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Two Dimensional NMR and NMR Relaxation Studies of Coal Structure

PROGRESS REPORT

including
the period July 1, 1992 to Sept. 30, 1992

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NOTICE

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. Methods such as dipolar dephasing or magic angle spinning separated local field spectroscopy differentiate carbon centers based on the number of dipolar couplings a given ^{13}C nucleus has to directly attached ^1H nuclei. Such methods work as long as one can assume that all ^{13}C-^1H dipolar couplings are basically of the same strength. When significant molecular mobility is present or a wide variation in dipolar couplings is encountered these techniques then fail. In the last report we presented the development of a new method using polarization inversion which can differentiate between CH_3, CH_2, CH and C centers. The new technique was different in that it did not rely heavily upon the strength of the dipolar couplings, but instead upon the number of protons attached to a given carbon center. The method is relatively user friendly and can be implemented on a wide range of commercial hardware. In this report we describe some extensions of the method and the first applications to the analysis of coal structure.

Application of CPMAS Spectral Editing to Coals

One of the new CP MAS spectral editing techniques we have developed permits us to obtain the methylene-only subspectrum. The editing techniques used include three different CPMAS pulse sequences: (1) Standard CPMAS (Figure 1a), (2) standard CP combined with polarization inversion (PI) as diagrammed in Fig. 1b. and finally (3) standard CP combined with depolarization for suppressing rigid protonated carbon signals (*Chem. Phys. Letters*, 162, 321 (1989).), as shown in Fig. 1c. There are slight modifications in these pulse sequences compared with the standard versions so that the carbon signals are spin-locked for the same period of time in the different experiments before the acquisition. This avoids possible distortions due to $T_{1\rho}$ effects. The total spin locking time used in these sequences is typically 300 μs.

For analysis, four spectra are recorded. (1) A standard CPMAS spectrum with about 1 ms of contact time, τ_{cp}. (2) A methylene-only subspectrum obtained with the pulse sequence shown in Fig. 1b and with the parameters τ_{cp} = 50 μs and polarization inversion time τ_{pi} = 36 μs. (3) A rigid-CH_n-

suppressed subspectum obtained with the pulse sequence shown in Fig. 1c and with the parameters τ_{cp} = 1 ms and depolarization time τ_D = 4 x 25 μs. (4) A short τ_{cp} spectrum with τ_{cp} = 50 μs, where rigid CH_n signals dominate. This last spectrum is necessary only when $T_{1\rho}$ of the protons is short, as in the case of coals.

The carbon signals of the standard CPMAS spectrum (spectrum 1) are supposed to have full intensity, which are taken as 100%. The relative intensities for the different kinds of signals in the three other spectra (spectra 2-4) are listed in the following table:

Table I

		relative intensity			
spectrum#	Name	C	CH	CH_2	CH_3
1	Standard CPMAS	100	100	100	100
2	Methylene-only	0	0	-23	0
3	Rigid-CH_n-suppressed	77	0	0	60
4	Rigid-CH_n-dominated	17	60	70	26
5	CH_3-suppressed	-28	100	100	0
6	C-suppressed	0	100	100	22

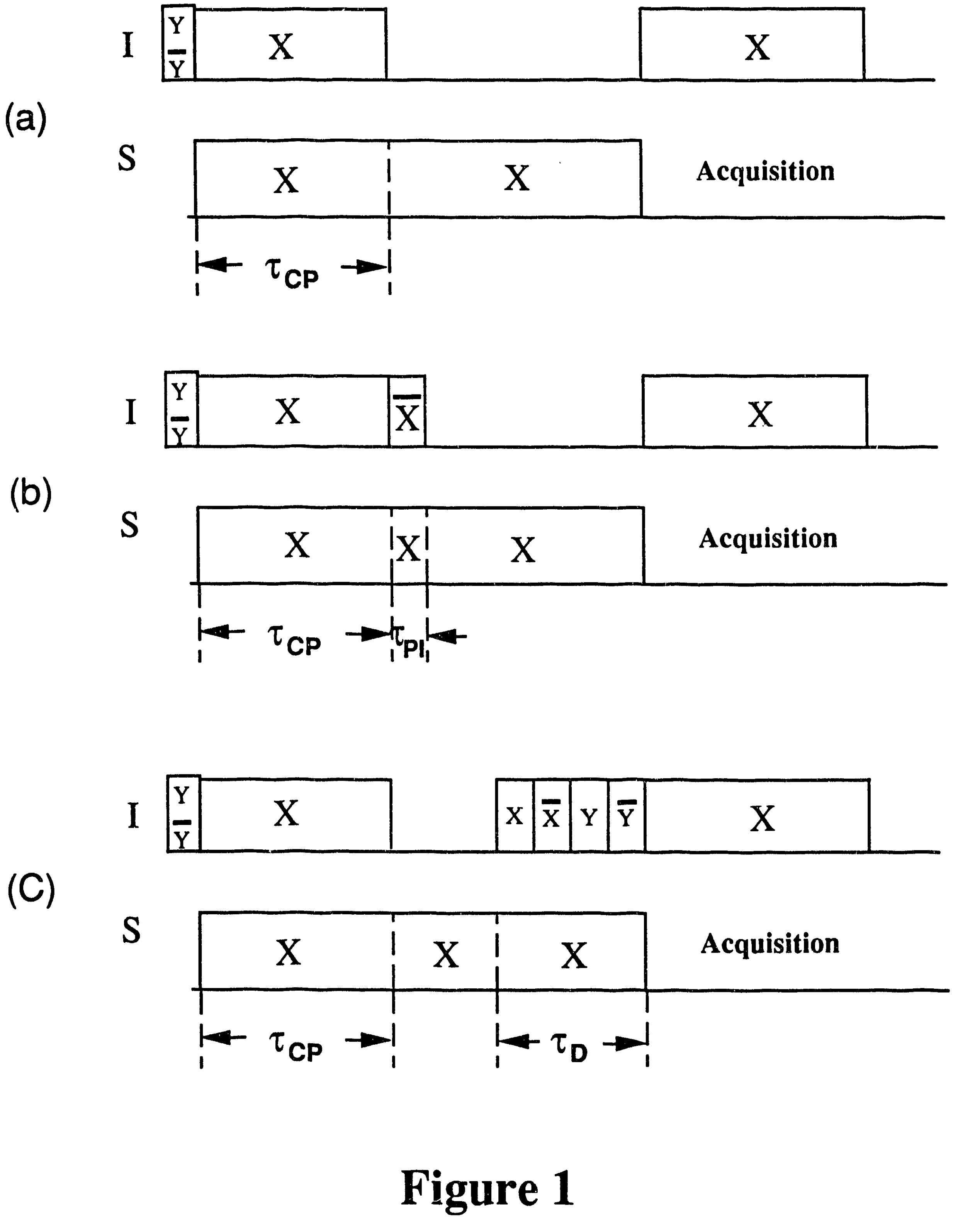
The four spectra (spectra 1 - 4) of a model sample, ethylfumaric acid, are displayed on Figure 2. From bottom to top, they are the standard CPMAS (spectrum 1), rigid-CH_n-suppressed (spectrum 3), rigid-CH_n-dominated (spectrum 4) and methylene-only (spectrum 2). For clarity the intensity of the methylene-only spectrum has been multiplyed by three.

Properly combining these four spectra according to the weights in Table I gives a possible approach to quantitative estimation of the different kinds of carbon signals. Of course, it is still difficult to separate the four kinds of signals completely, if they overlap. For example, a rigid-CH_n-only subspectrum cannot be obtained from spectrum 1 and spectrum 3, because the attenuation of C and CH_3 is different in spectrum 3. However, it is noted that in the aromatic region from 75 to 200 ppm, there are no CH_3 signals, and in the aliphatic region from 0 to 75 ppm, there is often little in the way of nonprotonated carbon signals (in coals). Thus partial separation is usually possible. For example, subtracting the rigid-CH_n-suppressed spectrum (spectrum 3) multiplied by 1.67, from the standard

CPMAS spectrum (spectrum 1), gives a edited spectrum (spectrum 5 in Table I) where the CH_3 signals disappear, rigid CH_n are unchanged, and the C signals become negative with a relative intensity of 28%. In this case, the total intensity of the rigid CH_n signals in the aliphatic area can be estimated. Similarly, one can get another edited spectrum (spectrum 6 in Table I) where the C signals disappear and the total intensity of the rigid CH_n in aromatic area can be estimated.

Figure 3 shows a set of spectra for a sample of PSOC 284 taken at a MAS speed of 4.5 kHz. Figure 4 shows a similar set of spectra of the same sample using TOSS to suppress the spinning sidebands. The order from bottom to top is the same as in Fig. 2. From these original spectra, some edited spectra can be obtained. Figures 5 and 6 display two examples for the sets shown in Figs. 3 and 4, respectively. In each of them the CH_3-supperessed spectrum (spectrum 5) is on the bottom and, for comparison, the methylene-only spectrum (spectrum 2) is on the top. It turns out that separating the rigid CH groups from the CH_2 groups in the aliphatic region is straightforward.

All these spectra were obtained on a 300 MHz instrument. At 4.5 kHz MAS, the intensity of the sidebands is fairly strong. In Figures 3 and 5, the sidebands from the aromatics overlap the aliphatic signal severely. At high MAS speed (>10 kHz) the sidbands disappear. However, the spectra obtained with the same techniques behave differently and quantitative estimation becomes difficult (for details see "Complete Spectral Editing in CPMAS NMR", preprint contained in report DOE/PC/91285-3, in press *J. Magn. Reson.*, May, 1993). By using TOSS, the sidebands disappear, as shown in Figures 4 and 6. However, TOSS results in a distortion of the intensities. To avoid this problem, we are going to go back to using a lower field instrument (100 MHz) for applications to coals for now. We intend to study the intensities in edited spectra on model compounds and coals at both low and high fields to determine the limitations of the technique for quantitative analysis of coal functionalities. Future reports will describe these results.


(a)
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Acquisition
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Figure 1

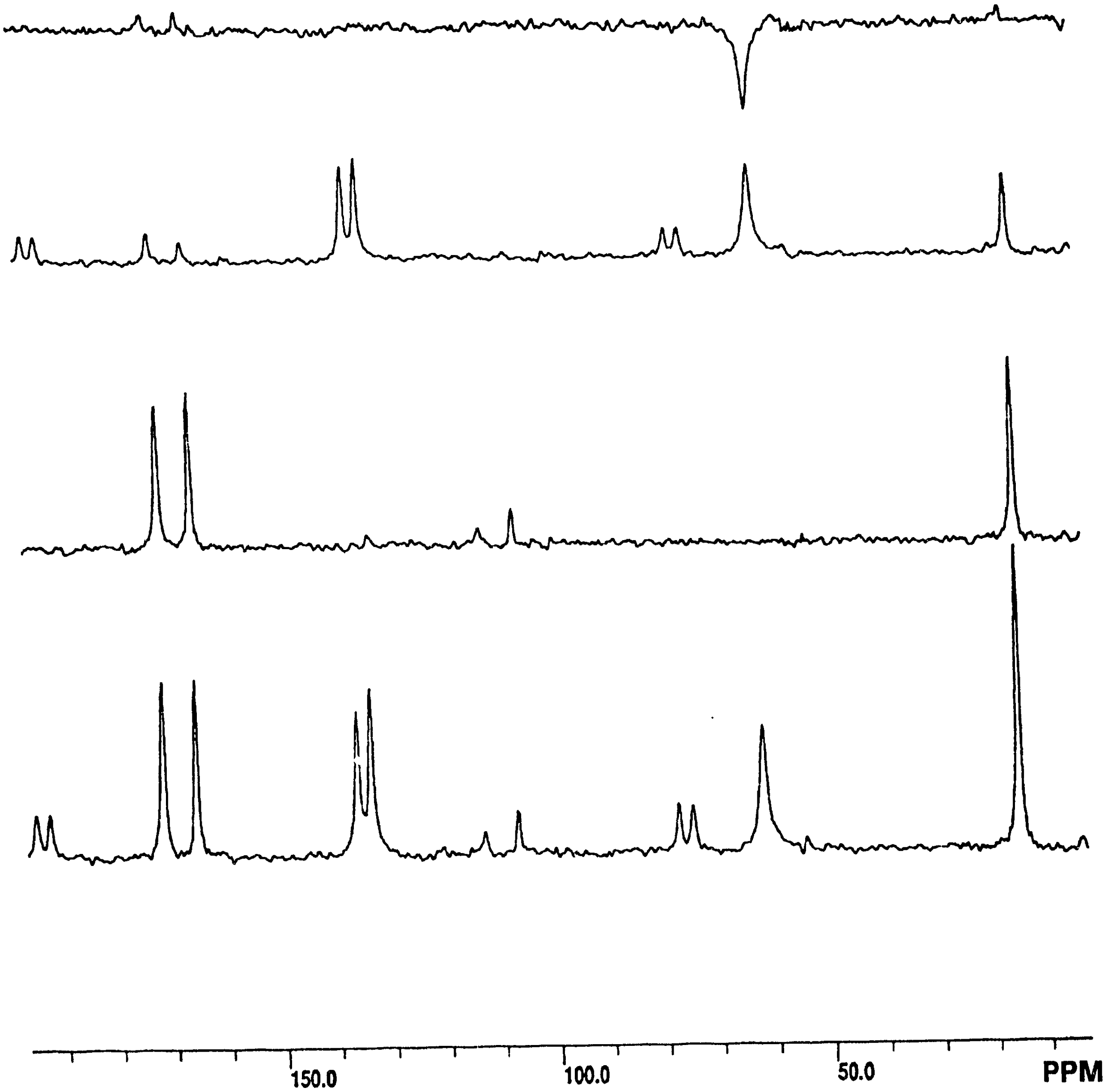

Figure 2

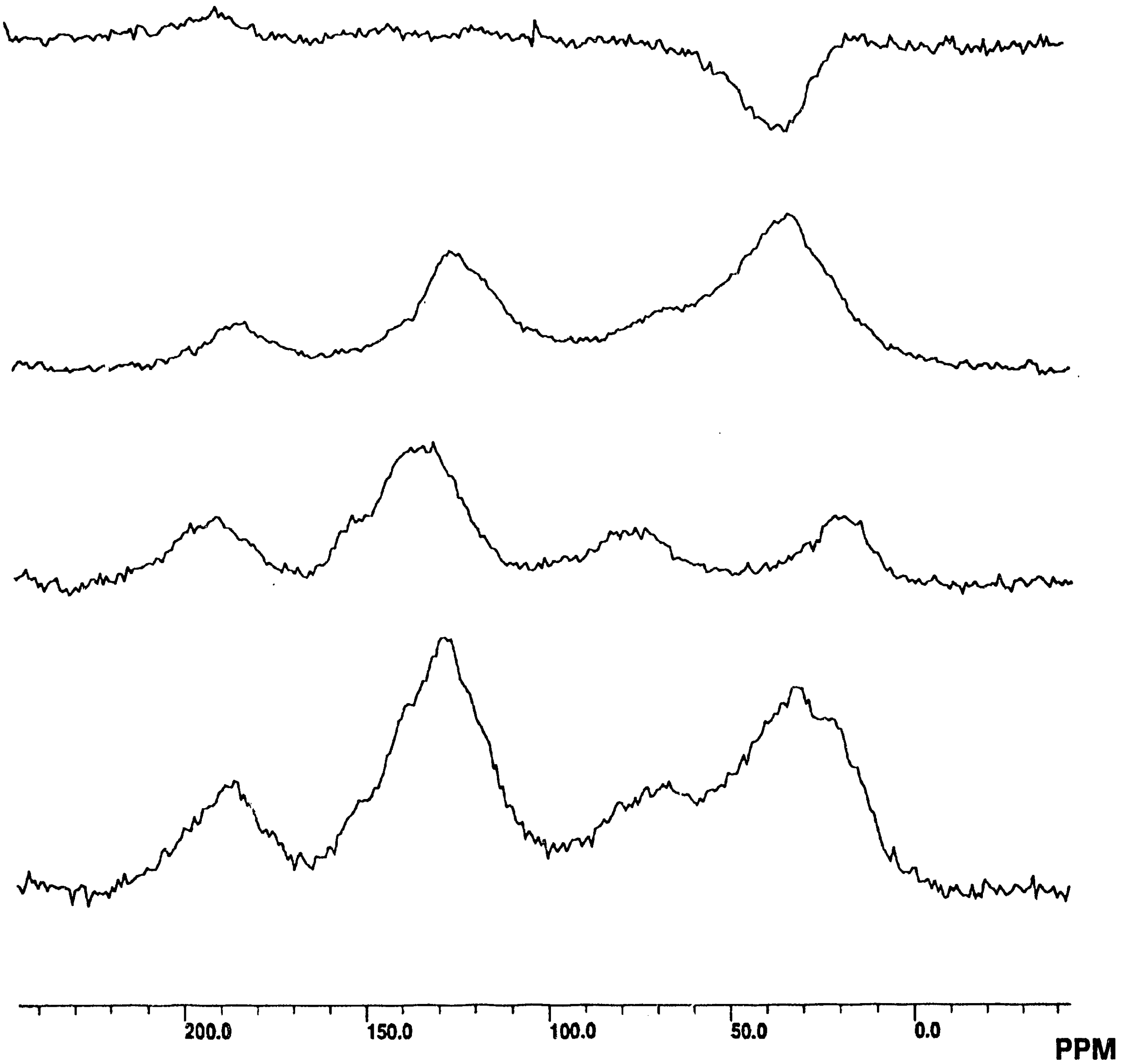

Figure 3

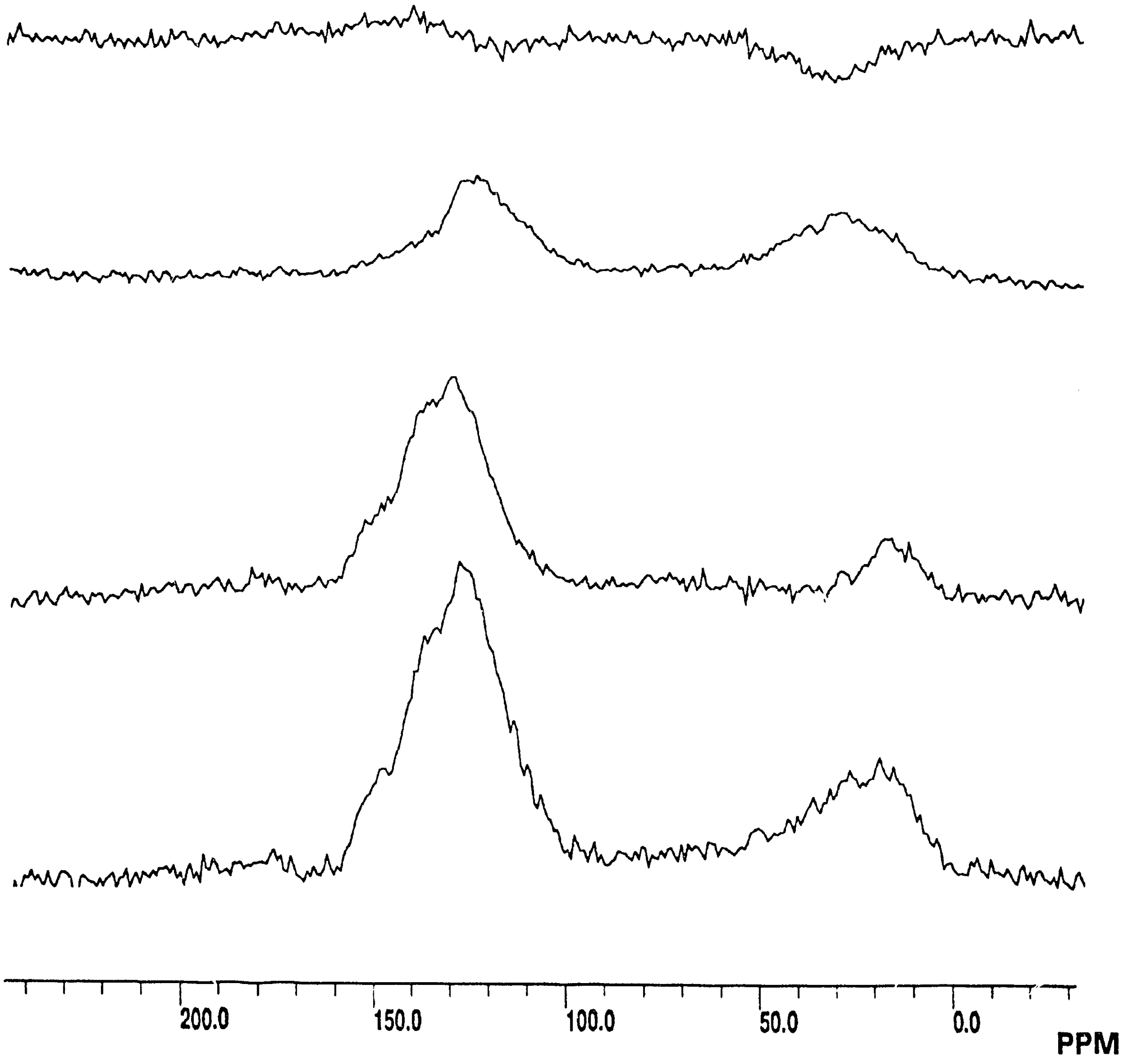

Figure 4

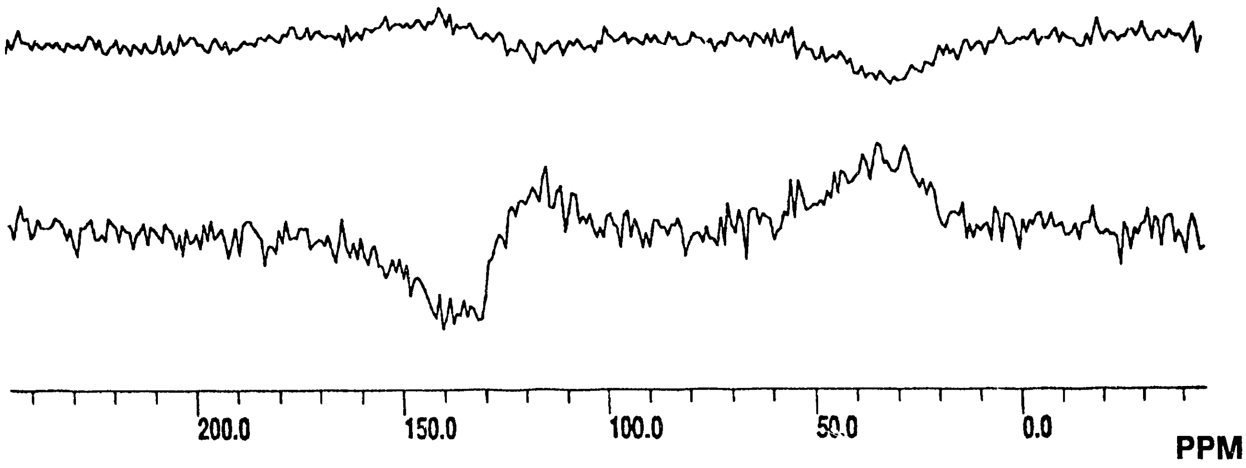

Figure 6

Figure 5

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