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**Two Dimensional NMR and NMR Relaxation Studies
of Coal Structure**

PROGRESS REPORT

including
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ABSTRACT

This report covers the progress made on the title project for the project period. Four major areas of inquiry are being pursued. Advanced solid state NMR methods are being developed to assay the distribution of the various important functional groups that determine the reactivity of coals. Special attention is being paid to methods that are compatible with the very high magic angle sample spinning rates needed for operation at the high magnetic field strengths available today. Polarization inversion methods utilizing the difference in heat capacities of small groups of spins are particularly promising. Methods combining proton-proton spin diffusion with ^{13}C CPMAS readout are being developed to determine the connectivity of functional groups in coals in a high sensitivity relay type of experiment. Additional work is aimed at delineating the role of methyl group rotation in the proton NMR relaxation behavior of coals.

Introduction

Quantitative differentiation of the various functional groups in coals by ^{13}C CPMAS NMR methods has provided a great deal of structural information which is not available from other spectral techniques. Previous reports described our work on the development of a new method using polarization inversion which can differentiate between CH_3 , CH_2 , CH and C centers. The new techniques are different in that they do not rely heavily upon the strength of the dipolar couplings, but instead primarily upon the number of protons attached to a given carbon center. The last report contained a preprint which described in some detail the first protocol for obtaining CH , CH_2 , CH_3 and non-protonated CPMAS subspectra in solids, and demonstrated the first application of the method to one of the Argonne Premium Coal samples.

This quarter we have completed the first round of data acquisition and analysis of the entire Argonne coal suite. The results and some preliminary interpretation are contained in the attached report. These data and this preliminary report will be worked into several full papers over the next six months.

Abstract

The results of the application of a new ^{13}C cpmas nmr spectral editing method to the study of coal is presented. From this method, one obtains four subspectra for each coal; representing the nonprotonated ^{13}C , ^{13}CH , $^{13}\text{CH}_2$, and $^{13}\text{CH}_3$ contributions to the normal cpmas spectrum. This new method was used to investigate the chemical functionality of the Argonne Premium Coal Samples (APCS). Particular attention was paid to the extraction of possible chemical structures present in the coal samples. This information was derived directly by assigning the chemical shifts from the spectra. Carbon and proton aromaticities, as well as the aromatic and aliphatic contributions to the H/C ratio are calculated and used to discuss the effectiveness of the method and the functionality of the coals.

INTRODUCTION

With the advent of methods designed to remove the resonance broadening effects of ^1H - ^{13}C dipolar interactions, the application of ^{13}C NMR spectroscopy to the study of coals was realized. High power proton decoupling combined with magic angle spinning (MAS) can be used to effectively narrow ^{13}C resonances. Combined with cross polarization (CP), these techniques represent the most popular NMR method used in the study of coals for the past fifteen years. Due to the complex heterogeneous nature of coal, it is most advantageous to attempt a characterization in terms of average structural parameters. These NMR experiments put the measurement of such structural parameters within the grasp of the coal scientist. Indeed, ^{13}C CPMAS NMR has come to be known as one of the most direct methods for measuring carbon aromaticity (f_a), defined as the fraction of carbon in aromatic environments. Over the last decade this method has provided a wealth of structural information on whole coals and coal macerals. Proton aromaticities (H_a), H/C ratios, and ratios of ^{13}CH to $^{13}\text{CH}_2$ to $^{13}\text{CH}_3$ groups can also be obtained from NMR measurements. ^{13}C NMR spectra of coals typically consist of two bands, one corresponding to aromatic carbon and another corresponding to aliphatic carbon. From spectra such as these, measurement of f_a can be accomplished by integrating the aromatic band and subsequently dividing the result by the integral of the entire spectrum. In this way, structural information can be obtained by correct interpretation of the NMR spectra. Furthermore, coal ^{13}C NMR spectra often exhibit shoulders or other sharp features that may be ascribed to specific carbon bonding environments. For instance, $>\text{C}=\text{O}$ groups contained in coal samples will often be manifest as small peaks downfield from the aromatic band. If these features are present additional structural information such as the relative amount of $>\text{C}=\text{O}$ groups present can be obtained directly.

Quantitative characterization of the functional groups in coals can provide a surprisingly rich description of their overall structure and chemistry. Research directed at measurement of such parameters provides the background needed to rationally design new approaches to coal depolymerization chemistry. Unfortunately, many of the most important average structural parameters determined in these studies are derived from several measurements. It is usually difficult to provide internal consistency checks for the parameters so derived, and propagation of errors often results in very large uncertainties for these parameters. For instance, aliphatic H/C ratios calculated from various combinations of ^{13}C or ^1H NMR data with IR and elemental analysis, have been found to differ by as much as a factor of two. Such large uncertainties make this data of limited utility and more direct spectral methods for determining such quantities would appear to be desirable. In this paper, we hope to show how average structural parameters for coals can be determined from a single method in which propagation of error is minimized.

THEORY

Spectra presented in this paper were obtained with the pulse sequences illustrated in figure 1. These pulse sequences form the basis for a new spectral editing scheme that enables one to obtain four ^{13}C CPMAS subspectra for a given compound. These subspectra represent the carbon resonances from the nonprotonated ^{13}C , ^{13}CH , $^{13}\text{CH}_2$ and $^{13}\text{CH}_3$ groups of the compound under investigation. Fundamental to the development of this editing technique is an understanding of the dynamics of cross relaxation between ^{13}C nuclei and ^1H nuclei. This cross relaxation, which was historically assumed to be single exponential, is now known to consist of two components, the faster of which is due to directly bonded carbon-proton interactions. Cross relaxation to nonprotonated carbons lacks this two stage feature. Similarly, in methyl groups, where the heteronuclear dipolar coupling is attenuated by internal rotation, the cross relaxation is also essentially single exponential. With this knowledge of the cross relaxation rates, one can design experiments to selectively polarize ^{13}CH and $^{13}\text{CH}_2$ groups. For those groups in which the cross relaxation is bi-exponential, the fast portion of the cross relaxation occurs on the tens of microseconds timescale. The slower portion, from less strongly coupled protons, occurs on the millisecond or hundred of microsecond timescale. In practice, one finds that after a CP contact of several milliseconds, the rare ^{13}C and the abundant ^1H nuclei achieve a common spin temperature. In comparison to the single pulse excitation (SPE) ^{13}C NMR signal, this CP ^{13}C signal will be

enhanced by about a factor of four. For CP contacts lasting several tens of microseconds, the situation is different. ^{13}C nuclei reach a quasi equilibrium with their directly attached ^1H 's. In this initial equilibrium, polarization is shared equally between the bonded nuclei. The ^{13}C signal rapidly achieves 1/2 its ultimate intensity for a ^{13}CH pair, or 2/3 in a $^{13}\text{CH}_2$ group. The final approach to a fully enhanced CP signal depends upon spin diffusion among the abundant protons. Since the degree of polarization of a ^{13}C nucleus in this quasi equilibrium depends upon the number of directly attached protons, it can serve as the basis for a spectral editing scheme

The realization that there are two distinct timescales for the ^1H - ^{13}C CP process isn't sufficient to devise a complete spectral editing scheme. With this knowledge, the best that can be done is to separate ^{13}C resonances into two groups; strongly coupled (^{13}CH , $^{13}\text{CH}_2$) and weakly coupled (^{13}C -, $^{13}\text{CH}_3$). To obtain further selectivity, polarization inversion (PI) and depolarization (DEP) are used. Polarization inversion is used to remove the ^{13}CH signal from an experiment that selects for the strongly coupled groups. In this way, a spectrum that contains only $^{13}\text{CH}_2$ signal can be obtained. Experimentally this is realized as follows. During polarization inversion, the phase of the proton RF field is shifted by 180° . This corresponds to an inversion of the spin temperature for the proton spins locked by that field. The situation is now such that the two types of spins have spin temperatures of opposite sign. Since the spins are still subject to cross polarization, the spin temperature will equilibrate. This results in no signal for a ^{13}CH group ($1+[-1]=0$) and a negative signal for a $^{13}\text{CH}_2$ group ($1+[-2]=-1$). Depolarization is accomplished by turning off the RF field in the proton channel and allowing the ^1H magnetization to dephase under T_2 . Then, the CP contact is reinstated and the ^{13}C 's are depolarized as the ^1H 's gain polarization. Of course, the rate of polarization change is a function of the strength of the dipolar coupling and depolarization times can be chosen to principally affect strongly coupled spin systems only. In practice, depolarization is used to "clean up" spectra by removing signal from the strongly coupled ^{13}CH and $^{13}\text{CH}_2$ groups. The resulting spectra can then be used in the editing procedure as sources of nonprotonated ^{13}C and $^{13}\text{CH}_3$ signal only.

The four subspectra obtained from application of this method are linear combinations of four experimental spectra. These four experimental spectra are derived from four pulse sequences (see figure 1). The first pulse sequence (figure 1a) is a short (40 μs) contact time cross polarization; abbreviated SCP. This yields a ^{13}CH and $^{13}\text{CH}_2$ dominated spectrum that contains traces of nonprotonated ^{13}C and $^{13}\text{CH}_3$ signal. The second pulse sequence (figure 1b) is

comprised of a short (40 μ s) contact time CP followed by 35 μ s of polarization inversion. This yields the $^{13}\text{CH}_2$ only subspectrum directly and is abbreviated SCPPI. The third pulse sequence (figure 1c) is called SCPDEP which stands for a short (40 μ s) CP followed by depolarization. This spectrum contains no ^{13}CH or $^{13}\text{CH}_2$ signal. The nonprotonated ^{13}C and $^{13}\text{CH}_3$ signals can be subtracted from the residual signals in the SCP spectrum to yield a spectrum that contains ^{13}CH and $^{13}\text{CH}_2$ only. The final pulse sequence is LCPDEP (figure 1d) which represents a long (1.0 ms) CP followed by depolarization. This spectrum contains no ^{13}CH or $^{13}\text{CH}_2$ signal. Provided the nonprotonated ^{13}C and $^{13}\text{CH}_3$ signals do not overlap, this spectrum can be separated into nonprotonated ^{13}C only and $^{13}\text{CH}_3$ only contributions. In general, the signals may or may not overlap. For these coal samples it is assumed that all of the nonprotonated ^{13}C intensity is due to aromatic (sp^2 hybridized) moieties. This assumption is supported by dipolar dephasing experiments done at 4 K on whole coals. These experiments indicate that none of the nonprotonated ^{13}C signal arises from aliphatic environments. This being the case, the separation of the spectrum appears justified. In practice, the separation of the LCPDEP spectrum to yield these two subspectra is accomplished by zeroing the appropriate section of the spectrum. This yields two separate subspectra; one containing nonprotonated ^{13}C signal only and the other containing $^{13}\text{CH}_3$ signal only. Multiplication by the appropriate scaling factors generates the corresponding intensity corrected subspectra.

EXPERIMENTAL

Samples from the APCS program were used as received. While under argon, each sample was opened and an aliquot transferred to a 7mm rotor. All experiments were performed at $B_0=2.35$ T using an Oxford Instruments room temperature bore superconducting solenoid magnet and a home-built spectrometer using a Nicolet 1280 data system. A doubly tuned single coil home built probe that utilized a MAS stator from Doty Scientific Ltd. was used for all measurements. Each sample was spun at the magic angle with a spinning speed of ca. 4 kHz. An RF field strength of 62 kHz was used for proton decoupling. In order to optimize the experimental parameters, a sample of mono ethyl fumarate was used. The Hartmann-Hahn match condition $\omega_C = \omega_H = 55$ kHz was established using this compound and a SCPPI spectrum (Short Cross Polarization - Polarization Inversion; see Theory section) was acquired to verify the setting. It was found that if the match was poorly set the ^{13}CH signal would not be completely suppressed

in this spectrum. After having passed this test, measurement of the coal spectra were performed. Simultaneous phase inversion was used in each pulse sequence to minimize sensitivity to the match. Contact times of 1.0 ms and 40 μ s were used for the long and short contact times respectively. Typically 1000 transients were acquired for the LCP spectrum; 2000 for the LCPDEP; 4000 for the SCP; 24000 for the SCPDEP, and 24000 for the SCPPI spectrum. A relaxation delay of 1.2 seconds was used for all spectra recorded. All chemical shifts are quoted in ppm relative to TMS (tetramethylsilane).

RESULTS

For each of the eight coals in the APCS bank, we have acquired the four spectra that comprise our editing method. Linear combinations, as outlined in the theory section, have been made to produce four subspectra for each coal. In addition to the subspectra, several other spectra are of interest. Figures 2 to 17 represent the spectra obtained from these experiments. These include the nonprotonated ^{13}C , ^{13}CH , $^{13}\text{CH}_2$, and $^{13}\text{CH}_3$ only subspectra; the 'normal' long contact time CPMAS spectrum; the synthetic CPMAS spectrum derived from the subspectra; and a spectrum representing the difference between these last two spectra. Taken together, the subspectra give a good indication of the functionalities present in a given sample. Comparison of the 'normal' CPMAS and synthetic CPMAS spectra via the difference spectrum provides an important check for consistency.

For each coal, the nonprotonated ^{13}C subspectrum consists of one broad peak. Spinning sidebands, with intensities of approximately 8% are also present. The single nonprotonated peak has significant intensity from ca. 100 to 170 ppm in most of the coal samples. Some samples also display nonprotonated ^{13}C resonances due to carbonyl groups. These carbonyl resonances fall in the region near 180 ppm. The range from 0 to 70 ppm has been set to zero to remove $^{13}\text{CH}_3$ signal.

The ^{13}CH subspectrum consists of one or two peaks, depending on the coal. Spinning sidebands are barely observable above the baseline in most of the ^{13}CH subspectra. The aromatic ^{13}CH signal falls in the 100 to 140 ppm range and the aliphatic signal in the 20 to 60 ppm range. In all cases, the sp^2 hybridized ^{13}CH intensity is greater than the sp^3 hybridized ^{13}CH intensity. For the Pocahontas sample, no aliphatic ^{13}CH intensity is observable. In each of the coals studied however, some aromatic ^{13}CH signal is present.

The $^{13}\text{CH}_2$ subspectrum consists of one peak in each case, with chemical shift of 0 to 60 ppm. No spinning sidebands are observable in any of the $^{13}\text{CH}_2$ subspectra.

The $^{13}\text{CH}_3$ subspectrum also consists of one peak around the 0 to 60 ppm range. In the $^{13}\text{CH}_3$ subspectrum, the range from 70 to 350 ppm is zeroed to remove signal from nonprotonated ^{13}C .

For each of the coals studied, there are several sharp features to the resonance bands present in the spectra. Knowledge of the chemical shift and proton multiplicity enables one to associate a possible carbon bonding environment (functionality) with each of these sharp features. Sample structures as shown in figures 18 to 21 will be used to discuss the carbon functionalities.

Subspectra of the Wyodak-Anderson coal sample contain several peaks which may be assigned to specific carbon functionalities. The nonprotonated ^{13}C subspectrum contains distinct chemical shifts at 184, 155, and 137 ppm (see figure 2). The peak at 184 ppm clearly corresponds to a carbonyl resonance. Since this peak appears in the nonprotonated ^{13}C subspectrum, the possibility of an aldehydic group can be ruled out. It is possible however that this resonance is due to an acid, ester, or ketone functionality. On the basis of chemical shift, it seems most reasonable to assign the resonance to an aliphatic acidic functional group. Structure J in figure 18 is an example of such a carbon center. The next peak of interest has a chemical shift of 155 ppm. This resonance must similarly correspond to a nonprotonated carbon center. The chemical shift suggests that an aromatic carbon atom with an attached ether oxygen is a possibility. This ether may be an aliphatic or aryl ether; a phenol is also a possibility. An example of such a carbon functionality is the nonprotonated carbon in methoxybenzene which is pictured as structure E in figure 18. Phenol (structure F, figure 18) is also a possibility. The final peak of interest here has a chemical shift of 137 ppm. This resonance can be assigned to nonprotonated carbon atoms in heteroaromatic rings. For example, one of the quaternary carbons of isoquinoline resonates at approximately this chemical shift (see structure C of figure 18).

In the ^{13}CH subspectrum of the Wyodak-Anderson coal, there are two peaks of interest. One of these peaks lies in the aliphatic region with a chemical shift of 45 ppm. The other peak corresponds to aromatic carbon resonances and is found at 120 ppm. On the basis of chemical shift, the aliphatic peak corresponds to methine resonances in decalin type moieties. Structure 9 in figure 19 corresponds to this type of carbon. The second peak in the ^{13}CH subspectrum of this coal corresponds to ^{13}CH groups in heteroaromatic molecules such as the ones labeled 'a' in structure 3 of figure 19.

The $^{13}\text{CH}_2$ subspectrum of this coal consists of a single peak with a chemical shift of 34 ppm. This resonance corresponds to methylene groups in aliphatic rings. Examples of this type of carbon environment are given in figure 20 as structures I and II.

For the Wyodak-Anderson coal, the $^{13}\text{CH}_3$ subspectrum contains two peaks that are of interest. These peaks have chemical shifts of 31 and 18 ppm. For the 31 ppm resonance, a methyl group environment in which the methyl carbon is attached to a carbonyl group is proposed. The methyl group in acetone resonates at 30.6 ppm and therefore meets these criteria. Structures ii & iii in figure 21 depict this molecule and neopentane, whose chemical shift is similar. The second methyl resonance, at 18 ppm, corresponds to methyls on aliphatic carbons such as the methyl labeled 'b' in structure vi of figure 21.

The next coal that will be considered is Pittsburgh No. 8. The nonprotonated ^{13}C subspectrum of this coal contains two peaks, at 155 and 135 ppm, that are of interest. As discussed above under the Wyodak-Anderson coal, nonprotonated carbon resonances at 155 ppm are assigned to aromatic ether carbons. This functionality is represented by structures E & F in figure 18. The resonance at 135 ppm corresponds to carbon atoms common to the two aromatic rings such as in structure B of figure 18. This resonance could also correspond to quaternary carbons in heteroaromatic polycyclic rings. In this case, the structure mentioned in the discussion of the 137 ppm nonprotonated ^{13}C resonance of the Wyodak-Anderson coal could also apply.

The ^{13}CH subspectrum of the Pittsburgh No. 8 coal shows three distinct chemical shifts at 126, 43, and 33 ppm. The first of these shifts corresponds to ^{13}CH groups in aromatic rings such as in structure 1 and structure 2(a) of figure 19. The peak at 43 ppm in this subspectrum corresponds to certain aliphatic ^{13}CH 's. An example of one compound with a similar chemical shift is given as structure 10 in figure 19. The third peak of interest in this subspectrum falls at 33 ppm. This resonance corresponds to tertiary aliphatic ring carbons such as the one identified in structure 12 of figure 19.

There is one peak of interest in the $^{13}\text{CH}_2$ subspectrum of the Pittsburgh No. 8 coal. The single resonance at 33 ppm arises from methylene groups in aliphatic chains or rings. These groups are depicted in structures III and V of figure 20 and, as noted for the Wyodak-Anderson coal, in structures I & II of the same figure.

The methyl only subspectrum of this coal contains resonances at 53 and 18 ppm. The 53 ppm resonance can be assigned to $^{13}\text{CH}_3$ groups attached to oxygen such as the aromatic ether in structure i of figure 21. The second methyl chemical shift of interest could correspond to a

methyl group on an aliphatic carbon center. The methyl group labeled 'b' in structure vi of figure 21 shows an example of this carbon functionality.

Subspectra of the Stockton-Lewiston sample provide similar insight into the carbon functionalities present in the coal. The nonprotonated ^{13}C only subspectrum contains a peak at 134 ppm. This peak can be assigned, analogous to the peak from the spectrum of the Pittsburgh No. 8 coal sample, to carbon atoms common to two aromatic rings. The figure references for this peak are identical to those given for the Pittsburgh sample.

Peaks at 125 and 47 ppm are present in the ^{13}CH subspectrum of the Stockton sample. The 125 ppm resonance corresponds to aromatic methine groups. Spectra of the Pittsburgh coal contain analogous resonances at 126 ppm and the reader is referred to the figures mentioned earlier. The 47 ppm resonance is assigned to aliphatic ring methine functionalities such as the group shown in structure 8 of figure 19.

The methylene only subspectrum for this coal consists of a single peak, centered at 32 ppm. This chemical shift corresponds to $^{13}\text{CH}_2$ groups in aliphatic chains. The chemical shift of the third carbon in octane (see structure V(b) in figure 20) is 32.1 ppm which is quite close to the value observed here. The third carbon of 2-methyl butane, as shown in structure III of figure 20, resonates at nearly this frequency as well. This similarity is sufficient to associate the methylene peak observed for the Stockton coal with this type of functionality.

There are two chemical shifts of interest in the $^{13}\text{CH}_3$ only subspectrum of this coal. The peak at 28 ppm corresponds to methyl groups attached to quaternary aliphatic carbon centers. An example of a molecule with such a methyl group is structure iv in figure 21. The second peak has a chemical shift of 19 ppm. This resonance can be assigned to the same carbon bonding environment as the 18 ppm methyl group resonance observed in spectra of the Pittsburgh No. 8 and Wyodak-Anderson coals.

The nonprotonated ^{13}C subspectrum for the Upper Freeport coal has a peak at 132 ppm. This chemical shift corresponds to quaternary carbon atoms common to two aromatic rings. An example of a molecule with a resonance at this frequency is structure A in figure 18.

In the ^{13}CH subspectrum of this coal, we find two resonances of interest. Peaks appearing at 126 and 51 ppm correspond to aromatic and aliphatic ^{13}CH resonances respectively. As discussed previously, the 126 ppm peak can be assigned to aromatic methine carbons. The 51 ppm peak corresponds to an aliphatic methine carbon with an attached aryl group. Structure 6 in figure 19 provides an example of a methine group with this chemical shift.

Two peaks are of interest in the $^{13}\text{CH}_2$ subspectrum of the Upper Freeport coal. The first peak has a chemical shift of 35 ppm and can be assigned to the same structures as the Wyodak-Anderson 34 ppm resonance. The second peak, with a chemical shift of 22 ppm, corresponds to $^{13}\text{CH}_2$'s between terminal methyl groups and secondary aliphatic carbons. This type of carbon functionality is present in octane as shown in structure V(a) of figure 20.

The final subspectrum contains the methyl resonances. For this coal, there is one methyl resonance of interest at 20 ppm. This chemical shift corresponds to a methyl group attached to a methine carbon that has an attached hydroxyl group. Structure vi in figure 21 shows such a methyl group.

The nonprotonated ^{13}C subspectrum of the Beulah Zap sample contains five distinct chemical shifts to which we will assign structures. Peaks at 181, 165, 155, 146, and 137 ppm are of interest. On the basis of chemical shift alone, one can conclude that the peaks at 181 and 165 ppm must be due to carbonyl resonances. The first of these peaks, at 181 ppm, corresponds to an aliphatic carboxylic acid. Structure I of figure 18 gives an example of an acid such as this. The 165 ppm peak can be assigned to an ester, with either an aromatic or aliphatic structure being a possibility. Structures G and H in figure 18 are plausible. The remaining three resonances are due to quaternary aromatic carbons. The 155 ppm peak was assigned in the discussion of the Wyodak-Anderson coal. The peak at 146 ppm corresponds to quaternary carbons next to nitrogens in aromatic molecules. An example of this bonding arrangement can be found in structure D of figure 18. The final peak, at 137 ppm, has also been previously assigned in the discussion of the Wyodak-Anderson coal.

The ^{13}CH subspectrum contains three peaks that will be discussed here. One aromatic peak with a chemical shift of 120 ppm and two aliphatic peaks at 55 and 48 ppm are of interest. The aromatic peak was assigned in the discussion of the Wyodak-Anderson coal. The second peak, at 55 ppm, can be assigned to aliphatic methine groups next to nitrogen. An example of one possibility is given in structure 5 of figure 19. The 48 ppm peak also corresponds to an aliphatic methine with an attached nitrogen. The methine carbon in structure 7 of figure 19 has a chemical shift of 48 ppm.

There is one peak at 33 ppm in the methylene only subspectrum for this coal. It corresponds to chain and/or ring methylene groups as discussed under the Wyodak-Anderson coal.

In the methyl subspectrum for the Beulah Zap coal, shifts at 57 and 22 ppm are of interest. The 57 ppm peak can be assigned to aromatic methyl ethers similar to the 53 ppm peak in the Pittsburgh No. 8 coal subspectrum. The 22 ppm peak corresponds to methyl's on isopropyl groups. Structure v in figure 21 is an example of a molecule with methyl group that has this chemical shift.

The nonprotonated ^{13}C subspectrum of the Illinois No. 6 coal contains a peak with a shift of 136 ppm. This peak corresponds to aromatic methine carbons as discussed for the Pittsburgh No. 8 coal.

The ^{13}CH subspectrum of this coal has four interesting peaks with chemical shifts of 124, 105, 71, and 41 ppm. The 124 ppm peak can be assigned to aromatic methine groups as in structures 2(b) and 3(b) of figure 19. The second peak, with a chemical shift of 105 ppm, corresponds to carbons in heteroaromatic rings such as the carbon indicated with a 'c' in structure 3 of figure 19. The 71 ppm peak corresponds to aliphatic methine carbons with attached hydroxyl groups. Structure 4 in figure 19 contains a carbon of this type. The final ^{13}CH resonance of interest for this coal lies at 41 ppm. This chemical shift corresponds to an aliphatic methine carbon like that of structure 11 in figure 19.

The methylene only subspectrum contains a single resonance at 32 ppm. This resonance corresponds to methylenes labeled 'b' in structure V of figure 20 and to the methylenes indicated in structure III of the same figure.

The $^{13}\text{CH}_3$ only subspectrum contains a peak with a chemical shift of 17 ppm. The assignment of this peak is identical to the assignment of the peak at 18 ppm in the corresponding subspectrum of the Wyodak-Anderson coal.

There are two peaks of interest in the nonprotonated ^{13}C subspectrum of the Blind Canyon coal. The first peak lies at 154 ppm and can be assigned to the same carbon functionality as was the 155 ppm peak for the Pittsburgh No. 8 coal. The second peak has a chemical shift of 137 ppm and was assigned in the discussion of the Wyodak-Anderson coal.

The methine only subspectrum for this coal has shifts of 124, 111, 43, and 32 ppm. The 124 ppm resonance can be assigned to the same carbon functionality as the 124 ppm peak in the Illinois No. 6 coal. The 111 ppm peak corresponds to the appropriate carbon (carbon 'd') in structure 3 of figure 19. The 43 ppm peak was assigned in the discussion of the Pittsburgh No. 8 coal. The 32 ppm resonance can be assigned to the same carbon environment as the 33 ppm resonance in the Pittsburgh No. 8 coal.

The $^{13}\text{CH}_2$ subspectrum for the Blind Canyon coal contains resonances at 33 and 30 ppm. The 33 ppm peak was assigned during the discussion of the Pittsburgh No. 8 methylene only subspectrum. The peak at 30 ppm corresponds to methylene groups in decalin rings such as structure IV in figure 20.

The methyl only subspectrum of this coal contains resonances at 31 and 22 ppm. The 31 ppm peak was assigned during the discussion of the Wyodak-Anderson coal and the 22 ppm peak was assigned to the 22 ppm resonance in the methyl only subspectrum of the Beulah Zap coal.

The final coal in the APCS series is the Pocahontas coal. The nonprotonated ^{13}C subspectrum of this coal has a peak at 132 ppm. This resonance was assigned during the discussion of the Upper Freeport coal.

The ^{13}CH only subspectrum contains a single resonance of interest at 124 ppm. This resonance was assigned during the discussion of the Illinois no. 6 coal.

The methylene only subspectrum has a peak at 32 ppm. This resonance was assigned during the discussion of the Stockton-Lewiston coal.

The methyl only subspectrum of the Pocahontas coal has a resonance at 20 ppm which can be assigned analogously to the 20 ppm resonance observed in the methyl only subspectrum of the Upper Freeport coal.

LIST OF FIGURES

Figure 1: Pulse sequences.

- a) Short CP sequence (SCP)
- b) Short CP combined with polarization inversion (SCPPI)
- c) Short CP followed by depolarization (SCPDEP)
- d) Long CP followed by depolarization (LCPDEP)

Figure 2: Edited subspectra and LCP spectrum of the Wyodak coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 3: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Wyodak coal.

- a) LCP spectrum
- b) Sum of figures 2 (b) to 2 (e)
- c) Difference spectrum -- 3(a)-3(b)

Figure 4: Edited subspectra and LCP spectrum of the Pittsburgh No. 8 coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 5: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Pittsburgh No. 8 coal.

- a) LCP spectrum
- b) Sum of figures 4 (b) to 4 (e)
- c) Difference spectrum -- 5(a)-5(b)

Figure 6: Edited subspectra and LCP spectrum of the Stockton coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 7: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Stockton coal.

- a) LCP spectrum

- b) Sum of figures 6 (b) to 6 (e)
- c) Difference spectrum -- 7(a)-7(b)

Figure 8: Edited subspectra and LCP spectrum of the Upper Freeport coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 9: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Upper Freeport coal.

- a) LCP spectrum
- b) Sum of figures 8 (b) to 8 (e)
- c) Difference spectrum -- 9(a)-9(b)

Figure 10: Edited subspectra and LCP spectrum of the Beulah Zap coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 11: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Beulah Zap coal.

- a) LCP spectrum
- b) Sum of figures 10 (b) to 10 (e)
- c) Difference spectrum -- 11(a)-11(b)

Figure 12: Edited subspectra and LCP spectrum of the Illinois No. 6 coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 13: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Illinois No. 6 coal.

- a) LCP spectrum
- b) Sum of figures 12 (b) to 12 (e)
- c) Difference spectrum -- 13(a)-13(b)

Figure 14: Edited subspectra and LCP spectrum of the Blind Canyon coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 15: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra Blind Canyon coal.

- a) LCP spectrum
- b) Sum of figures 14 (b) to 14 (e)
- c) Difference spectrum -- 15(a)-15(b)

Figure 16: Edited subspectra and LCP spectrum of the Pocahontas coal.

- a) LCP spectrum
- b) nonprotonated ^{13}C only subspectrum
- c) ^{13}CH only subspectrum
- d) $^{13}\text{CH}_2$ only subspectrum
- e) $^{13}\text{CH}_3$ only subspectrum

Figure 17: Spectrum representing the sum of the subspectra, the LCP spectrum, and the difference between these two spectra for the Pocahontas coal.

- a) LCP spectrum
- b) Sum of figures 16 (b) to 16 (e)
- c) Difference spectrum -- 17(a)-17(b)

Figure 18: Structures assigned to nonprotonated ^{13}C subspectra.

Figure 19: Structures assigned to ^{13}CH subspectra.

Figure 20: Structures assigned to $^{13}\text{CH}_2$ subspectra.

Figure 21: Structures assigned to $^{13}\text{CH}_3$ subspectra.

Figure 22: Summary of results section.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18: Structures assigned to nonprotonated ^{13}C subspectra.

Figure 19: Structures assigned to ^{13}CH subspectra.

Figure 20: Structures assigned to $^{13}\text{CH}_2$ subspectra.

Figure 21: Structure assigned to $^{13}\text{CH}_3$ subspectra.

FIGURE 22: Summary of results.

Wyodak-Anderson

Subspectrum	Shift	Structure	Fig.
^{13}C	184	J	18
	155	E or F	18
	137	C	18
^{13}CH	120	3(a)	19
	45	9	19
$^{13}\text{CH}_2$	34	I or II	20
$^{13}\text{CH}_3$	31	ii or iii	21
	18	vi	21

Pittsburgh No. 8

Subspectrum	Shift	Structure	Fig.
^{13}C	155	E or F	18
	135	B or C	18
^{13}CH	126	1 or 2(a)	19
	43	10	19
	33	12	19
$^{13}\text{CH}_2$	33	I,II,III,V(b)	20
$^{13}\text{CH}_3$	53	i	21
	18	vi	21

Stockton

Subspectrum	Shift	Structure	Fig.
^{13}C	134	B or C	18
^{13}CH	125	1 or 2(a)	19
	47	8	19
$^{13}\text{CH}_2$	32	III or V	20
$^{13}\text{CH}_3$	28	iv	21
	19	vi	21

Upper Freeport

Subspectrum	Shift	Structure	Fig.
^{13}C	132	A	18
^{13}CH	126	1 or 2(a)	19
	51	6	19
$^{13}\text{CH}_2$	35	I or II	20
$^{13}\text{CH}_3$	22	V	20
	20	vi	21

Beulah Zap

Subspectrum	Shift	Structure	Fig.
^{13}C	181	I	18
	165	G or H	18
	155	E or F	18
	146	D	18
	137	C	18
^{13}CH	120	3(a)	19
	55	5	19
	48	7	19
	33	I or II	20
$^{13}\text{CH}_2$	33	I or II	20
	57	i	21
$^{13}\text{CH}_3$	22	v	21

Illinois No.6

Subspectrum	Shift	Structure	Fig.
^{13}C	136	B or C	18
^{13}CH	124	2(b) or 3(b)	19
	105	3(c)	19
	71	4	19
	41	11	19
$^{13}\text{CH}_2$	32	III or V(b)	20
$^{13}\text{CH}_3$	17	vi	21

Blind Canyon

Subspectrum	Shift	Structure	Fig.
^{13}C	154	E or F	18
	137	C	18
^{13}CH	124	2(b) or 3(b)	19
	111	3(d)	19
	43	10	19
	32	12	19
$^{13}\text{CH}_2$	33	I,II,III,V(b)	20
	30	IV	20
$^{13}\text{CH}_3$	31	ii or iii	21
	22	v	21

Pocahontas

Subspectrum	Shift	Structure	Fig.
^{13}C	132	A	18
^{13}CH	124	2(b) or 3(b)	19
$^{13}\text{CH}_2$	32	III or V(b)	20
$^{13}\text{CH}_3$	20	vi	21

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