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Two Dimensional NMR and NMR Relaxation Studies
of Coal Structure

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PROGRESS REPORT

including
the period January 1, 1993 to March 31, 1993

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Prepared for the Department of Energy
Agreement No. DE-FG22-91PC91285

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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 (3 and 4) 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. In the attached preprint we describe an extension of this work to produce another new method for spectral editing of complex solid state $\text{C-}^{13}\text{NMR}$ spectra. The technique appears to provide a reliable means of assessing the number of methylene groups in a complex organic solid.

Methylene-only subspectrum in CPMAS NMR

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The CPMAS spectrum can be edited by using cross polarization (CP) (1) combined with polarization inversion (PI) (2-4). In the CPPI spectrum obtained with a long CP time and 35 μ s PI time, ^{13}CH signals disappear, $^{13}\text{CH}_2$ signals become negative and have a relative intensity about 1/3, and methyl and nonprotonated ^{13}C signals are attenuated to about 62 and 86%, respectively (5). The four kinds of signals are easy to distinguish. However, in more complicated spectra, where the different kinds of lines overlap severely, it is not easy to edit the signals with perfect selectivity, especially when a quantitative analysis is desired.

This communication will show that, if CP and PI times in the CPPI scheme are chosen properly, $^{13}\text{CH}_3$, nonprotonated ^{13}C as well as ^{13}CH signals can be suppressed completely, while the remaining $^{13}\text{CH}_2$ signals are still strong enough to produce a methylene-only subspectrum.

The pulse sequence used is that of the standard cross polarization (CP) combined with polarization inversion (PI) as shown in Fig. 1a. The abundant I spin represents ^1H , and the rare S spin ^{13}C . Unlike in the previous proposals (5), the CP time used in the new scheme is very short, about 40 μ s. For rigid SI_n groups, 40 μ s is long enough for the S spin and its directly bonded I spins to reach a quasi-equilibrium state and to share the magnetization offered by the I spins in the SI_n subsystem (6,7). Thus 40 μ s CP time results in a spectrum where the ^{13}CH signals reach 50% of its

maximum intensity, while $^{13}\text{CH}_2$ signals reach 66.7%. In contrast, the methyl and nonprotonated carbon signals vary much slowly and in a single-exponential fashion. Their signal intensity, M_{cp} , as a function of the CP time τ_{cp} , can be expressed as :

$$M_{\text{cp}} = M_0 (1 - \exp(-\tau_{\text{cp}}/T_{\text{IS}})). \quad (1)$$

Here M_0 is the maximum signal intensity that can be obtained if the CP time is chosen to be much longer. T_{IS} is the CP rate constant, which is about 150 μs and 800 μs for typical $^{13}\text{CH}_3$ groups and nonprotonated ^{13}C sites, respectively. Thus after a 40 μs CP time, the signal intensity for typical $^{13}\text{CH}_3$ groups and nonprotonated ^{13}C sites are approximately 23.5% M_0 and 5% M_0 , respectively. They are weaker than the rigid protonated $^{13}\text{CH}_n$ signals, yet the $^{13}\text{CH}_3$ signals are still noticeable.

After 40 μs CP, the phase of the I spin channel is then shifted by 180° , as shown in Fig. 1a. As the spin temperature of the I spins is inverted, the quasi-equilibrium state of the rigid SI_n subsystem is broken and polarization transfer between the S and I_n occurs again. The I and S spins reach a new quasi-equilibrium state after a 35 μs PI time. During the PI process, the polarizations of the $n \times \text{I}$ spin and the S spin cancel each other so that at the end of the PI time ^{13}CH signals are nulled, while $^{13}\text{CH}_2$ signals become negative with a relative intensity -1/3 with respect to that before PI. The $^{13}\text{CH}_3$ and nonprotonated ^{13}C signals, M_{pi} , will vary according to the equation:

$$M_{\text{pi}}(\tau_{\text{pi}}) - M_{\text{cp}} = (-M_0 - M_{\text{cp}}) (1 - \exp(-\tau_{\text{pi}}/T_{\text{IS}})). \quad (2)$$

Where τ_{pi} is the PI time. Combining Eqs. [1] and [2] gives the expression:

$$M_{pi} = M_0 \{2\exp[-\tau_{pi}/T_{IS}] - \exp[-(\tau_{cp} + \tau_{pi})/T_{IS}] - 1\}. \quad (3)$$

When both τ_{cp} and τ_{pi} are much shorter than T_{IS} ,

$$M_{pi} \sim M_0 (\tau_{cp} - \tau_{pi})/T_{IS}. \quad (4)$$

Equation [4] tells us that the S signals are approximately equal to zero if τ_{cp} and τ_{pi} both are short and are roughly equal to each other. For nonprotonated ^{13}C signals, Eq. [4] is sufficiently accurate. For $^{13}\text{CH}_3$ Eq. [3] should be used, as 40 μs is not a significantly shorter time than 150 μs . From Eq. [3] it is easy to deduce that for $T_{IS} = 150$ μs , a combination of a 40 μs CP time and a 35 μs PI time makes M_{pi} equal to zero. Under this condition, a methylene-only subspectrum is obtained.

Experiments were performed on a homebuilt NMR spectrometer controlled by a Nicolet data system and using an Oxford Instruments 2.35 T, 110 mm room-temperature bore superconducting solenoid. A homebuilt CPMAS probe using a stator of Doty Scientific Inc. has been used. The simultaneous phase inversion (SPI) were used for both CP and PI, as shown in Fig. 1b, which relaxes the requirement of a well-matched Hartmann-Hahn condition (7-9). The durations τ_{cp1} and τ_{pi1} were set equal to τ_{cp2} , and τ_{pi2} , respectively. The setup requirements for these experiments were essentially identical to those used for routing CPMAS

experiments. All the spectra were obtained with MAS rates of 4 kHz and under the Hartmann-Hahn condition. During the contact time, both RF field strengths were 60 kHz, while the ^1H decoupling field strength was 75 kHz.

A methylene-only subspectrum for a model sample, fumaric acid monoethyl ester, is shown in Fig. 2d, top. For comparison, three other spectra are also displayed, which are: (a) a standard CPMAS spectrum with 1.5 ms CP time, (b) a CPPI spectrum with 1.5 ms CP time and 35 μs PI time, and (c) a spectrum obtained with 40 μs CP time.

Table 1 shows the relative intensities for each peak in the four spectra shown in Fig 2, where the intensities of spectrum (a) are taken as 100%. In spectrum (b), the two methine lines near 135 ppm are nulled, while $^{13}\text{CH}_2$ signals at 60 ppm become negative with a relative intensity of 27%, as described before (5). In spectrum (c), the methylene and methine lines have relative intensities 68 and 55%, respectively. They are slightly stronger than 66.7 and 50%, because the $^{13}\text{CH}_n$ subsystems are not ideally isolated from the neighboring protons and ^1H - ^1H spin diffusion also occurs during the short CP time.

A similar set of four spectra of cholesteryl acetate are shown in Fig. 3. The numbers of scans for each spectrum are different as indicated in the figure. The $^{13}\text{CH}_2$ peaks in spectra (d) and (c) have opposite polarization but nearly identical apparent amplitudes, as in spectra (b) and (a).

Figure 4 shows the 10-50 ppm region of the same set of spectra. In the aliphatic region, the CPPI spectrum with a long CP

time (b) contains many positive and negative peaks. It is possible to identify some $^{13}\text{CH}_2$ signals from the negative peaks, but the severe overlap makes a complete assignment very difficult. In contrast, all methylene lines can be clearly identified in spectrum (d).

The method proposed here has all the advantages of the usual CPPI spectral editing method: it is very simple to apply; no adjustments of the instrument other than those for routine CPMAS are required. It offers a reliable semi-quantitative measurement of the rigid methylene groups. The underlying principle makes use the facts that (a) cross-relaxation rates of rigid SI_n groups are much faster than that containing non-protonated or methyl carbons, and (b) the ratio of the heat capacities between the S and I spins in the SI_n subsystem is different for ^{13}CH and $^{13}\text{CH}_2$ groups. These facts are generally insensitive to molecular motion. Of course, if some $^{13}\text{CH}_2$ groups are involved in substantial motions, their signals will be lost in the methylene-only subspectrum. As a result, this technique provides the minimum number of methylene groups in a given sample.

The choice of the short CP and PI time is not very critical, as the slow variation stage of the rigid SI_n signals in the cross-relaxation process begins after approximately 35 ~ 40 μs . A few μs variation makes no significant difference in the results.

The CPPI technique proposed here works best at moderate MAS speeds, for example, from 3 to 5 kHz (5). If necessary, it can be easily combined with other techniques to suppress spinning sidebands.

We come to the conclusion that the CPPI spectral editing technique can give a reliable methylene-only subspectrum. For typical rigid samples, the optimum parameters are: 40 μ s CP time and 35 μ s PI time. The methylene-only subspectrum has a relative intensity of -25% compared with the standard CPMAS spectrum.

Combined with other available techniques, it seems possible to get several subspectra, where only one kind of carbon signals dominates in each. This makes the complete spectral editing of CPMAS spectra more practical. These techniques have been used on some coal samples, where the different kinds of ^{13}C sites have wide chemical shift distributions. Spectral overlap makes such an analysis especially challenging. Our preliminary results indicate that these new techniques are quite promising even for such complex samples. Further work is in progress.

ACKNOWLEDGEMENTS

Support of this work by the U. S. Department of Energy under grant DE-FG22-91PC91285 is gratefully acknowledged.

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TABLE 1

RELATIVE INTENSITY

SPECTRA	^{13}C	^{13}CH	$^{13}\text{CH}_2$	$^{13}\text{CH}_3$
(a)	100	100	100	100
(b)	86	3	-27	62
(c)	8	55	68	22
(d)	0	0	-25	0

Figure Captions:

Fig. 1. The pulse sequences utilized. (a) Standard CPMAS combined with polarization inversion (CPPI). (b) Simultaneous phase inversion (SPI) is used during both the CP and the PI times.

Fig. 2. The methylene-only subspectrum of fumaric acid monoethyl ester (d), top, which was obtained by using $\tau_{cp1} = \tau_{cp2} = 20 \mu s$, $\tau_{pi1} = \tau_{pi2} = 17.5 \mu s$. The other three spectra were obtained under the conditions: (a) $\tau_{cp1} = \tau_{cp2} = 750 \mu s$. (b) $\tau_{cp1} = \tau_{cp2} = 750 \mu s$, $\tau_{pi1} = \tau_{pi2} = 17.5 \mu s$. (c) $\tau_{cp1} = \tau_{cp2} = 20 \mu s$.

Fig. 3. Four spectra for cholesteryl acetate, which were obtained under the similar conditions as described in Fig. 2. The numbers of scans are different as indicated to the right. The apparent amplitudes of the $^{13}CH_2$ peaks in spectra (d) and (c) are nearly identical, as in spectra (b) and (a).

Fig. 4. The expansion, from 10 to 50 ppm, of the spectra shown in Fig. 3. In spectrum (b), a complete assignment of methylene lines is difficult due to the severe overlap. In contrast, all methylene lines can be clearly identified in spectrum (d).

Table caption:

Table 1. Relative intensities of the four spectra shown in Fig. 1. The methylene-only subspectrum has a relative intensity of -25%.

Figure 1

Figure 2

Figure 3

Figure 4

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