SCIENTIFIC AND TECHNICAL REPORT ON

"Temperature Effects on Chemical Structure and Motion in Coal"

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(1) A New 2D Spin Diffusion Experiment

As summarized in previous reports, we observed that proton spin-exchange and/or spin-diffusion occurs on a time scale similar to that of ^1H dipolar-dephasing processes in coals. 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. Proton 2D spin diffusion experiments based on MREV-8 have been successfully used to study the miscibility and morphology of polymer blends^[1]. 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 ^1H CRAMPS spectra, as we have demonstrated in our previous dipolar-dephasing experiments. Therefore, spin exchange processes among spins with overlapping chemical shifts but different mobilities cannot be investigated directly using standard 2D spin exchange/diffusion experiments. To solve this problem, we designed a new 2D spin exchange pulse sequence. This sequence, as shown in Figure 1, 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 will select relatively mobile protons, discriminating against protons in rigid, proton-rich environments. Thus, gradients of Zeeman spin order among protons of different mobilities and different chemical shifts are established prior to the mixing period. Spin exchange between rigid and mobile protons

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with unresolved chemical shifts can be detected from the broadening of peaks along the ω_2 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 diffusion pulse sequence. To minimize baseline distortion and "pedestals" due to spins locked along the direction of the effective field of the average Hamiltonian, composite pulses 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 are also inserted before the mixing period to return the magnetization back to the xy plane of the laboratory frame and bring the y component of magnetization to the direction of B_0 (z). The composite pulse used in this pulse sequence is just one of many possible composite pulses that can be used to serve the same purpose. Pure absorption 2D exchange spectra can be easily realized by setting the carrier frequency outside the spectral range and performing real Fourier transformation with respect to t_1 . If quadrature detection in both dimensions is desired, which is unnecessary in most cases, the TPPI scheme can be easily adapted

Figure 1. A new mobility-selective 2D spin diffusion pulse sequence designed to probe spin diffusion pathways among spins with different mobilities and chemical shifts.

to the new pulse sequence to obtain pure absorption 2D spectra.

Figure 2 shows a set of 2D spin diffusion spectra of Argonne premium coal 601 obtained at 25 °C using the new pulse sequence. According to our previous dipolar-dephasing experiments, we know that the dephasing time constant for protons in a rigid structure is around 10 μ s and for mobile protons is around 50 μ s. We used a dipolar dephasing time of 26 μ s to achieve a 93% suppression of signal from rigid protons. Spin diffusion pathways among protons with different mobilities can be seen clearly from Figure 2. Spin diffusion between aliphatic and aromatic protons can also be identified from cross peaks in Figure 2. With the mixing time ranging from 0 μ s to 5 ms, the spin diffusion processes in coal 601 are clearly demonstrated through this set of spectra. We also carried out variable temperature 2D exchange experiments. Complete analysis of the results will be presented in a later report.

(2) Some Important Improvements in the Software for NMR Spectrometer Control and Data Processing

As we have been carrying out very time-consuming time-domain experiments and 2D experiments, we needed a way to automatically schedule multiple experiments in order to make best use of spectrometer time. Unfortunately, the spectrometer being used for this work did not have such capabilities. By modifying and adding some programs to the software that controls the spectrometer, we successfully implemented a capability for scheduling multiple experiments on the spectrometer. We also fixed some bugs in the software, which could have interfered with data acquisition during experiments, when another set of data was being processed at the same time.

We had relied on using an offline NMR data processing package in another lab to process 2D data collected in our laboratory, a very cumbersome arrangement. Hence, another important improvement to our NMR data processing software is the enhancement of the 2D data processing capability. Specifically, we wrote an HPGL graphics driver and integrated it into the existing NMR data processing package for graphics hardcopy of NMR spectra, including 2D spectra. We can now take full advantage of workstations in our lab to process 2D NMR data with high efficiency.

Figure 2. 2D spin diffusion spectra of Argonne premium coal 601 obtained at 25 °C using the new pulse sequence. The dipolar-dephasing period was set as 26 μ s. The mixing time for the spectra are (A) 0 μ s; (B) 50 μ s; (C) 500 μ s; and (D) 5 ms.

(3) RF Heating Experiment

Recently, we have been focusing on expanding our high temperature ^1H CRAMPS capability to a temperature range from 250 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, using a RF heating technique. This involved constructing another RF channel for RF heating. The frequency of the RF heating channel is set to only 200 kHz away from the proton resonance frequency to simplify the electronic design. The regular proton channel and the RF heating channel are connected to a home-built RF switch, which is controlled by the pulse programmer of the NMR spectrometer. Both channels share the same RF power amplifiers. It was reported that the platinum coating procedure on NMR tubes is very critical for RF heating^[2]. Specifically, it was claimed that good coating can be made only from a glass blower's oven, not a small lab furnace. After experimenting with various conditions, we found the proper procedures for preparing good platinum coatings on both Pyrex and quartz NMR tubes, using a regular small, lab furnace. In preliminary RF heating experiments, we can now achieve a temperature of 650-700 $^{\circ}\text{C}$ for static samples, using a RF power of about 16W with 80% duty cycle. We are now searching for proper temperature sensing methods for a sample under magic-angle spinning conditions.

References:

1. P. Caravatti, P. Neuenschwander, and R. R. Ernst, *Macromolecules*, **18**, 119 (1985).
2. D. Ferguson and J. F. Haw, private communication.

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