QUANTITATIVE ASPECTS IN CP/MAS EXPERIMENTS ON WHOLE COALS AND MACERALS*

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Introduction

Solid–state NMR spectra are now being obtained routinely for a wide variety of fossil–fuel materials, including coals, using cross–polarization (CP) techniques combined with high–power decoupling and magic–angle sample rotation (MAS).[1] However, the quantitative reliability of CP/MAS experiments on coals has recently received considerable attention.[2–8] Because coals are heterogeneous by nature, a single CP experiment can give inadequate quantitative information and may be very misleading. Problems can arise because the efficiency of cross polarization to different carbons in the sample depends upon their characteristic polarization transfer times (T_{CH}) and on the behavior of their respective proton reservoirs with regard to spin–lattice relaxation in the rotating frame ($T_{1\rho}{}^{H}$). With regard to the analysis of coals, there is the additional complication that carbons in the vicinity of free radicals may not be detected due to dipolar interactions.

The purpose of the present investigation is to identify the important experimental parameters which govern NMR signal intensities in solid–state experiments on whole coals and separated coal macerals and, subsequently, to devise computer–assisted methods which allow absolute signal intensities to be calculated from the data. New methods have also been developed to evaluate the number of carbon spins that are detected in solid–state NMR experiments. Any missing carbon signal intensity has been attributed to the presence of paramagnetic centers or to inefficient carbon polarization.

Experimental

Solid–state ^{13}C spectra were obtained at 25.18 MHz on a Bruker CXP–100 spectrometer with a doubly–tuned single coil probe and a dual air–bearing spinning apparatus. The spinners were made of ceramic with an internal volume of 0.3 ml and were spun at approximately 4 kHz. Relaxation time experiments were carried out employing contact times between 0.05 and 10 ms, a 2 s pulse repetition rate, and a 67 kHz proton decoupling field. Carbon signal intensities were determined for aromatic (110–160 ppm) and aliphatic (0–60 ppm) absorption bands. For the aromatic carbons, signal intensities of the spinning sidebands were added to the intensity of the centerband. The fit of the contact–time magnetization curves was obtained using a non–linear least squares computer program developed in these laboratories. Typically, 11–22 contact times were selected for a single analysis.

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Carbon spin–counting experiments were carried out by physically mixing approximately 12 percent hexamethylbenzene (HMB) by weight with the sample to be measured. Experimental conditions used for the measurements were a contact time of 4 ms, a 3 s pulse repetition rate, a 50 ms acquisition time, and a 67 kHz proton decoupling field.

The five maceral samples studied were a resinite from Utah, Blind Bear Canyon mine, a sporinite isolated from PSOC 828, two vitrinites isolated from Illinois No. 2 hvC bituminous and PSOC 1103 coals, and a fusinite isolated from Illinois No. 2 hvC bituminous coal. The coal samples studied were a Victorian Brown coal (pale lithotype) from Australia, a Wyoming lignite, an Illinois hvC bituminous coal (Herrin No. 6), and a medium–volatile bituminous coal (PSOC 403). Analytical data for the separated coal macerals have been presented elsewhere.[9] The samples designated PSOC were obtained from the Penn State Coal Sample Bank.

Results and Discussion

Conventional CP/MAS experiments with a contact time of 1 ms initially were performed on the Illinois No. 2 vitrinite sample in order to establish which instrumental parameters were critical for quantitative analysis. Varying the proton decoupling field from 40–80 kHz or changing the pulse repetition rate from 0.5–3 s had little effect on the derived carbon aromaticity values. However, even a slight misadjustment of the Hartmann–Hahn matching condition resulted in a substantial reduction in the observed carbon aromaticity.

In a second set of experiments, the variation of the aromatic and aliphatic carbon signal intensities with contact time was investigated. Previous studies on coals have shown that treating all aromatic or all aliphatic carbons as having single relaxation behavior provides a reasonable model for computational analysis of the data.[4] Figure 1 shows the magnetization curves for four maceral samples. Absolute values for the carbon intensities (M_0) then are calculated by fitting the variation in carbon magnetization to equation 1 below:

$$M = M_0 \exp(-t/T_{CH}) \left(1 - \exp(-bt/T_{1\rho}{}^{H}) \right), \qquad (1)$$

$$\text{where } b = 1 - T_{CH}/T_{1\rho}{}^{H}.$$

Our studies on model polymers have demonstrated that computed intensities for different carbon functional groups from variable contact–time experiments are accurate to within 3%. Calculated carbon aromaticities in Table 1 for a series of whole coals and maceral concentrates show the expected trends: aromaticity increases with increasing rank of the coals and, for macerals, in the order resinite < sporinite < vitrinite < fusinite. More importantly, each maceral sample in Figure 1 exhibits a unique, intensity response profile to the variation in contact time. The plots for the various macerals indicate that the intensity maxima of the aromatic carbons occur typically at longer contact times than those of aliphatic carbons. Hence, to select a single contact time which gives representative aromatic–aliphatic intensity ratios for the entire suite of macerals is difficult, if not impossible. Consequently, differences in relaxation behavior from sample to sample

are hard to reconcile from a single cross–polarization experiment and can lead to significant errors in the estimation of aromaticity values. The advantage of the computational method lies in its ability to determine carbon intensities which are independent of relaxation effects.

Carbon–spin counting experiments on the coal and maceral samples involve physically mixing a suitable intensity reference, hexamethylbenzene (HMB), with the sample to be measured. The ratio of the total carbon magnetizations of the sample over the reference calculated using equation 1 and normalized with respect to weight–percent carbon gives a good estimate of the proportion of carbon spins detected for the sample. Comparing results from Bloch–decay (SPE) and CP experiments allows one to distinguish what portion of the undetected signal intensity is due either to the presence of paramagnetic species in the sample or to inefficient carbon polarization. Figure 2 shows the results from a CP experiment on a resinite and a vitrinite sample, each containing approximately the same weight percent of HMB. The sharp signals at 20 and 135 ppm in each spectrum respectively represent the methyl and aromatic carbons of HMB. Visual inspection of the overall signal intensities of the two samples (in relation to the reference) reveals that a substantially lower number of carbons are detected for the vitrinite sample. When the integrated intensities are mathematically corrected for relaxation effects and compared to those calculated for the standard, the results indicate that 70% of the carbons in the resinite sample are being detected and only 35% for the vitrinite. These can be compared with values of 70% and 50%, respectively, obtained from Bloch–decay experiments. Therefore, one half of the carbons in the vitrinite sample are not observed due to paramagnetic line–broadening effects, while another 15% go undetected due to inefficient cross polarization. Moreover, the vitrinite data suggest that cross–polarization experiments largely discriminate against aromatic carbons, and thus, they provide minimum values for carbon aromaticity. The general trend observed for the entire suite of coal and maceral samples presented in Table 2 is a decrease in detected carbons with increasing carbon content of the sample.

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Table 1. Carbon Aromaticities(f_a) Derived from Contact Time Experiments using Equation 1.

Sample	f_a
Resinite(Hiawatha)	0.16
Sporinite(PSOC 828)	0.56
Vitrinite(Ill No. 2)	0.70
Vitrinite(PSOC 1103)	0.69
Fusinite(Ill No. 2)	0.82
Australian(Pale Lith)	0.37
Wyoming Lignite	0.55
Herrin No. 6(HVC Bit)	0.67

Table 2. Carbon Spin–Counting Experiments

Sample	% C Observed SPE[a]	CP[b]	% C[c]
Resinite(Hiawatha)	70	70	83.8
Vitrinite(Ill No. 2)	50	35	72.0
Fusinite(Ill No. 2)	43	26	79.3
Wyoming Lignite		56	66.4
Herrin No. 6(HVC Bit)		55	62.8
MV Bit(PSOC 403)		40	78.0

[a] SPE = single–pulse excitation.

[b] CP = cross polarization.

[c] Carbon % on dmmf basis.

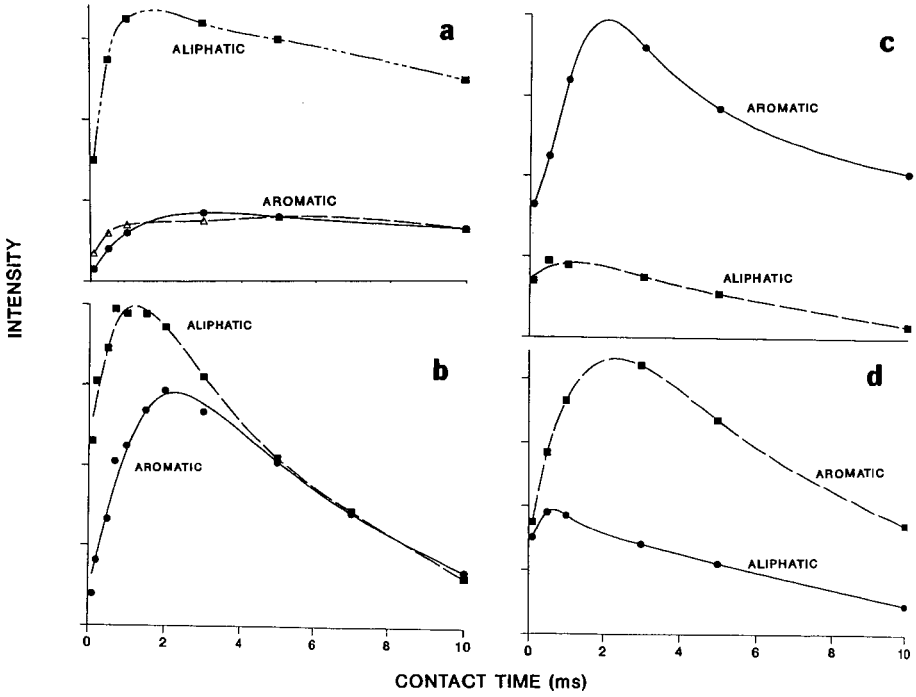

Figure 1. Variation in Carbon Signal Intensity with Contact Time for Maceral Concentrates a)Resinite, b)Sporinite, c)Fusinite and d)Vitrinite.

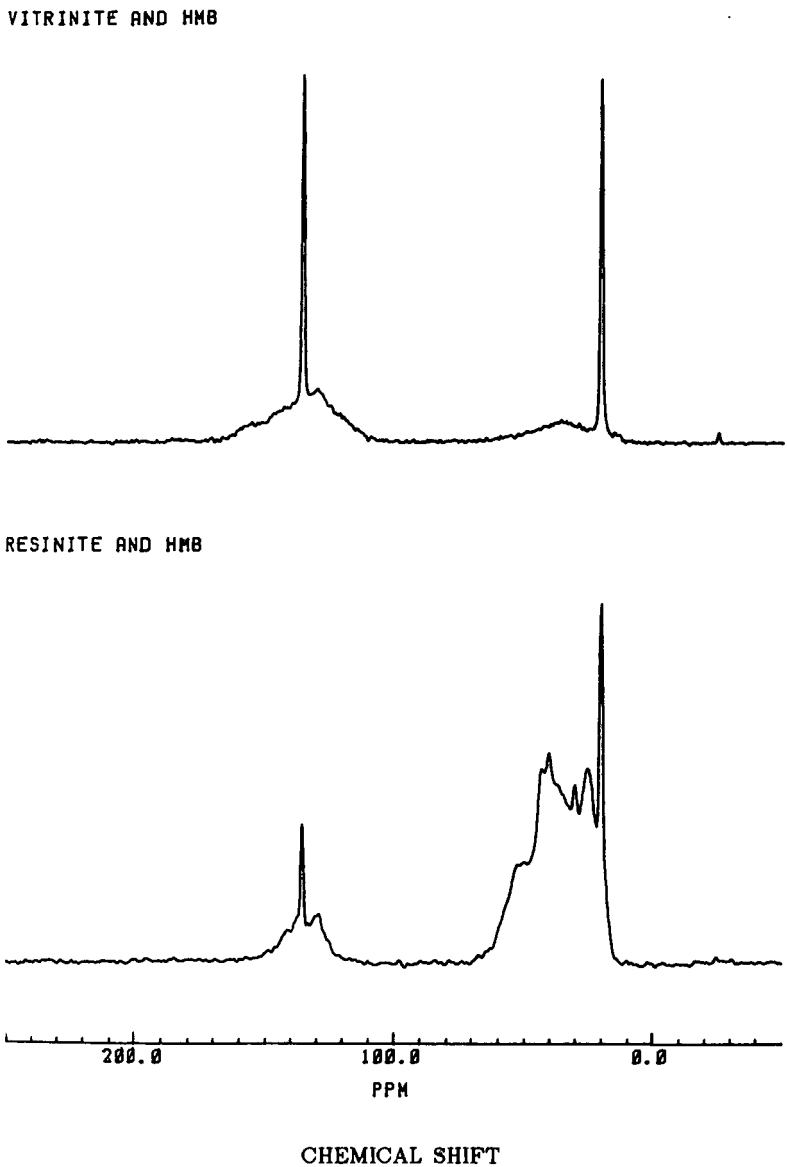

Figure 2. CP/MAS ^{13}C–NMR Spectra of Vitrinite and Resinite Samples with added HMB as the Intensity Standard.