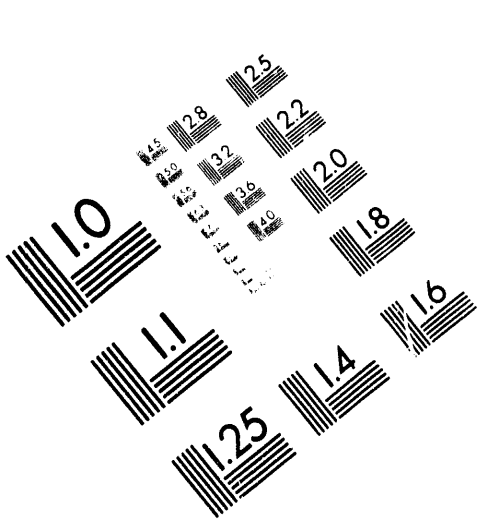

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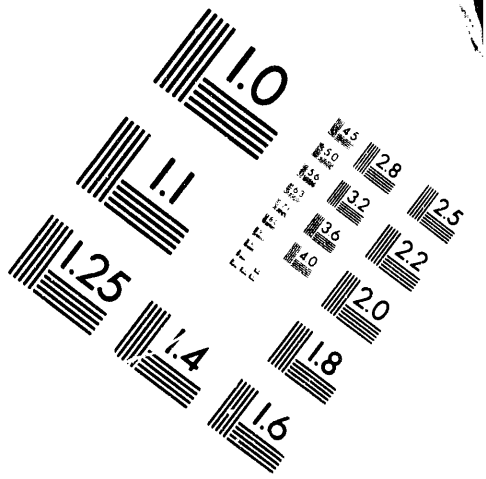

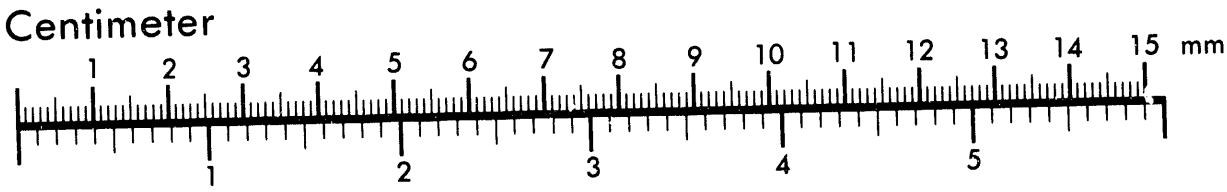

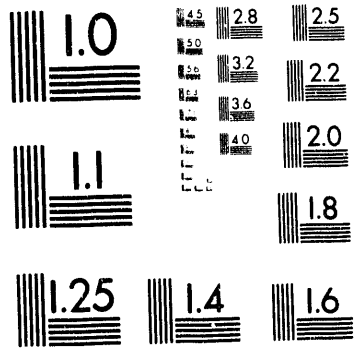

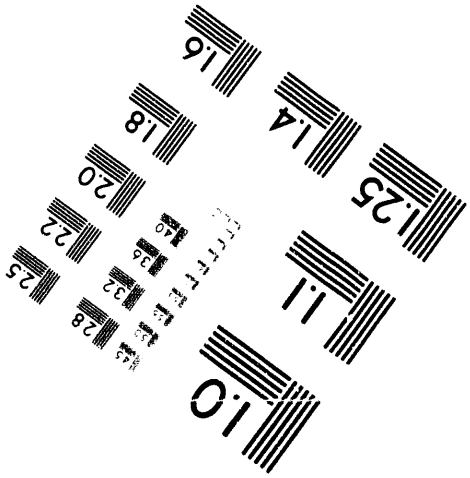

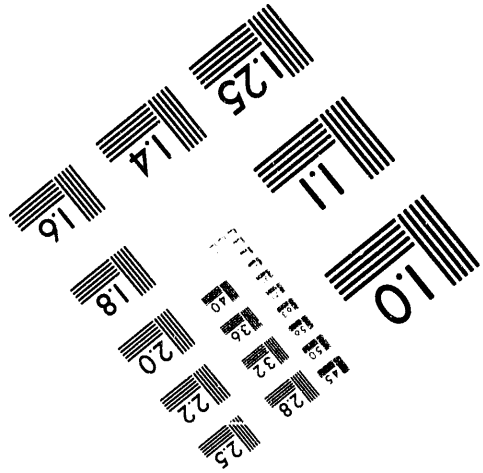

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Two Dimensional NMR and NMR Relaxation Studies of Coal Structure

PROGRESS REPORT

including

the period October 1, 1992 to December 31, 1992

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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

As the field strengths available for NMR magnets have increased, it has become increasingly important to develop solid state NMR methods which will take advantage of the increases in sensitivity and dispersion these advances make possible. For a number of varied reasons we expect multiple pulse homonuclear decoupling methods to work significantly better as field strengths increase. Applications combining multiple pulse methods with magic angle sample spinning (MAS), also known as CRAMPS, are especially attractive. In this report we briefly outline some of the experiments we have been doing recently to investigate the problems inherent in combining MAS and multiple pulse decoupling. It has long been held that as long as the sample rotation period was several times as long as the multiple pulse cycle time, that the line narrowing produced by these techniques would be additive. In fact we have found a number of instances in which this reasonable assumption is totally at odds with experiment. As we produce ever faster sample spinners to accomodate higher field operation, this problem will become increasingly severe. Therefore, a better understanding of this problem is central to the continued development of 2D NMR methods for solids that will work at high field. The following report describes some of the results collected during the last quarter in our investigation of this problem.

Multiple-pulse proton homonuclear decoupling under MAS.

Solid state ^{1}H - ^{13}C 2D heteronuclear chemical-shift correlation experiments (HetCor) have recently been the focus of more attention. We have proposed that this kind of experiment could be used on coals to give more structural information. One of the key elements in getting a high degree of resolution in the proton dimension is effective proton homonuclear decoupling. This is accomplished by using multiple-pulse sequences. It is generally believed that 2 - 4 kHz MAS speeds are low enough to avoid MAS interference with multiple-pulse decoupling of homonuclear interactions. In practice, a series of ^{1}H CRAMPS spectra are first performed and the experimental conditions for good I-I decoupling, such as the rotor speed, are optimized accordingly. Then the ^{1}H-^{13}C 2D HetCor spectra are obtained under the same conditions, except for the different pulse sequence. Usually, the multiple-pulse sequence used in the HetCor is different from that used in CRAMPS. It is supposed that the different multiple-pulse sequences should behave similarly under the same spinning conditions.

Recent work in our laboratory has found that multiple-pulse I-I decoupling under MAS is more complicated than previously thought. The MAS interference with multiple-pulse I-I decoupling may still be very strong even at 2 - 4 kHz MAS. Under a certain condition, one multiple-pulse sequence works very well, while another may be very bad.

Experiments were performed on adamantane. Under MAS, the ^{1}H-^{13}C J coupling can be clearly observed in the ^{13}C spectrum when I-I decoupling is applied during the acquisition time. Figure 1a shows a typical J coupling resolved ^{13}C spectrum. The decoupling power was about 50 kHz, which corresponds to a 5 microsecond 90° pulse. The different multiple-

pulse sequences used were (a) Semi-windowless MREV-8 with a cycle time 60 microseconds, (b) BLEW-24 with a cycle time 240 microseconds and (c) MREV-8 with a cycle time 120 microseconds.

Figure 1 shows the different ^{13}C spectra obtained under 2.23 kHz MAS with different I-I decoupling multiple-pulses. Spectra a, b and c correspond to the three pulse sequences mentioned above. Windowless MREV-8 works perfectly, while BLEW-24 is very bad. As a measure of the decoupling efficiency we define R=A/B where A is the distance from the baseline to the lowest point between the two peaks of the doublet and B is the average height of the two peaks. Table 1 shows the results for the different multiple-pulse sequences and the slightly different MAS speeds.

Table 1 R values

MAS speed (kHz)	a	b	c
2.23	0.22	2.40	0.60
2.42	0.44	0.56	0.91
2.50	0.25	0.50	0.65

These data show that a slight variation of the MAS speeds can make a very big difference for the same pulse sequence. For example, at 2.42 kHz MAS, BLEW-24 works fine. However, slowing down by 190 Hz makes BLEW-24 very bad.

The preliminary work has indicated that the I-I decoupling under MAS is more complicated than once thought. More work is in progress in our laboratory to have a better understanding, and to design better procedures for performing the 2D HetCor and other relevant experiments.

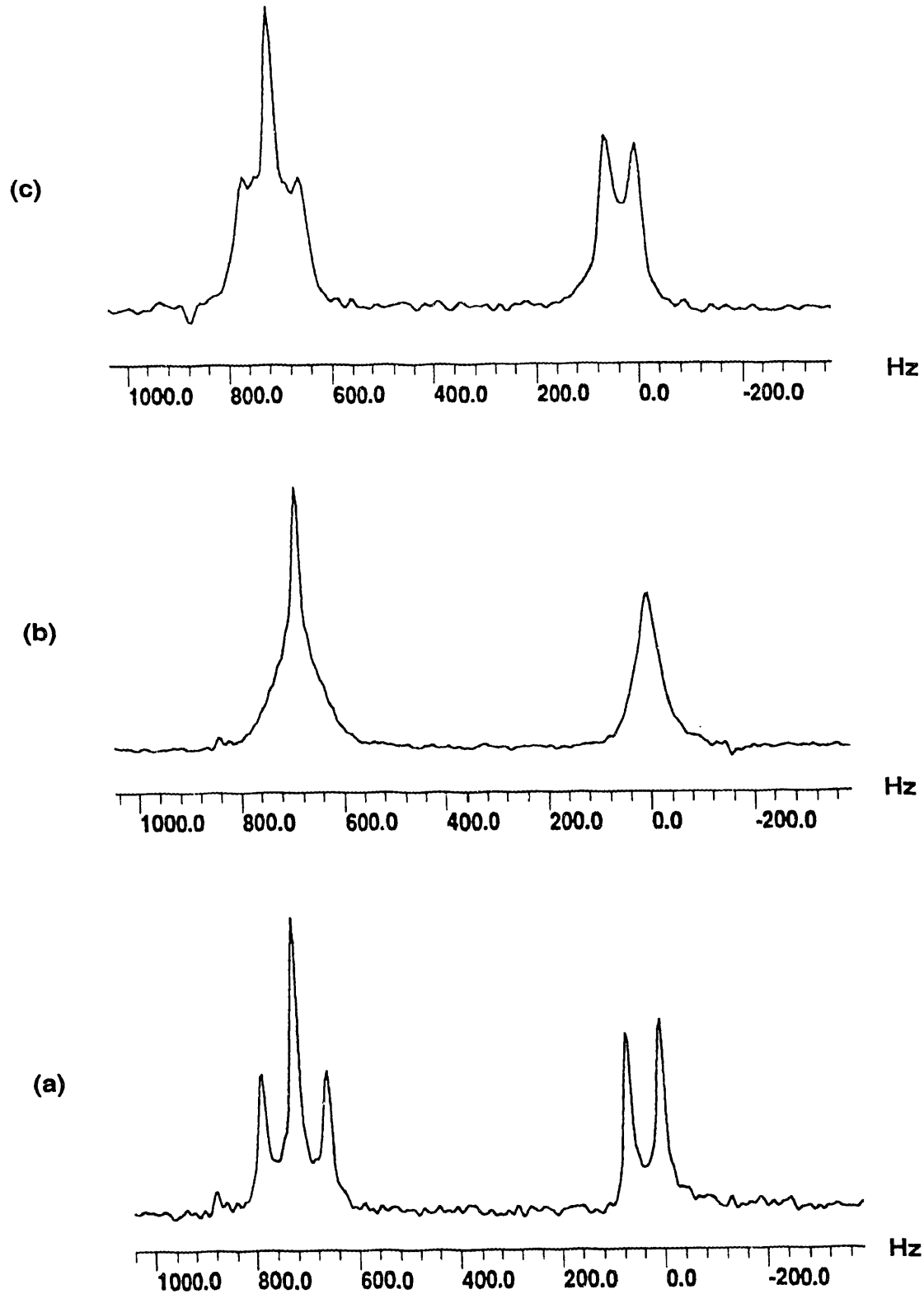
(c)
1000.0
800.0
600.0
400.0
200.0
0.0
-200.0
Hz
(b)
1000.0
800.0
600.0
400.0
200.0
0.0
-200.0
Hz
(a)
1000.0
800.0
600.0
400.0
200.0
0.0
-200.0
Hz

Figure 1

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