exchange pulse sequence is well suited for studying spin-exchange process among mobile protons of different chemical shifts.

Figure 30 shows contour plots of 2D spin-exchange spectra of C$_3$D$_3$N-saturated premium coal 601 obtained at 25 °C with mixing times of 10 ms and 100 ms. A dipolar dephasing period of 200 μs was used to filter out signals from rigid Gaussian dephasing components.

In a 2D experiment, data points collected in the $t_1$ dimension are usually limited by the available experimental time and may be severely truncated. Therefore, resolution in the $\omega_1$ dimension is usually worse than that in the $\omega_2$ dimension, and severe distortions of the baseline around a strong and narrow peak in the $\omega_1$ dimension may be observed. In this case small peaks on $\omega_1$ dimension may be difficult to identify. This is the case for the strong diagonal aliphatic peak at 1.0 ppm in Figure 30. Cross peaks between this aliphatic peak and the aromatic peak are clearer in the upper right corners of Figure 30 than in the lower left corner, because of the distortions along the $\omega_1$ dimension.

As the aliphatic peak of C$_3$D$_3$N-saturated coal 601 at 1.0 ppm is much stronger than other peaks in the $^1$H CRAMPS spectrum, especially after a substantial dipolar-dephasing period, we have to set a very low contour level in the contour plot in order to present the 2D spin exchange spectra properly. As a result, small distortions around the bottom of the strong aliphatic peak can show up in the 2D spectrum. That is the origin of much of the off diagonal spectral intensity in Figure 30. It is usually easy to distinguish a real cross peak from small spectral distortions by examining slices cut from the 2D spectrum.
Another thing worth mentioning here is that Lorentzian and Gaussian peaks in a pure absorption-mode 2D spectrum show distinctively different contour shapes in a 2D contour plot. A Gaussian peak shows circular contours, while a Lorentzian peak shows a star shaped contour. The strong aliphatic peak at 1.0 ppm in the 2D spin-exchange spectra (Figure 30) of C₅D₃N-saturated coal is close to Lorentzian in shape. At the bottom of the aliphatic peak, the contour extends along the ω₁ and ω₂ axes. This kind of feature can be seen in Figure 30.

One can clearly see that there is no significant build-up of cross peaks with a mixing time of 10 ms (Figure 30a). This fact is consistent with results of the dipolar-dephasing experiments described above. If spin exchange among mobile protons were very efficient within 10 ms, we would not have been able to identify two Lorentzian components with distinctly different dipolar-dephasing constants. These results also suggest that intramolecular dipolar coupling between structurally different types of protons (aliphatic and aromatic) is weak. This implies that the Lorentzian dephasing components undergo very rapid rotational motion, which effectively averages intramolecular dipolar interactions.

With a mixing time of 100 ms (Figure 30b), small cross peaks between the aliphatic peak and the aromatic peak are clearly identified. As we have found that there is no detectable spin diffusion between the Lorentzian dephasing components and the Gaussian dephasing components within 100 ms, the cross peak should be mainly due to the intramolecular dipolar couplings between protons attached to aromatic rings and protons in aliphatic...
substituents of aromatic structures of Lorentzian dephasing components. Therefore, the intensity ratio of the cross peak to the diagonal aromatic peak provides a measure of the degree of substitution of aromatic ring systems of Lorentzian dephasing components. The intensity ratio of the cross peak to the diagonal aliphatic peak reflects the ratio of protons in aliphatic substituents on aromatic structures to protons in aliphatic molecules.

The relative intensity of the cross peak to diagonal aliphatic and aromatic peaks can be clearly seen in slices cut parallel to the \( \omega_1 \) and \( \omega_2 \) axes. From a slice cut parallel to the \( \omega_1 \) axis of Fig. 30 at 1.0 ppm (not shown here), one sees that the cross peak in the aromatic region is much smaller than the diagonal aliphatic peak at 1.0 ppm. By magnifying the vertical scale of the slice by 10 times, the cross peak is easily recognizable. From a slice cut along \( \omega_2 \) at 6.9 ppm (not shown here), one sees the intensity of the cross peak shown in the aliphatic region is close to that of the diagonal aromatic peak at 6.9 ppm. This result suggests that most of the mobile aliphatic protons with Lorentzian dephasing characteristics are in structures consisting of only aliphatic moieties. However, the mobile aromatic protons showing Lorentzian dephasing behaviors are likely to be distributed in aromatic structures with substantial aliphatic substituents. This is consistent with the recent studies on the molecular structure of pyridine extracts of coal\textsuperscript{91,134}. Our dipolar-dephasing results strongly suggest that most of the fast Lorentzian dephasing aromatic protons are associated with mobile macromolecular chains in coal. The spin exchange results imply that a significant fraction of the flexible aliphatic side chains present are attached to the mobile aromatic main chains of macromolecular structures in coal, which undergo rapid segmental motion.

Analogous results (not shown here) were obtained on the same sample at a higher temperature, 90 °C, with a mixing time of 100 ms. Cross peaks between aliphatic and aromatic protons can still be identified. Although the aromatic cross peak is hardly recognizable at a quick glance of the slice cut parallel to \( \omega_1 \) at 1.0 ppm, the cross peak is clearly identified in a vertically magnified view of the same slice. One can see that the intensity ratio of cross peak to diagonal aliphatic peak at 90 °C is lower than the corresponding one at 25 °C. These observations are consistent with VT dipolar dephasing studies on C,D,N-saturated premium coal 601 discussed earlier in this report. When the temperature is increased from 25 °C to 90 °C, the Lorentzian dephasing components (the sum of both fast and slow dephasing components) of aliphatic protons are increased from 35% to 46% (Table 21), while Lorentzian dephasing components of aromatic protons are increased from 14% to 19%. The 2D spin exchange results suggest that the increase of mobile Lorentzian dephasing aliphatic protons at 90 °C is mainly due to structures with low aromaticity. However, the cross-peak intensity in the slice cut parallel to \( \omega_1 \) at 6.9 ppm is close to the intensity of the diagonal aromatic peak. The intensity ratio of the cross peak to the diagonal aromatic peak at 25 °C is very close to the ratio at 90 °C. This result implies that the degree of substitution of aromatic structures of Lorentzian dephasing components at 25 °C is very close to that at 90 °C.
The 2D spin-exchange studies presented in this report clearly demonstrate the power and potential of the new 2D spin-exchange pulse sequence for elucidating structural and dynamical details of very complicated heterogeneous systems.

Summary of variable-temperature $^1$H NMR studies of premium coals

We have carried out the first systematic variable-temperature in situ $^1$H CRAMPS studies of untreated coal and C$_3$D$_3$N-saturated coal samples between 25 °C and 230 °C, focusing on the molecular structural and dynamical changes in coal induced by thermal treatment and solvent saturation via various time-domain and two-dimensional NMR experiments. These studies provide new insights into an important research area in coal science, i.e., how non-covalent associative interactions in coal are affected at the molecular level by thermal treatment and solvent saturation.

We have made major improvements in $^1$H CRAMPS methods and techniques in this work. New hardware and software were designed, developed and implemented to improve the reliability, robustness and efficiency of $^1$H CRAMPS techniques. One of the major improvements that we have made in this work on various time-domain CRAMPS experiments is the design and implementation of appropriate composite pulse(s) and phase cycling procedures for multiple-pulse cycles. These advances have significantly improved the baseline quality of $^1$H CRAMPS spectra of coal, which is crucial for reliable quantitation.

Based on the improved hardware and techniques, we carried out the first systematic in situ $^1$H CRAMPS studies of untreated premium coals 301, 501 and 601 between 25 °C and 230 °C. We showed, through a time-suspension experiment based on the CMG-48 sequence and a new 2D $^1$H-$^1$H spin exchange experiment based on the BR-24 sequence, that the resolution of $^1$H BR-24 CRAMPS spectra of coal is limited mainly by inhomogeneous line broadening. Contrary to what we expected, a slight resolution deterioration of $^1$H CRAMPS spectra of coal was observed at high temperature. This is due to the interference of molecular motion, induced by thermal activation, with the coherent averaging of dipolar couplings and chemical shift anisotropies by CRAMPS.

To examine explicitly the dependence of molecular motion on the temperature, we carried out various time-domain NMR experiments based on CRAMPS detection at high temperature. We found that two Gaussian dephasing components are needed to describe the $^1$H dipolar dephasing behavior of untreated coals in most cases. The $^1$H dipolar dephasing time constants do not change much with temperature. However, the fraction of the slow dephasing component is increased dramatically with increasing temperature. The slow dephasing component corresponds to protons in relatively mobile structures with a correlation time of random motion on the order of tens of microsecond. The dipolar dephasing behavior of protons in coal depends on the chemical environment (aliphatic or aromatic protons) and the rank of coal (HVB or LVB), as well as temperature. Although the dipolar dephasing experiments demonstrate that molecular
motion is indeed promoted by thermal treatment, the promoted molecular motion is anisotropic in nature, and is not fast enough to improve the resolution of $^1H$ CRAMPS spectra of coal.

We also carried out Zeeman spin-lattice relaxation time ($T_1$) measurements on coals. For coal samples that have been exposed to air, we confirmed that paramagnetic oxygen is the main source of proton spin-lattice relaxation. $^1H$ $T_1$ measurements provide information on the structural heterogeneity of coal on a spatial scale larger than 350 Å. We found that high temperature spin-lattice relaxation experiments help to reveal the structural heterogeneity of coal because of reduced electron-electron and proton-proton spin diffusion rates at high temperature. Large domains with distinctively different paramagnetic oxygen concentrations were found in all three coal samples. In particular, we found that very large aliphatic-rich domains exist in premium coal 601.

Rotating-frame spin-lattice relaxation time ($T_{1p}$) measurements provide dynamical and structural information on a $^1H$ spin system on time and spatial scales that are intermediate between those relevant to dipolar dephasing experiments and Zeeman spin-lattice relaxation measurements. The observed dependence of $^1H$ $T_{1p}$ on the strength of the spin-lock field supports the view that the main relaxation mechanism is time-dependent $^1H$-$^1H$ dipolar interactions in untreated coals. From this dependence, we estimated that the correlation time of molecular motion that is responsible for rotating-frame proton spin-lattice relaxation in untreated coals is on the order of 10 μs, which is in agreement with conclusions drawn from proton dipolar-dephasing experiments. Two $T_{1p}$ values were identified for each of the three untreated coal samples studied. This result indicates the existence of structural heterogeneity in coal on a spatial scale of ~ 50 Å.

To compare the effect of thermal treatment with the effect of solvent saturation on the structure and dynamics of coals, we carried out VT $^1H$ CRAMPS studies on C,D,N-saturated samples of an original coal and its extraction residue. With the enhanced $^1H$ CRAMPS resolution provided by pyridine saturation, we were able to elucidate much more detailed chemical functionalities in coals. A moderate increase of temperature from 25 °C to 90 °C does not lead to a further dramatic change of the resolution of $^1H$ CRAMPS of C,D,N-saturated coal. However, a pronounced change in molecular dynamics was detected through dipolar-dephasing experiments, when the temperature was increased from 25 °C to 90 °C. Up to four dipolar dephasing components were identified in C,D,N-saturated coals. In addition to one or two Gaussian dephasing components, similar to what we observed in untreated coals, two Lorentzian dephasing components, with dephasing time constants ranging from 0.13 ms to 11 ms, were determined in C,D,N-saturated coals. This result suggests that pyridine saturation can dramatically promote molecular motion with correlation times as short as tens of nanoseconds to microseconds even at room temperature, while thermal treatment alone is much less effective in promoting molecular motion even at 180 °C. A new model for explaining the enhancement of molecular mobility induced by thermal treatment and solvent saturation was proposed and discussed in terms of our new experimental results.
Correlations among molecular structure, molecular mobility and solvent-extraction components were established through comparative variable-temperature \(^1\)H CRAMPS studies on C\(_2\)D\(_3\)N-saturated samples of premium coal 601 and its pyridine-extraction residue. A critical review of the molecular/macromolecular (M/M) structural model of coal was made on the basis of our new results. The nature of the molecular phase and macromolecular phase in coal has been reexamined. The relationships between the molecular/macromolecular phases and molecular mobility is found to be much more complicated than previously thought. There is no simple one-to-one correspondence between them. We have developed a coherent view of the molecular structure and dynamics in coal on the basis of the new experimental results. Many discrepancies in the literature on these issues are well resolved by this view, and the resolution enhancement due to solvent saturation is also satisfactorily explained.

The structural heterogeneity in coal has been addressed in this work directly via the first 1D and 2D \(^1\)H-\(^1\)H spin-exchange studies based on \(^1\)H CRAMPS detection. A new 2D \(^1\)H-\(^1\)H spin-exchange experimental technique has been developed in this work for probing complicated spin-exchange pathways among protons with different mobilities and chemical shifts in a heterogeneous system. This new 2D spin-exchange experiment was also shown to be very useful for studying intramolecular spin exchange among protons in highly mobile structures of C\(_2\)D\(_3\)N-saturated coals. Information on the degree of substitution of aromatic rings of the mobile component in C\(_2\)D\(_3\)N-saturated coals was obtained from such studies.

Proton spin diffusion coefficients in coal were estimated on the basis of equations derived for calculating spin diffusion coefficients from proton dipolar dephasing constants. We found that spin diffusion between protons with similar chemical shifts but different mobilities is very efficient and can be detected in untreated coal samples with a mixing time as short as 50 \(\mu\)s. Spin diffusion among various types of protons with different chemical shifts and molecular mobilities is almost complete within 2 ms. Results of 1D and 2D spin exchange experiments on untreated premium coal 601 suggest that the size of aromatic structural unit is not large (less than 35 \(\AA\)) and large aliphatic-rich domains (larger than at least 80 \(\AA\)) exist in the untreated coal.

We have found no detectable proton spin diffusion between rigid Gaussian dipolar-dephasing components and mobile Lorentzian dephasing components in C\(_2\)D\(_3\)N-saturated coals within a mixing time of 100 ms. This result suggests that mobile Lorentzian dephasing components may be distributed in large pores (with dimensions on the order of 100 \(\AA\) or larger) of the macromolecular matrix of coal, created from disruption of hydrogen bonding bridges in coal by pyridine molecules. This result supports our proposed model of pyridine/coal interactions based on VT time-domain experiments on untreated and C\(_2\)D\(_3\)N-saturated coals.

This work clearly demonstrates the power and potential of \textit{in situ} VT \(^1\)H CRAMPS techniques, combined with various time-domain and two-dimensional experiments, for revealing structural and dynamical details of extremely heterogeneous systems like coals.
References


