ADVANCED SOLIDS NMR STUDIES OF COAL STRUCTURE AND CHEMISTRY

FINAL PROGRESS REPORT

including
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ABSTRACT

This report covers the progress made on the title project for the final project period and summarizes the completion of the grant. The study of coal chemical structure is a vital component of research efforts to develop better chemical utilization of coals, and for furthering our basic understanding of coal geochemistry. In this grant we are addressing several structural questions pertaining to coals with advances in state of the art solids NMR methods. The final activities of the grant focused on moving the analytical methods developed over the duration of the grant from the low field instrumentation used to newly acquired very high field NMR instrumentation. The project accomplishments and output are summarized.

Background

The work during the first 2 1/2 years of this project have focused on developing solids NMR as a means of non-destructively probing the organic structures present in coals and kerogens. We have specifically developed a suite of spectral editing methods which we use to acquire the spectra of carbons having differing multiplicities, i.e. we acquire spectra for the CH₃, CH₂, CH and non-protonated C fractions separately (subspectra). In general these methods have been quite successful at the low field strengths (100 MHz for ¹H) that have commonly employed in solids NMR of organic source rock and kerogens. Initial work on developing methods for moderate field strengths (300 MHz for ¹H) have been carried out. Rather than continue in this vein, we instead have decided to pursue development of methods suitable for the highest fields strengths available today (800 MHz for ¹H). Adaptation of spectral editing methods for the highest possible field strengths will require very different approaches than were successful at low fields, and our final activities in this grant have focused on identifying the problems that will have to be addressed.

High Field Double Resonance NMR

Our editing methods that have proven so useful in delineating the breakdown of coal structure by functional groups rely upon the differential cross polarization dynamics for ¹³C with differing numbers of attached ¹Hs. At moderate to low field strengths this has proven a robust approach. At much higher field strengths however the requirement of very high magic angle sample spinning (MAS) rates makes this a more difficult proposition. We have recently installed the first 18.9 T NMR instruments for solids NMR. At the operating frequency of 800 MHz for ¹H and 201 MHz for ¹³C, MAS rates in excess of 20 kHz are required if spinning sidebands are to be suppressed. These high rates in themselves are sufficient to decouple the ¹H and ¹³C nuclei, and significantly alter the spin dynamics of cross polarization.

The first stages of this work involved development of a new NMR probe for CPMAS NMR of ¹³C in solids at 800 MHz. This probe was completed and uses a 2.5 mm rotor with a sample capacity of only 10 mg. The small size is required to make it possible to attain the high spin rates required - in excess of 30 kHz - if spinning side bands are to be eliminated. An additional feature of this small sample size in combination with the exceptional sensitivity

afforded by the high field strength is that it makes study of maceral concentrates possible with an order of magnitude less material than possible before.

A consequence of the high spin rates is a significant effect on the cross polarization (CP) dynamics. An indication of the effect is shown in Figure 1. These two plots compare a theoretical expectation and the experimental result for the CP efficiency as a function of the Hartmann-Hahn matching condition. At zero or low spin rates magnetization transfer from ^1H to ^{13}C by CP occurs most efficiently when the amplitude of the radio frequency (RF) spinlocking fields are matched. At higher spin rates it is well known that the matching condition becomes modified; the two RF field amplitudes must differ by once or twice the spin rate ω_r . If a CP experiment is done using a fixed CP mixing time, the size of the signal will vary according to how well the matching conditions are met. In the upper trace the theoretical expectation for this matching curve is shown at a spin rate of ~ 20 kHz. There are 4 matching conditions corresponding to the ^{13}C RF field amplitude differing from the ^1H field by $-2\omega_r$, $-\omega_r$, ω_r , or $2\omega_r$. The width of these "resonances" in the Hartmann-Hahn matching spectrum depends upon the size of the ^{13}C - ^1H dipolar coupling, chosen here to reflect the situation in a sample of adamantane.

The lower trace is a collection of actual ^{13}C spectra at this spinning rate, plotted side-by-side as a function of the ^{13}C RF field strength. The overall pattern predicted by theory is grossly followed, but there are important differences. The approach of a resonance is sharp as expected, for instance consider the $+\omega_r$ matching condition. However, as the field is increased further the size of the signal does not drop as expected, and signal is observed in between matching conditions far in excess of what is expected.

This has now been investigated at some length. One of the problems not addressed in the top theoretical trace is that the RF fields are somewhat inhomogeneous across the sample as the sample coil is a finite solenoid. Figure 2 depicts what one might expect for the profiles of the ^{13}C and ^1H RF fields and their difference δ as a function of position within the coil. The profiles are expected to be the same shape, therefore the requirement for a fixed δ between the two RF fields cannot be simultaneously met in the entire sample. Simulations taking this into account however still fail to explain the experimental result. To better understand what is happening here the fields have been mapped by applying a static field gradient across the sample while measuring the field strengths with a nutation array. Fits of this experimental data show that the

field profiles in fact are as shown in Figure 3. The surprising observation is that the two RF field profiles are physically displaced from one another in space. This occurs even though the two fields are produced by the same RF coil, and is a result of the high frequency of operation for ^1H . At 800 MHz the electric fields of the coil interact strongly with the high dielectric constant zirconia ceramic rotor. At the end the coil is driven by the ^1H RF, this interaction is much stronger than at the opposite end held at ground. In this unbalanced mode the resulting RF field is then peaked strongly at one end of the coil instead of the middle. Figure 4 depicts a simulation of the matching profile through one of the matching resonances showing that this indeed explains the observed effect.

In order to be able to perform our spectral editing methods at this field strength then we need to make the RF fields more symmetrical and have them centered in the coil center at both frequencies. Since the ^{13}C field at its 4x's lower frequency is not effected, our main concern is to re-centred the ^1H RF field. In principal this can be accomplished by adopting a balanced configuration for the ^1H circuit. The difference is shown in Figure 5a and 5b. Figure 5a shows the equivalent circuit for the ^1H channel now being used. By adopting one such as in Figure 5b the voltage rise across the coil will be kept symmetrical. Neither end is held at ground as the resonating capacitor is split in two across the coil. Figure 5c depicts a circuit which retains the balanced configuration, but also provides the possibility of double tuning the sample coil at the ^{13}C frequency as well. Development of a probe incorporating this new circuit is the next step to extending our previous methods to much higher field operation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

^1H NMR in Solids at 800 MHz

Another motivation for moving to very high field for solids NMR is the expectation that multiple-pulse line narrowing methods should be easier in some ways to implement at higher frequency. Since the ^1H shift dispersion increases linearly with field strength, while the experimentally limiting factors either remain constant or decrease with $1/B_0$, resolution should by all rights increase. A method we have developed for using ^1H shifts is a solid state ^{13}C - ^1H shift correlation method based on the Frequency Shifted Lee Goldberg (FSLG) technique. We have previously used this type of 2D spectroscopy on coals at 100 MHz using MREV-8 for ^1H line narrowing. The FSLG method is more compatible with high speed MAS rotation, so it has instead been pursued to see whether this technique will become more useful for fossil fuel samples at high field.

The pulse sequence we have devised is shown in Figure 6. FSLG accomplishes ^1H line narrowing by applying an effective RF field at the magic angle in the rotating frame. This is accomplished by moving the ^1H RF off resonance to satisfy the magic angle condition $\Delta\omega/\omega_1 = 0.707$. The ^1H - ^1H dipolar decoupling is improved by alternating between an offset at $+\Delta\omega$ and $-\Delta\omega$. In practice this is accomplished by programming a fine phase shifter to phase shift the ^1H RF an amount $\Delta\phi$ each Δt , result in the frequency offset $\Delta\omega$ from the carrier. With the small sample coil in our probe large RF fields can be produced (over 130 kHz for $\omega_1/2\pi$), producing very large FSLG effective fields and thus very short cycle times. At 20 kHz a series of five FSLG cycles can be nested within a single rotor period thereby providing for lack of interference between the FSLG decoupling and the MAS rotation.

Figure 7 shows a result for a moderately large model compound, brucine. The plot shows a contour map of the ^{13}C - ^1H shift correlation spectrum, with projections of the ^1H and ^{13}C spectra along the side and top. There are several notable results in this spectrum. First the ^1H lines are uniformly 0.3 ppm or less in width. This is half that typically obtained in this experiment on our lower field instruments, and the implementation here has not yet been fully optimized. Secondly, we note that the lines even for methylene protons are narrow. For instance the two diastereotopic protons on carbon number 15 are fully resolved. This has never been accomplished to our knowledge before. Lastly it should be noted that some of the ^{13}C resonances are actually better resolved in the ^1H dimension. Again this has not been observed before; the higher inherent

Figure 6

Figure 7

resolution of the solid state ^{13}C spectrum has always been relied upon to resolve the broader ^1H resonances. This preliminary result is a very hopeful glimpse of how high field operation will make ^1H spectroscopy in organic solids of real utility.

Summary of accomplishments

During this project a set of spectral editing methods were refined for delineating the structural components of coals and kerogens according to functional group via carbon multiplicity and chemical shift. The methods were tested for their quantitative response in organic mixtures. For the low field methods developed it was found that the results are as quantitative as CPMAS spectroscopy is in coals. That is to say, no additional quantitative errors were introduced by these new methods over those already inherent in ^{13}C CPMAS NMR. A series of protocols were developed to optimize the acquisition of spectral editing data, forming a theoretical framework in which one can treat the experimental errors. Application to the coals in the Argonne sample data bank provided a rich amount of information as to the chemical nature of these coals, and several trends were evident as coals of increasing rank were compared. The results in general were consistent with previous work using chemical degradation and direct ^{13}C polarization MAS NMR methods. However the NMR methods developed in this grant are more rapid, and have built in consistency checks. Comparison to work using IR spectroscopy and solid state ^1H NMR using CRAMPS methods showed that these methods are apparently in error in overestimating the aliphatic hydrogen content.

Extension of these methods to higher field strength operation has first been investigated at 300 MHz and most recently at 800 MHz operating frequencies for ^1H . In general the approaches developed should be amenable to higher frequency operation, however they will need to be significantly modified at the highest fields to accommodate the requirement of very fast MAS rates.

Future Plans

Our group will continue to develop these methods at high fields, but our emphasis will be shifted towards a wider range of naturally occurring organic polymers. As the nationwide interest in fossil fuels remains low, our effort will focus more on basic geochemical issues. These

techniques should find significant application in study of the biogenic origins of organic kerogen in source rocks, delineating the chemical compositions of ocean sediments, and in study of the weathering of kerogens with implications for the global carbon cycle.

Project Output:

Publications:

1. Zilm, K.W. "Spectral Editing in C-13 Spectra of Hydrocarbon Solids" *Encyclopedia of Nuclear Magnetic Resonance*, John Wiley and Sons Ltd., 4498-4504 (1995).
2. Augustine, M. P., and Zilm, K. W., "Observation Of Bulk Susceptibility Effects In High-Resolution Nuclear Magnetic Resonance", *Journal of Magnetic Resonance Series A*, 123, 145 (1996).
3. Augustine, M. P., and Zilm, K. W., "Optical Pumping Magnetic Resonance In High Magnetic Fields: Characterization Of Nuclear Relaxation During Pumping", *Journal of Chemical Physics*, 105, 2998 (1996).
4. Augustine, M. P., and Zilm, K. W., "Optical Pumping Magnetic Resonance In High Magnetic Fields: Characterization Of The Optical Properties Of Rb-Xe Mixtures", *Molecular Physics*, 89, 737 (1996).
5. Augustine, M. P., and Zilm, K. W., "Optical Pumping Magnetic Resonance In High Magnetic Fields: Measurement Of High Field Spin Exchange Cross Sections", *Chemical Physics Letters*, 280, 1 (1997).
6. Wiberg, K. B.; Hammer, J. D.; Keith, T.A.; Zilm, K. W. "¹³C NMR Chemical Shifts of Methyl Cation and Anion: A Relationship Between Chemical Shift and Charge" *Tetrahedron Letters*, 38, 323-326 (1997).
7. Han, O. H., Larsen, G., Haller, G. L., and Zilm, K. W., "Carbon-13 Nuclear Magnetic Resonance Spectroscopic Studies Of (CO)-C-13 Adsorbed On Platinum Particles In L-Zeolites", *Bulletin of the Korean Chemical Society*, 19, 934 (1998).
8. Han, O. H., Haller, G. L., and Zilm, K. W., "Reconstruction Of Pd Particles Supported On Silica In The Presence Of CO As Studied By Carbon-13 NMR", *Bulletin of the Korean Chemical Society*, 19, 942 (1998).
9. Wiberg, K. B., Hammer, J. D., Zilm, K. W., Cheeseman, J. R., and Keith, T. A., "NMR Chemical Shifts. 1. The Role Of Relative Atomic Orbital Phase In Determining The Sign Of The Paramagnetic Terms: Clf, CH₃F, CH₃NH₃⁺, FNH₃⁺, And HC≡CF", *Journal of Physical Chemistry A*, 102, 8766 (1998).
10. Wiberg, K. B., Hammer, J. D., Zilm, K. W., and Cheeseman, J. R., "NMR Chemical Shifts. 3. A Comparison Of Acetylene, Allene, And The Higher Cumulenes", *Journal of Organic Chemistry*, 64, 6394 (1999).
11. Sean T. Burns, S.T., Wu, X., Zilm, K.W. "Improvement of Spectral Editing in Solids: A Sequence for Obtaining ¹³CH + ¹³CH₂ -Only ¹³C Spectra" *Journal of Magnetic Resonance*, 143, 352-359 (2000).

Project output cont.

Ph. D. Thesis

1. Matthew Augustine, "Theoretical Treatment of Time Dependent Phenomena and the Investigation of Highly Magnetized Systems", Yale, 1995.
2. Sean Burns, "Spectral Editing in Solid State NMR", Yale, 1998.
3. I-Wen Wu, "Solid-State NMR Characterization of Heterogeneous Catalysts", Yale, 1998.

Invited Talks Acknowledging Support of this Grant:

1. "Quantum Exchange and Rotational Tunneling in Transition Metal Polyhydrides" and "NMR in Highly Polarized Samples", Dept. of Chemistry, Cornell Univ.
2. "NMR of Highly Polarized Samples" NMR Gordon Conf., Wolfeboro, NH, July 1995
3. "Solids NMR of Complex Mixtures and Macromolecules" 37th Rocky Mountain Conference, Denver, CO, July 1995.
4. "Solids NMR of Uniformly Labeled Macromolecules" presented at the Eastern Analytical Symposium, Somerset, NJ, Nov. 13, 1995.
5. "Differentiating Oil-Prone and Gas-Prone Source Rocks by Solids NMR" presented at Exxon Research and Engineering Corp., Nov. 1995.
6. "Differentiating Simple Models for Quantum Exchange: What Can We Test Experimentally?" presented at the 2nd International Conference on Hydrogen and Metals, Santa Fe, NM, Dec. 13, 1995.
7. "New Approaches to Teaching Chemistry: Dealing with a Diverse Student Body" presented at the Gordon Conf. on Innovations in Chemical Education, North Hampton, NH, June 1996.
8. "Advances in NMR Instrumentation" presented at DuPont Experimental Station, Wilmington, DE, March 1996.
9. "High Field CPMAS NMR" presented at the 38th Rocky Mountain Conference, Denver, CO, July 1996.
10. "Spectral Editing in CPMAS NMR" presented at the Otsuka Electronics Solid State NMR Workshop, Estes Park, CO, July 1996.
11. "High Field CPMAS NMR: Problems and Prospects" presented at the Eastern Analytical Symposium, Somerset, NJ, Nov. 11, 1996.
12. "Investigation of High Speed CP MAS and Dipolar Recoupling Techniques on Fully Labeled Compounds", presented at the 37th Experimental NMR Conference, Asilomar CA, March 1996 by A. Mehta
13. "Quantitative Aspects of Solids NMR Spectral Editing", presented at the 37th Experimental NMR Conference, Asilomar CA, Mar. 1996 by I-Wen Wu
14. "Improvement of Spectral Editing in Solids: A Sequence for Obtaining CH + CH₂ Only ¹³C Spectra", presented at the 37th Experimental NMR Conference, Asilomar CA, March 1996 by S. Burns
15. "New Approaches to Structure Determination by Solid State NMR: Horizons in Structural Biology presented at the Department of Chemistry, California Institute of Technology, Pasadena, CA, May 13, 1997.
16. "Decoupling and Recoupling Spin Dynamics Under High Speed Magic Angle Spinning" to be

- presented at the Eastern Analytical Symposium, Somerset, NJ, Nov. 14, 1997.
17. "Applications of Al-27, P-31 and V-51 MAS Double Resonance Experiments in Catalysis" to be presented at the 24th annual FACCS meeting, Providence, RI, Nov. 26, 1997.
 18. "Advances in High Speed MAS NMR" presented at the Workshop on Biological Solid-State NMR Spectroscopy, , University of Pennsylvania, Philadelphia, PA, June 28-29, 1997.
 19. "Solids NMR of Uniformly C-13 Labeled Macromolecular Building Blocks: Assignment Strategies and Problems at High Fields" presented at the Chicago Area NMR meeting, Argonne National Laboratory, Nov. 1997.
 20. "Solids NMR of Uniformly C-13 Labeled Macromolecular Building Blocks: Assignment Strategies and Problems at High Fields" presented at the Department of Chemistry, University of Nebraska, Lincoln NE, Nov. 1997.
 21. "High Field CPMAS NMR: Problems and Prospects", colloquium presented at the Department of Chemistry, University of Nebraska, Lincoln, NE, Feb. 1998.
 22. "High Field CPMAS NMR: Problems and Prospects", presented at the Department of Chemistry, SUNY-Brookhaven, Brookhaven, NY, Feb. 1998.
 23. "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at 1998 Experimental NMR Conference, Asilomar, CA, Mar. 1998
 24. "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at the Department of Chemistry, University of West Virginia, Mar. 1998
 25. "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at NOVA Chemicals, Calgary, CA, Sept. 1998.
 26. "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at the Department of Chemistry, Purdue University, Oct. 1998
 27. "Solids NMR of Uniformly Labeled Macromolecular Building Blocks", presented at the Symposium on Magnetic Resonance, Schlumberger-Doll Research Center, Ridgefield, CT, Nov. 1998.

Personnel Supported on this project:

Graduates Students:

Anil Mehta
 Sean Burns
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 Brett Tounge
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current position

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