

THE MEASUREMENT OF  $^{13}\text{C}$  CHEMICAL SHIFT TENSORS IN COMPLEX  
POLYCYCLIC AROMATIC COMPOUNDS AND COALS BY AN EXTREMELY SLOW  
SPINNING MAS EXPERIMENT

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#### INTRODUCTION

The  $^{13}\text{C}$  CP/MAS experiment has proven to be a powerful technique for obtaining high resolution spectra in complex solids such as coal (1). MAS narrows the chemical shift anisotropy (CSA) to its isotropic shift when the sample spinning speed is greater than the anisotropy. While the isotropic chemical shift is useful in characterizing chemical structure, the principal values of the chemical shift tensor provide even more information. These principal values are available from the powder pattern obtained from a stationary or slowly spinning sample. Unfortunately, the overlap of many broad powder patterns in a complex solid often prevents the measurement of the individual principal values.

In an effort to address this problem of spectral overlap, many 2D techniques have been developed to simultaneously obtain the dispersion by isotropic shift, such as produced by MAS, in one dimension and the tensorial information as separate powder patterns in the second dimension (2-6). A very successful technique is the slow spinning modification of the magic angle hopping experiment (2) recently proposed by Gan (5), which we call the Magic Angle Turning (MAT) experiment (6). This experiment has a number of advantages over earlier 2D methods. The use of very slow spinning speeds (<50 Hz) favors the quantitative polarization of all carbons and allows the use of a large volume sample rotor resulting in a typical 2D spectrum acquisition requiring less than 24 hours. The mechanical device for slow spinning is very stable and high resolution in the isotropic chemical shift dimension can be easily obtained. The MAT experiment could be done on a suitably stable MAS probe. The only disadvantage of the original MAT experiment is that data acquisition starts right after the last pulse, causing distortion in the evolution dimension (the second dimension) even if a delay as short as 20 $\mu\text{s}$  is used.

In this paper, a triple-echo MAT sequence, previously described (6,7), is employed which improves the 2D baseline. Two additional experiments, using short contact times and dipolar dephasing techniques, are also employed to further separate the powder patterns of protonated and nonprotonated carbons in complex compounds. Experimental results on representative model compounds as well as coals are presented in this paper.

#### EXPERIMENTAL DETAILS

The experiments were performed on a Varian VXR-200 NMR spectrometer. A large-sample-volume slow-spinning MAS probe was constructed for the experiment. The probe holds approximately 5  $\text{cm}^3$  of sample and has a very stable sample spinning rate ranging from 20 to 300 Hz. A spinning rate of 44 Hz was used for the experiments discussed below. 1,2,3-trimethoxybenzene (TMB) and 2,3-dimethylnaphthalene were used as received from Aldrich and the coal samples were obtained from Argonne Premium Coal Sample Bank.

#### RESULTS AND DISCUSSION

The triple-echo and dipolar dephased MAT sequences are given in Fig. 1. The 2D spectrum obtained in this manner and plotted in a square has the bands inclined relative to the acquisition dimension axis at an angle  $\arctan(\omega_2/(3\omega_1))$ , where  $\omega_1$  and  $\omega_2$  are the evolution and acquisition spectral widths, respectively. In order to obtain a 2D spectrum whose projection along one axis gives the isotropic shift spectrum, these data must be sheared through the inclination angle. For all experiments reported in this paper, the evolution-time increments are chosen to be three times the acquisition dwell times, so that the spectral widths for the acquisition dimensions are three times those for the evolution dimensions. This results in 2D spectra with bands inclined at an

angle of  $\arctan(1) = 45^\circ$ . After a  $45^\circ$  shearing operation, the isotropic shift spectrum is obtained from the projection on one axis, while the powder patterns are taken as the perpendicular slices at the isotropic shift positions. The resultant contour plot spectrum of 1,2,3-trimethoxybenzene (TMB) is shown in Fig. 2. The resolution achieved for the isotropic chemical shift dimension is about 1 ppm, as illustrated in Fig. 2, where the resonance for M1 and M3, separated by 1 ppm, are resolved (8). The flat baseline in the isotropic shift projection of Fig. 2 indicates the quality of the 2D baseline achieved, which is essential for the quantitative measurement of the aromaticity ( $f_a$ ) of coal. The individual powder patterns, from which the principal values of the chemical shift tensor can be extracted, are displayed in Fig. 3.

Results from a triple-echo MAT spectrum of 2,3-dimethylnaphthalene (2,3-DMN) are given in Fig. 4 and Table 1. The methyl carbon isotropic shift at 21 ppm is well-separated from those of the ring carbons, and is easily assigned. Assignment of the closely-spaced aromatic carbon shifts is more difficult. An expansion of the aromatic region of the MAT isotropic-shift projection and a similar portion of the MAS spectrum are shown in Figure 4(a). These spectra are interpreted as showing isotropic shift peaks at 124 ppm, 128 ppm, 133 ppm, and 134 ppm. The 128 ppm peak has double intensity, but it is no wider than the single intensity peak at 124 ppm, indicating that two pairs of chemically equivalent carbons have virtually identical isotropic shifts in the solid. A dipolar-dephasing MAS spectrum (not shown) indicates that the nonprotonated carbons are those with isotropic shifts of 133 ppm and 134 ppm. A tentative assignment of the aromatic carbons can be made by assuming that the order of the solid isotropic shifts is the same as that in solution. The chemical shift assignments for 2,3-DMN in solution reported by Wilson and Stothers (9) are given in Table 1. On the basis of the isotropic shift order the 124 ppm shift is assigned to C<sub>6,7</sub>, the 133 ppm shift to C<sub>4a,8a</sub>, and the 134 ppm shift to C<sub>2,3</sub>. These assignments are consistent with the dipolar-dephasing MAS data. The isotropic shifts of C<sub>1,4</sub> and C<sub>5,8</sub> have moved together in the solid to form the double-intensity peak at 128 ppm. Assignment of C<sub>1,4</sub> and C<sub>5,8</sub> requires examination of the principal values of the tensors and the details for the assignments of all carbons are given in reference 6. The important point of note from the example of 2,3-DMN is that the triple-echo MAT experiment provides sufficient resolution to deconvolute overlapping tensor principal values.

The combination of triple-echo MAT, dipolar dephasing triple-echo MAT, and short-contact-time triple-echo MAT experiments can be used as a basic technique for extracting  $^{13}\text{C}$  tensor information in complex powdered solids, e.g. coal. The flat 2D baseplanes produced by these modified sequences and the quantitative cross polarization of the MAT technique are especially important to this application. Shown in Figure 5(a) is the 2D contour plot of a spectrum of Pocahontas coal obtained with the triple-echo MAT pulse sequence; the projection onto the isotropic shift axis is given in Figure 5(b). The aromaticity ( $f_a$ ) obtained by a volume integration of the spectrum in the aliphatic and aromatic regions is 0.86, in good agreement with the value of 0.86 obtained by a variable contact time of  $^{13}\text{C}$  MAS experiment at a field of 2.35T (1). Pocahontas coal powder pattern slices are shown in Figure 6. The normal triple-echo MAT powder pattern at an isotropic shift of 20 ppm in Figure 6(a) corresponds to methyl carbons on aromatic rings. The dipolar dephasing triple-echo MAT powder pattern at 139 ppm in Figure 6(e) arises from the substituted aromatic carbons, some of which cluster in the 135-139 ppm range. Figure 6(b) shows the normal triple-echo MAT powder pattern from the overlapping protonated and nonprotonated aromatic carbons at 124 ppm. These overlapping patterns are successfully separated in Figures 6(c) and 6(d) by the short contact time and the dipolar dephasing experiments, respectively, into patterns characteristic of protonated and nonprotonated (bridgehead) carbons. Nonprotonated and protonated structural types can thus be distinguished in coal by these MAT techniques. The principal values of the tensors for different types of carbons obtained by measuring the shift at the peaks and half-heights of the breakpoints are given in Table 2. The principal values are in good agreement with those obtained by a 1D variable-angle spinning experiment (10). The extraction of the methyl powder pattern, difficult to see in a coal by any other technique, further demonstrates the power of the MAT experiment.

With the MAT experiment we have examined a number of anthracite coal as well as the coals from the Argonne Premium Sample Bank.

It is clear that a great deal of information is available in the experimental data and we are evaluating methods for analysis of the principal value data. The quantitative aspects of the MAT experiment on coals in portrayed in Fig. 7. The triple-echo MAT values of aromaticity correlate closely with those reported by Solum (1). A careful analysis of the quantitative nature of the experiment will be pursued in the future.

#### CONCLUSIONS

The data presented in this study demonstrate that the Magic Angle Turning experiment enables the measurement of  $^{13}\text{C}$  principal values in complex powdered solids by separating tensor powder patterns according to their isotropic shifts. Furthermore, the principal values of different types of tensors are recognizable even when the isotropic shifts overlap. The triple-echo MAT experiment produces 2D spectra with flat baseplanes which are well-adapted to quantitative analysis. Protonated and nonprotonated carbons may be separated by the short-contact-time and dipolar-dephasing variants of the triple-echo MAT experiment. The major problems associated with obtaining MAS spectra at high fields, the very high spinning speeds required to suppress or separate sidebands and the consequent difficulty in uniformly polarizing all spins, are eliminated by the MAT experiment. The triple-echo MAT experiment effectively suppresses spinning sidebands at low rotation frequencies, and the slowly rotating sample appears to promote the polarization of all spins. To date, none of the experiments performed in this laboratory on a wide range of model compounds exhibit recognizable magic angle holes. The MAT experiments described above are particularly promising for the investigation of complex solids such as coal at high fields. Hence, it appears that the MAT experiment will be very useful in the study of a wide range of complex materials. A particular advantage is found in the relatively high resolution features of the experiment. In the isotropic chemical shift dimension the spectral resolution is comparable to that of a traditional CP/MAS experiment, while the uncertainty in the principal values in the powder pattern projections is estimated at  $\pm 2$  ppm.

#### ACKNOWLEDGMENTS

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**Table 1.**  
Carbon-13 Chemical Shift Tensors in 2,3-Dimethylnaphthalene and Naphthalene.

Carbon	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$\delta_{iso.}$	$\delta_{sol.}^b$
<b>2,3-Dimethylnaphthalene<sup>c</sup></b>					
Methyl	30	25	8	21	20.1
C1, 4	218 <sup>d</sup>	132	34	128	127.3
C2, 3	232	157	14	134	135.2
C5, 8	222 <sup>d</sup>	142	20	128	126.7
C6, 7	225	135	11	124	124.8
C4a, 8a	207	197	-4	133	132.3
<b>Naphthalene<sup>e</sup></b>					
C1, C4	224.7, 223.9	140.3, 145.6	22.8, 20.4	129.6	127.7
C2, C3	227.6, 227.6	139.3, 138.2	11.1, 10.4	125.7	125.6
C4a	208.5	202.2	-5.9	134.9	133.3

a. Shift obtained from isotropic projection and MAS spectrum.

b. Solution shifts from Reference 9.

c. Solid shifts in ppm from TMS. Estimated error in solid data is  $\pm 2$  ppm. The shifts are referenced via the methyl carbon of hexamethylbenzene at 17.3 ppm from TMS.

d. Calculated from  $\delta_{22}$ ,  $\delta_{33}$ , and  $\delta_{isotropic}$ .

e. Solid shifts taken from Reference 11; the single crystal environment exhibits  $C_i$  symmetry and has two values for the alpha and beta carbons.

**Table 2. <sup>13</sup>C chemical shift tensors in Pocahontas coal.<sup>a</sup>**

Carbon type	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_{ave.}$	$\delta_{iso.}$
	1	2	3		
<b>Methyl</b>			5		
	35	22		20.7	20.3
<b>Protonated</b>	223	13	20	124.7	126.
		1			7
<b>Nonprotonated</b>	197	18	-8	124.3	124.
		4			0
<b>Substituted</b>	228	16	32	141.0	139.
		3			4

a. Shifts in ppm from TMS referenced via methyl carbon of hexamethylbenzene at 17.3 ppm from TMS.

b. Average of three principal value shifts.

c. Chemical shift of slice used.

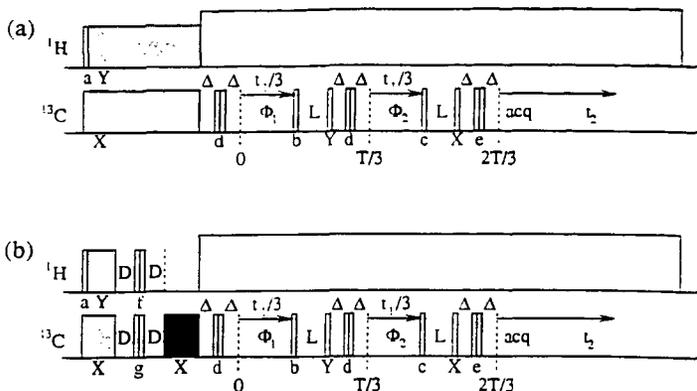


Figure 1. Pulse sequences for the 2D MAT experiments.  $90^\circ$  pulses are represented by single rectangles; two adjacent rectangles denote a  $180^\circ$  pulse. The cross-polarization pulses are shaded. The time  $T$  is an integral number of rotor periods (excluding a multiple of three rotor periods). The magnetization precesses in the transverse plane during the periods labeled  $f_1$  and  $f_2$ , and is along the longitudinal axis during the periods labeled  $L$ .

(a) Normal triple-echo MAT pulse sequence.  $\Delta$  is an echo delay time determined by the probe ring-down and receiver recovery time. The character above each pulse indicates the entry in the phase cycle table (reference 6) which gives the phase of the pulse.

(b) Dipolar dephasing triple-echo MAT pulse sequence. The spin-lock pulse is darkened. The character above each pulse indicates the entry in the phase cycle table (reference 6) which gives the phase of the pulse.

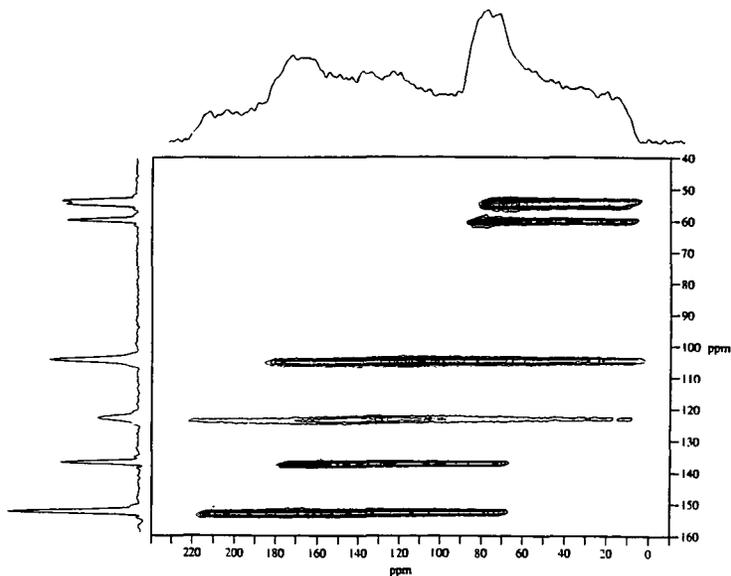


Figure 2. Contour plot of the central portion of the 1,2,3,-TMB 2D spectrum obtained by shearing the spectrum by  $45^\circ$ . The contour interval is 4% of the maximum peak height. The position of the breakpoints and peaks in the bands are given correctly by the ppm scale on the horizontal acquisition dimension axis. The isotropic shifts of the carbons can be read from ppm scale on the vertical axis. A 1.5 ppm Gaussian line broadening was applied in both dimensions, except that the isotropic shift projection was prepared from a 2D spectrum with no line broadening.

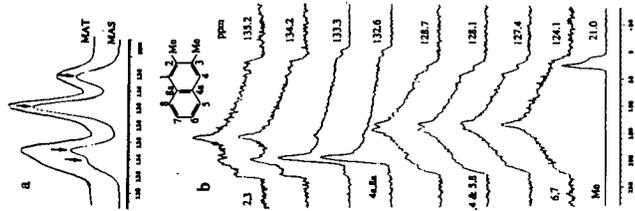


Figure 4. (a) The projection along the isotropic shift dimension and the CP/MAS spectrum of the aromatic carbons of 2,3-DMN with the isotropic shifts of the resolved resonances highlighted. (b) Powder pattern slices taken from normal triple-echo MAT spectrum of 2,3-DMN at indicated values of the isotropic chemical shift. The spectrum was obtained using a 4 ms contact time, spectral widths of  $\omega_2=3\omega_1=32000$  Hz, a 12 s recycle delay, 32 scans for both real and imaginary FIDs, 120 evolution increments with a 93.75  $\mu$ s increment time, and 26 hours total experimental time.

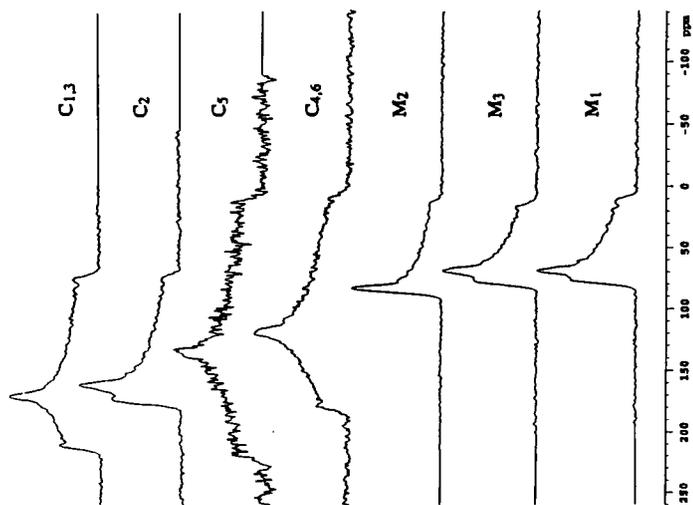


Figure 3. 1,2,3-TMB powder patterns from slices of the triple-echo MAT 2D spectrum in Figure 2.

## AROMATICITY VALUES IN ARGONNE PREMIUM COAL SAMPLES

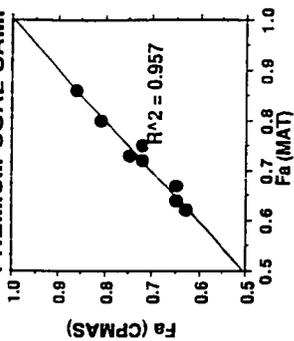


Figure 7. Comparison of the carbon aromaticity values ( $f_a$ ) for the Argonne Premium Coals as determined by the variable contact time CP/MAS technique (reference 1) and the triple echo MAT technique.

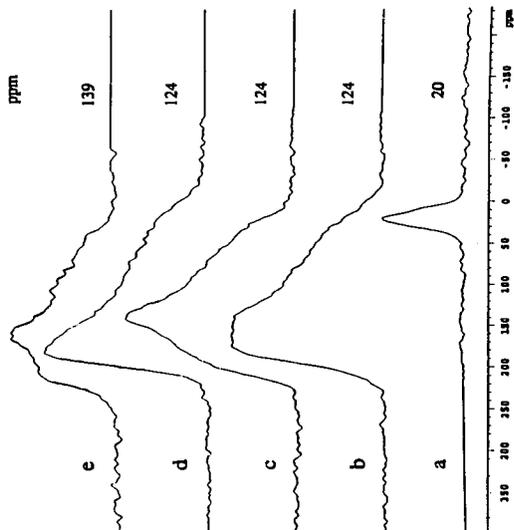


Figure 6. Pocahontas coal triple-echo MAT spectrum slices at selected isotropic shift values.  
 (a) Normal triple-echo MAT spectrum slice showing the aliphatic carbons centered at 20 ppm/  
 (b) Normal triple-echo MAT spectrum slice showing the overlapping protonated and nonprotonated (bridgehead) carbons centered at 124.0 ppm.  
 (c) 50  $\mu$ s contact time triple-echo MAT spectrum slice showing the protonated carbons centered at 124 ppm.  
 (d) Dipolar dephasing triple-echo MAT spectrum slice with  $D = 30$   $\mu$ s and a spin lock pulse of 1.5 ms showing the nonprotonated carbons centered at 124 ppm.  
 (e) Dipolar dephasing triple-echo MAT spectrum slice with  $D = 30$   $\mu$ s and a spin lock pulse of 1.5 MS showing the nonprotonated carbons centered at 139 ppm.

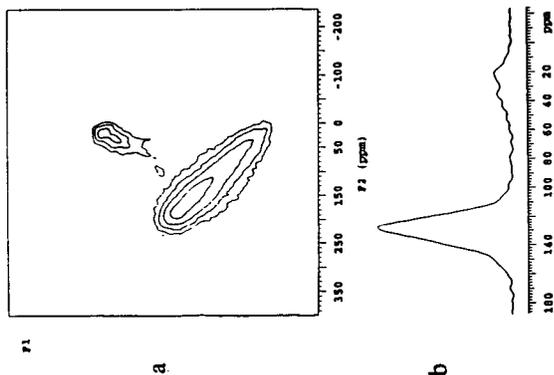


Figure 5. Pocahontas coal triple-echo MAT spectra.  
 (a) 2D spectrum obtained using a sample rotation rate of 4440.025 Hz, a  $\Delta$  of 60  $\mu$ s, a contact time of 2 ms, a recycle delay of 2 s, an acquisition dwell time of 31.25  $\mu$ s, a  $t_1$  increment of 93.75  $\mu$ s, and 25  $t_1$  increments. Data was acquired for 512 scans in the real data set and 512 scans in the imaginary data set for a total measuring time of approximately 8 hr. A 2 ppm full-width-at-half-maximum Gaussian line broadening was applied in both dimensions.  
 (b) Projection of the 2D spectrum in (a) onto the isotropic shift axis.