

Applications of the ^{13}C NMR Magic Angle Turning Experiment to Coal Studies

R. J. Pugmire^a, W. Wang^b, M. S. Solum^b, D. M. Grant^b, and J. Z. Hu

Departments of Chemical and Fuels Engineering^a and Chemistry^b
University of Utah, Salt Lake City, Utah 84112, USA
and Wuhan Institute of Physics., Chinese Academy of Science, Wuhan, The People's
Republic of China

Keywords: ^{13}C NMR, Two Dimensional Spectroscopy, Coal Structure

INTRODUCTION

One of the important contributions of high resolution ^{13}C CP/MAS to coal science is the measurement of the structural parameters of coal.¹⁻² It has been demonstrated³⁻⁵ that the structural parameters directly derived from ^{13}C CP/MAS experiments can be utilized to predict the details of coal devolatilization and char formation processes. One of the advantages of spinning a solid sample at the magic angle is the reduction of the line broadening contributions due to the chemical shift anisotropy (CSA). The chemical shift anisotropy is proportional to the strength of the external magnetic field and the CSA of aromatic carbons (200-240 ppm) is greater than that of the aliphatic carbons (20-100 ppm). When the sample is spun at the magic angle the CSA induced powder patterns break up into spinning sidebands and, in order to obtain a ^{13}C CP/MAS spectrum in which the aromatic carbon sidebands do not overlap the aliphatic carbon signals, it is necessary to spin the sample at approximately 4 KHz at a magnetic field of 2.35 Tesla. At a higher magnetic field strength a greater spinning rate is required. High speed magic angle spinning not only reduces the contributions of the spinning side bands but it also destroys very useful information on the local electronic environment that is embedded in the principal values of the CSA tensors.

The CSA exhibits three frequency components for each carbon in a powdered sample, the principal values, and spinning the sample at the magic angle averages these three values to the isotropic chemical shift of each nucleus. Hence, elimination of the CSA contribution increases the spectral resolution in conventional CP/MAS experiments but also throws away two thirds of the available data for each carbon. Thus, a major dilemma exists between spectral resolution and the richness of the data that is contained in powdered samples such as coal. Fortunately, the recently developed two-dimensional (2D) magic angle turning (MAT) experiments, (the triple echo-MAT⁶ and PHORMAT⁷) when applied at an extremely slow rotation rate, can provide both types of information without serious penalty. In the MAT experiments, a sideband free isotropic chemical shift spectrum which has resolution in the isotropic shift dimension comparable to the standard CP/MAS spectrum is obtained by projecting the 2D data onto the evolution frequency axis. Concurrently, an essentially static powder pattern is projected onto the acquisition frequency axis and the powder pattern for each individual isotropic chemical shift is obtained by simply taking a spectral slice at the specified isotropic chemical shift value in the acquisition dimension.⁶⁻⁸ In this paper, the power of the MAT experiments is further explored in a study of coals at a magnetic field strength of 9.4 Tesla.

EXPERIMENTAL

The experiments were performed on a Chemagnetics CMX-400 spectrometer with a ^{13}C frequency of 100.6 MHz. The probe used was a Chemagnetics pencil rotor design and samples were spun at *ca.* 30 Hz in a 9.5 mm rotor with a specially built low speed drive tip. The proton decoupling field strength on this probe is 50 KHz. The spinning speed was maintained within 0.25 Hz with a Chemagnetics speed control unit and the pulse sequences used are described elsewhere.⁶⁻⁸

Results and Discussion

The usefulness of the MAT experiments can best be described by examining the data obtained from a model compound with a diversity of carbon types. The PHORMAT pulse sequence⁷ was used to generate the composite data in Figure 1 in which the two-dimensional (2D) contour plot of p-ethoxyphenylacetic acid is displayed. All ten carbons are clearly resolved in the contour plot. The isotropic chemical shifts of these carbons are projected onto the evolution axis while the composite powder pattern data are projected onto the axis representing the acquisition dimension. As previously described,⁶⁻⁸ the principal values of the CSA tensors of each carbon can be found by examining the powder patterns taken at the individual isotropic chemical shift frequencies. Figure 3 displays a stacked plot of the powder patterns at the isotropic chemical shift frequency of each carbon. In this case none of the carbons overlap and, hence, no ambiguity is encountered in identifying the types of carbons associated with each powder pattern. Orendt, et. al.² have described the general shapes of powder patterns associated with different types of aromatic carbon functional groups, e.g., protonated, alkyl substituted, aryl ethers, and bridgehead carbons. The powder

patterns for the methyl, CH₂, and CH₂O- groups in p-ethoxyphenylacetic acid also exhibit characteristic shapes which can be used to identify overlapping carbon signals. The analysis of overlapping powder patterns in carbons with accidental degeneracy of the chemical shifts has been described by Hu, et. al.⁶ and Wang, et. al.⁹ for model compounds and for coals.⁸

The application of the triple-echo version of the MAT experiment to coal samples has been previously reported.^{6,8} The PHORMAT version of the MAT experiment does not require spectral shearing, as in the triple-echo MAT experiments, which simplifies the extraction of the principal values. The 2D PHORMAT data for Pocahontas #3 coal is presented in Figure 2. At first glance, one could assume that the useful information obtainable from the data is no greater than that of the standard CP/MAS experiment. However, by examining the spectral slices obtained at different isotropic chemical shifts, one can readily recognize the contributions from different types of carbon atoms. Figure 4 exhibits spectral slices taken at selected isotropic chemical shift values in the aromatic region from the data portrayed in Figure 3. One can easily recognize the characteristic line shapes of powder patterns due to substituted, bridgehead, and substituted aromatic carbons. One can also identify the features of composite patterns derived from overlapping signals from different structural types of carbons, i. e., protonated/bridgehead (slices at 120, 125, and 130 ppm), bridgehead/substituted (slices at 130 and 135 ppm), and substituted (slices at 135, 140, and 145 ppm). In Figure 4 the heavy vertical lines represent the frequency for the δ_{22} components of the protonated, bridgehead, and substituted carbons.

2D data set on experimental data in model compounds. Versions of these tools have been used for analysis of the spectral slices in coals and efforts are under way to expand these capabilities to include the entire 2D data set. It is interesting to note that the MAT experiments can also be used on polymer systems to refine the structural analysis and assess crystalline and non-crystalline components.

Acknowledgments

Support for this work was made available by the National Science Foundation through the Advanced Combustion Engineering Research Center, the U. S. Department of Energy Pittsburgh Energy Technology Center through the Consortium for Fossil Fuel Liquefaction Science (Contract No. DE-FCC22-93PC93053), and by Basic Energy Sciences, Office of Energy Research, U. S. Department of Energy (Contract No. DE03-94ER14452).

REFERENCES

1. M. S. Solum, R. J. Pugmire and D. M. Grant, *Energy & Fuels*, 3 (2), 187-193 (1989).
2. A. M. Orendt, M. S. Solum, N. K. Sethi, R. J. Pugmire and D. M. Grant, "Advances in Coal Spectroscopy" Edited by Henk L. C. Meuzelaar, Plenum Press - New York and London, 1992, Page 215-223.
3. T. H. Fletcher, A. R. Kerstein, R. J. Pugmire, M. S. Solum and D. M. Grant, *Energy Fuels*, 6 (4), 414-431 (1992).
4. T. H. Fletcher, M. S. Solum, D. M. Grant, and R. J. Pugmire, *Energy Fuels*, 1992, 643-650.
5. D. M. Grant, R. J. Pugmire, T. H. Fletcher and A. R. Kerstein, *Energy Fuels*, 3 (2), 175-186 (1989).
6. J. Z. Hu, A. M. Orendt, D. W. Alderman, R. J. Pugmire, C. Ye and D. M. Grant, *Solid State NMR*, 1994, 3, 298.
7. J. Z. Hu, W. Wang, F. Liu, M. S. Solum, D. W. Alderman, R. J. Pugmire, and D. M. Grant, *J. Magn. Reson.*, 1995, A113 (in press).
8. J. Z. Hu, M. S. Solum, R. J. Pugmire, C. Ye, and D. M. Grant, *Energy & Fuels*, 1995 (in press).
9. W. Wang, J. Z. Hu, D. W. Alderman, R. J. Pugmire, and D. M. Grant, *Solid State NMR*, 1995, 4 (in press).

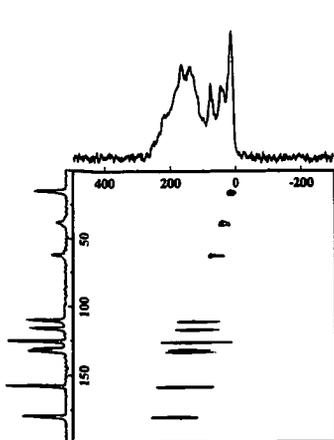


Figure 1. Two dimensional MAT data for p-ethoxyphenylacetic acid. The isotropic chemical shifts are projected on the evolution dimension while the powder patterns are projected on the acquisition dimension.

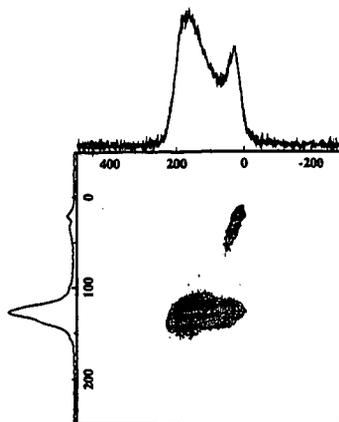


Figure 2. Two dimensional MAT data for Pocahontas #3 coal from the Argonne Premium Coal Sample Bank.

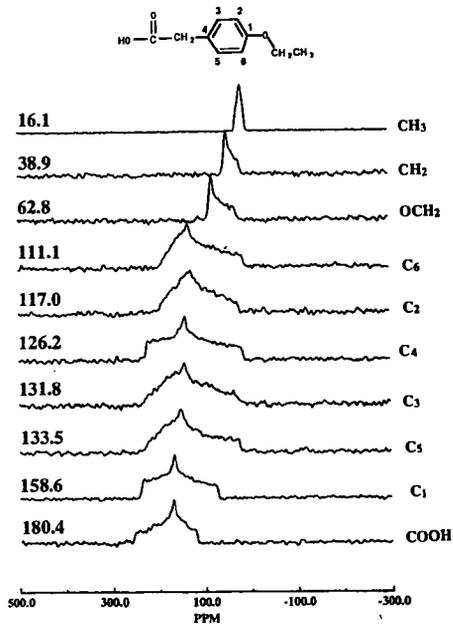


Figure 3. Powder patterns obtained from spectral slices taken from Figure 1.

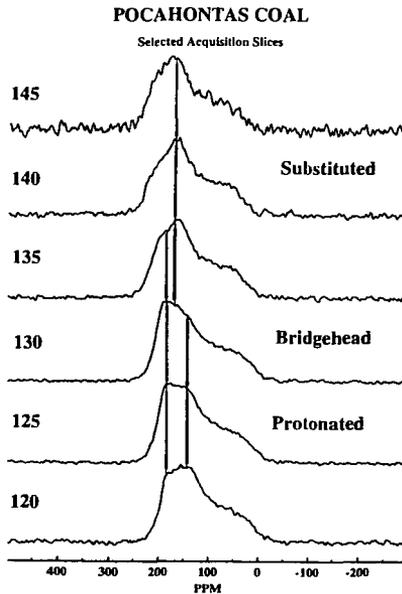


Figure 4. Powder patterns taken from Figure 2 at selected spectral slices illustrating composite patterns that still have features which can be attributed to protonated, bridgehead, and substituted aromatic carbons. The heavy vertical lines represent the approximate frequencies of the δ_{22} component of the principal values of the chemical shielding tensor for the different types of aromatic carbons.