

## Zero Field and 2D NMR Methods: Applications to Fossil Fuels

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### Introduction

A knowledge of the chemical structures present in coals is essential for developing a better understanding of coal chemistry. Therefore, the study of coal structure is important to the successful synthetic conversion of coal to a chemical feedstock or high quality fuel. A great deal has been inferred about coal structure from the study of liquid coal products by both classical chemical methods and modern spectroscopic techniques. This approach is attractive as most modern analytical methods are applicable only to liquid samples and are not suitable for solids. However, because of the heterogeneity of coals and the complexity of coal chemistry it is often difficult to extrapolate back to the structure of a whole coal solely from the characterization of liquid products and extracts. Over the last decade this has spurred the development of spectroscopic methods suitable for nondestructively analyzing the structures of whole coals in the solid state. The two most useful techniques to emerge so far have been Fourier transform infrared spectroscopy and carbon-13 solid state nuclear magnetic resonance. The latter technique in the form of the combination of cross polarization and magic angle sample spinning (CP/MAS) spectroscopy has proven the most useful in characterizing the functionalities present in the organic portion of coals(1,2). This method provides the best direct measure of carbon aromaticities and can also measure the relative amounts of protonated versus nonprotonated carbon when combined with dipolar dephasing techniques. Much more information is, in principle, contained in carbon-13 CP/MAS spectra, but the resolution typically obtained does not permit as detailed an analysis as is possible in the NMR of liquids. The situation for coal CP/MAS spectra is similar to that found in the NMR of complex biomolecules where the large number of resonances and broad natural linewidths result in incompletely resolved spectra. In solution studies these difficulties can often be overcome by the application of two dimensional (2D) NMR methods (3,4). In 2D NMR experiments a complex spectrum is separated into component subspectra on the basis of a second spectroscopic parameter. The subspectra are simpler, more resolved and thus easier to interpret.

Standard 2D NMR methods are not directly applicable to organic solids for a number of reasons, the main one being the strong dipolar couplings among the abundant protons. In this paper two 2D NMR methods are presented that overcome these problems and are suitable for solids. The first is an adaptation of heteronuclear shift correlation spectroscopy to solids (5,6). In this method the carbon-13 and proton chemical shifts of a solid are correlated with one another. This allows the spectroscopist to generate the carbon-13 spectra of all the species with a particular proton chemical shift and vice versa. The second method is a new variant of the dipolar-shift spectroscopy (DIPSHIFT) methods that have been developed to measure C-H distances from carbon-13 proton dipolar couplings (7). Since bonded C-H distances in organic solids are all very close to 1.09Å, the dipolar coupled patterns observed in DIPSHIFT spectra are principally determined by the number of directly attached protons. In this way the dipolar interaction is used to give the number of protons attached to a carbon-13 with a particular chemical shift. The last approach to high resolution solid state spectroscopy described here is deuterium zero field NMR (ZF-NMR) (8). In most solid state NMR methods the large anisotropic solid state interactions are suppressed to give liquid like high resolution chemical shift spectra. However, by doing NMR in zero magnetic field these interactions can be used to spectroscopically discriminate

among different functionalities. For deuterium the spectra are determined by the electric field gradient tensor which is a measure of the amount of s-character in a C-D bond. The spectra so obtained give information equivalent to normal proton NMR spectra, however the resolution is now as good in the solid state as in solution. These methods have shown great promise in model systems and should prove useful in studies of coal structure. The first of these methods has already had some success when applied to coal. Hopefully the finer structural information made available by these techniques will make it possible to apply more sophisticated and selective chemistry to coal. In the following paragraphs the basic principles underlying these experiments are examined and some applications are given. The interested reader is referred to the papers referenced above and to the references contained therein for a more complete description of the theory and the experimental requirements of these methods.

#### Heteronuclear Shift Correlation Spectroscopy

The pulse sequence used in heteronuclear shift correlation is indicated in figure 1. The basic idea of this method is to separate the overlapping carbon-13 resonances on the basis of the differences in the chemical shifts of the protons attached to the carbon-13 nuclei and vice versa. During the  $t_1$  interval the protons are allowed to evolve under their chemical shifts. To give optimal resolution the carbon-13 nuclei are decoupled from the protons and MREV-8 homonuclear decoupling is employed to remove the dipolar couplings among the protons. At the end of  $t_1$  the proton evolution must be transferred to the carbon-13 nuclei. In solids this can be accomplished by applying a proton spinlocking radio frequency (RF) field and then cross polarizing. When the proton spinlocking RF is turned on only that portion of the magnetization that is parallel to the RF field is spinlocked. For the protons on resonance all of the magnetization is spinlocked independent of the initial  $t_1$  period. On the other hand the protons off resonance go in and out of phase with the spinlocking field. This results a spinlocked magnetization that oscillates at the off resonance frequency as a function of  $t_1$ . Since the carbon-13 signal produced in the CP step depends on the size of the spinlocked proton magnetization, the carbon-13 signal will also oscillate as a function of  $t_1$  at the proton resonance offset. The Fourier transform of the carbon signal amplitude versus  $t_1$  then gives the proton chemical shift. To produce a 2D spectrum a set of carbon-13 spectra for successively longer values of  $t_1$  is acquired. A second Fourier transform versus  $t_1$  results in a 2D spectrum in which the proton and carbon-13 chemical shifts are correlated. The CP mixing time is kept short to minimize the contribution to the carbon-13 signal from non-bonded interactions. This ensures that only directly bonded pairs are correlated. This short mixing time also reduces the spin diffusion among the protons during cross polarization which can degrade the resolution in the proton dimension. As a result, this experiment is sensitive only to the subset of carbons that have a directly attached proton. In addition the proton spectra are only representative of that portion of the protons in the coal attached to a carbon.

The most natural way to portray 2D spectra is in a contour plot with the contours being paths of constant amplitude. Peaks appear as sets of concentric contours in this type of plot. In figure 2 is the contour plot of the heteronuclear shift correlation spectrum of an Illinois #6 coal (6). Along the top and sides are the summations of the data set onto the two axes. These spectra are the same as the normal short contact time CP/MAS spectrum and the combined multiple pulse MAS proton spectrum. In the contour plot there are three clearly resolved peaks and two weaker peaks labelled 1-5. For the aromatic region there is one peak at  $\delta^1\text{H} = 6.8$  ppm,  $\delta^{13}\text{C} = 128$  ppm as expected for the protonated aromatics. The results in the aliphatic region are much more revealing. Here the two most clearly resolved peaks, 4 and 5, are attributed to methylenes with  $\delta^1\text{H} = 2.1$  ppm,  $\delta^{13}\text{C} = 29$  ppm, and to methyls with  $\delta^1\text{H} = 1.0$  ppm,  $\delta^{13}\text{C} = 18$  ppm. These peaks are clearly resolved in both proton and carbon shift in the 2D spectrum. As the spectra along the top and sides indicate this resolution is not possible in either the proton or carbon-13 one dimensional spectra. In addition there are two

other weak peaks, 2 and 3, that are observed as shoulders in the 2D spectrum, one at  $\delta^1\text{H} = 3.5$  ppm,  $\delta^{13}\text{C} = 40$  ppm, and a second at  $\delta^1\text{H} = 0.8$  ppm,  $\delta^{13}\text{C} = 35$  ppm. These peaks are probably due to methyl groups with the first corresponding to heteroatom substituted methyls of some type and the second to sterically hindered methyls. Taking into account the bias in intensities that the short CP mixing time produces, the relative amounts of methyl to methylene to aromatic hydrogen can be estimated as 1.0 : 0.9 : 0.7 respectively.

From this 2D spectrum one can easily appreciate the increase in resolution that the method has over the usual CP/MAS technique. It is also apparent that the distribution of protons in the organic portion is easily accessible without spectral interference from water or mineral protons as would be encountered in direct solid state proton spectroscopy of coals. As shown above the method should be particularly useful in disentangling the overlapping bands in the aliphatic portion of coal CP/MAS spectra.

#### Dipolar Resolved Chemical Shift Spectroscopy- DIPSHIFT

The previous method used solid state pulse sequence trickery to adapt a liquid state method to the solid state. In the method diagrammed in figure 3, the solid state interactions are actually put to good use rather than considered just a nuisance. Let us begin by first considering some of the fundamentals of the magic angle spinning experiment.

In an MAS experiment the sample spinning is typically used to average the anisotropic chemical shifts to their isotropic values producing liquid like spectra. If the spin rate does not exceed the width of the shift anisotropy in Hertz, the spectrum will contain spinning sidebands. In the limit of very slow MAS spinning the envelope of the sideband pattern is the same as the static powder pattern. If MREV-8 decoupling is used to remove the proton-proton dipolar couplings in a solid, the remaining carbon-proton dipolar interaction also acts like a shift anisotropy. The combination of MREV-8 decoupling and MAS then gives dipolar coupled carbon-13 spectra broken up into sideband patterns. From the envelope of the sidebands the dipolar couplings can be determined. This is the principle behind the DIPSHIFT methods used to measure C-H distances via carbon-proton dipolar couplings and their  $1/r^3$  dependence. In the current application the strategy is to take advantage of the constancy of C-H distances in organic solids and to realize that the dipolar coupled spectral patterns thus depend only on the number of protons attached to a given carbon center. In figure 4 are typical dipolar coupled patterns for methylene, methine, rapidly rotating methyl and quaternary carbons using MREV-8 proton decoupling with CP/MAS. Note that the methylene pattern is approximately twice as wide as the methine pattern and that both are much wider than the methyl or quaternary patterns. The different widths of these patterns can be used to cleanly separate overlapping carbon-13 resonances that have different numbers of attached protons. Consider the case where the resonances for a methylene, methine and methyl carbon all overlap. In the MREV-8 decoupled CP/MAS spectrum the outermost sidebands will come only from the methylene carbon. Since the sideband intensity ratios in each pattern are fixed by the size of the carbon-proton dipolar coupling and the spin rate, the contribution of the methylene to the rest of the spectrum can be subtracted. In this resultant spectrum the outermost sidebands will now only be due to the methine. The subtraction operation used for the methylene can be repeated for the methine leaving only the methyl carbon spectrum. In this way the contributions to a line from methylene, methine and methyl plus quaternary carbons can be separated. This is a significant improvement over dipolar dephasing which cannot separate methylenes from methines. Also, since all carbons are observed at the same time, this type of technique avoids the problems with quantitation encountered in dipolar dephasing.

For a complex solid the dipolar coupled patterns are best obtained from a 2D experiment as in figure 3. During  $t_1$  the carbon-13 nuclei evolve under the effect of MREV-8 decoupling and the carbon-proton dipolar coupling. Afterwards in  $t_2$  the carbon signal is acquired under the influence of strong dipolar decoupling.

As before a set of carbon-13 spectra for successively longer values of  $t_1$  is acquired. The second Fourier transform gives a 2D spectrum with the normal carbon-13 chemical shift along one axis and chemical shift plus dipolar couplings along the second axis. In other DIPSHIFT methods the chemical shifts are removed during the  $t_2$  interval with a  $\pi$  refocussing pulse. To refocus the anisotropic as well as the isotropic shift the  $\pi$  pulse must be applied at an integral multiple of the MAS spinning cycle. Since accurately controlling MAS spin rates is difficult, an alternative method is attractive. In the new method presented here the chemical shift is kept in both  $t_1$  and  $t_2$ . Spectral distortions will occur in this experiment from the so-called phase twist problem (3) unless the carbon magnetization is projected at the end of  $t_1$ . This is done by flipping a portion of the carbon-13 magnetization up along the applied field, waiting a short dephasing time to destroy any transverse magnetization, and flipping the spins back down into the x-y plane. This method has the advantage that none of the experiment need be done synchronously with the MAS rotation. In addition the MREV-8 sequence can be incremented a piece at a time giving a greatly increased bandwidth in the dipolar dimension. The pulses used in the projection step are also phase cycled in 90 degree increments for each successive point to simulate the effect of having the detector off-resonance during  $t_1$ . This allows the carrier frequency to be placed in the center of the spectrum while appearing to be at the extreme edge and makes the most effective use of the available bandwidth in  $t_2$ . This feature is especially important for methylenes because their dipolar coupled patterns are so wide.

By using the subtraction scheme outlined above on the 2D spectrum the methylene only, methine only and methyl plus quaternary only spectra can be generated. With suitable software routines the relative numbers of methylenes, methines and methyls plus quaternary carbons can also be extracted for the different resolvable spectral regions. Application of this method in model polymer systems has allowed separation of overlapping resonances such as the methine and methylene that overlap in polystyrene. Whereas the peak in question seems to be a single resonance in the normal CP/MAS spectrum, the dipolar slices taken in the 2D experiment clearly show that this line is a superposition of a methylene and methine. The advantage of this method over the heteronuclear shift correlation technique is that all carbons are detected as a long mixing time can be used and therefore the signal to noise obtained in a given amount of time is much better. The information obtained is complementary being in terms of proton multiplicity rather than chemical shift. For coals the method should prove particularly useful for separating and assigning the resonances observed in CP/MAS spectra.

#### Zero Field NMR

Another method that should prove useful in the study of coal structure is zero field NMR (ZFNMN). In the 2D methods described so far the basic strategy has been to use carbon-13 chemical shifts to identify different functional types of carbon. Then either proton chemical shifts or carbon-13 proton dipolar couplings are used to separate resonances that occur at the same shift. In ZFNMN a very different approach is used. Instead of suppressing the large solid state anisotropic interactions such as dipolar or quadrupolar couplings to obtain liquid like chemical shift spectra, these interactions themselves are used as the principal means of resolving different chemical species.

Consider the case of a spin 1 nucleus in a large static magnetic field. The main interaction that this nucleus feels is the coupling to the static field giving the usual Zeeman splittings observed in an NMR experiment. In a rigid solid a spin 1 nucleus also has a quadrupole coupling that produces an additional splitting of the energy levels. For deuterium in organic solids this interaction is a measure of the s-character in the C-D bond and in a sense is analogous to a chemical shift. Deuterium quadrupole couplings typically range from tens to hundreds of kHz. This is much larger than the spread of deuterium chemical shifts that span only 750 Hz at the highest fields available today. Thus quadrupole couplings could potentially be the basis for a deuterium spectroscopy with much

greater resolving power than standard NMR. Unfortunately the quadrupolar interaction does not simply add to the Zeeman interaction and the size of the splitting at high field depends on the orientation of the electric field gradient tensor with respect to the applied field. In a randomly oriented powder sample this results in a range of observed splittings and the spectra are broad overlapping powder patterns.

The application of a strong magnetic field produces powder broadening because it polarizes the nuclei along a particular direction in space. However in the absence of an applied field, all deuterium nuclei of the same type experience the same splitting of their energy levels independent of their absolute orientation in space and the spins are quantized in a molecule fixed frame. Thus the zero field deuterium NMR (ZFDNR) spectrum of a randomly oriented powder is the same as for a single crystal and has narrow resolved lines. This is the basic idea behind pure nuclear quadrupole resonance (NQR) spectroscopy as well. The trick is to do a high sensitivity experiment in the absence of an applied field. Several clever field cycling and double resonance techniques have previously been developed for pure NQR spectroscopy of nuclei such as deuterium (8). However all of the standard methods are either continuous wave techniques or involve low frequency detection. The ZFNMR method is more generally applicable to nuclei such as deuterium with relatively small quadrupole couplings. The method uses high frequency detection for good sensitivity and is also a Fourier transform technique. This latter feature gives ZFNMR a better inherent resolution than any of the continuous wave methods (8).

The magnetic field cycle used in the ZFNMR method is shown in figure 5. The first step is to polarize the nuclei in a high field magnet to produce a measurable signal. The sample is then mechanically removed to an intermediate region in the fringe field of the high field magnet. If this is done rapidly compared to the characteristic relaxation times of the sample, the high field polarization is maintained in the intermediate field system. As long as the intermediate field is chosen to give a Zeeman splitting several times larger than the quadrupole splittings, the polarization will continue to be aligned with the applied field axis. This intermediate field is suddenly removed by a set of pulsed coils that can collapse the field rapidly compared to the inverse of the NQR frequencies of the sample. The magnetization that was initially along the applied field axis now finds itself influenced solely by the quadrupolar interaction. Since the polarization at zero field would prefer to be aligned in the internal axis system of the electric field gradient tensor, any portion that is not so oriented now oscillates at the zero field NQR frequencies. If a receiving coil was in place around the sample at this point, a zero field free induction decay (FID) would be observed. The Fourier transform of this zero field FID would give the ZFNMR spectrum. Because of the low frequencies involved, it is better to turn this oscillation into a high field observable. This requires a 2D type of data taking sequence with the zero field time as  $t_1$ . At the end of the zero field interval the intermediate field is suddenly pulsed back on trapping the component of the magnetization parallel to the applied field. After the sample is returned to the NMR magnet this component can be measured as a high field NMR signal. The amplitude of this signal naturally oscillates as a function of the length of time  $t_1$  that the sample spent at zero field. A Fourier transform of the high field signal amplitude versus  $t_1$  then results in the ZFNMR spectrum. Although a 2D type of data set is actually acquired, a full 2D transform is not performed since the high field spectra do not provide any additional information.

A typical result is shown in figure 6 where the ZFDNR 6a and high field MAS NMR 6b spectra of perdeuterated dimethoxy benzene are compared. In spectrum 6a the methyls give a resonance at about 40 kHz and the aromatics appear in the region around 135 kHz. This resolution is comparable to the resolution of the methyl and aromatic carbon-13 resonances in the CP/MAS spectrum. The two types of deuterium are barely resolved in spectrum 6b with the aromatics appearing at 2 and 4 ppm from the methyl. This set of spectra dramatically demonstrates the superior

resolving power of ZFDNR over the more conventional high field MAS technique. In fact the resolution of ZFDNR is comparable to high field deuterium NMR in solution and can discriminate among different functionalities as well as carbon-13 CP/MAS spectroscopy can. Thus the method should be the technique of choice for determining the different types of hydrogen in organic solids. For instance proton aromatics in coals could accurately be measured with ZFDNR. The successful application of this method will undoubtedly require additional developments to increase the sensitivity of the method such as combining ZFDNR with dynamic nuclear polarization (1) or indirect detection of the deuterium via the abundant protons (8). All experiments to date have used isotopically enriched samples because of the low natural abundance of deuterium. At present natural abundance studies are not feasible and in the immediate future the most fruitful contributions to coal chemistry will involve chemically modified coals either by using deuterated reagents or exchanging labile hydrogen for deuterium.

#### Conclusions

The increase in resolution made possible by these new 2D NMR and zero field NMR methods should make it possible to determine the chemical structures present in coals to a much finer degree than previously possible. With a better knowledge of the functional units in coals it should be possible to develop more sophisticated chemistry for converting coal to a chemical feedstock or fuel. These NMR methods are still in an early stage of development but have already had some success in application to polymers and coal. The question of quantitative response has yet to be fully addressed but at present there is no evidence to indicate that this will be any more of a problem than in standard carbon-13 CP/MAS spectroscopy. More development is needed to make these techniques generally accessible to the practicing chemist and work in this area is being actively pursued.

#### Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS for partial support of this work. Other financial support for this work was provided by the Department of Energy under grant number DE-FG22-83PC60791.

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Fig. 1

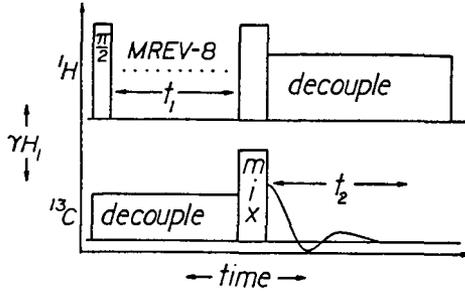


Fig. 2

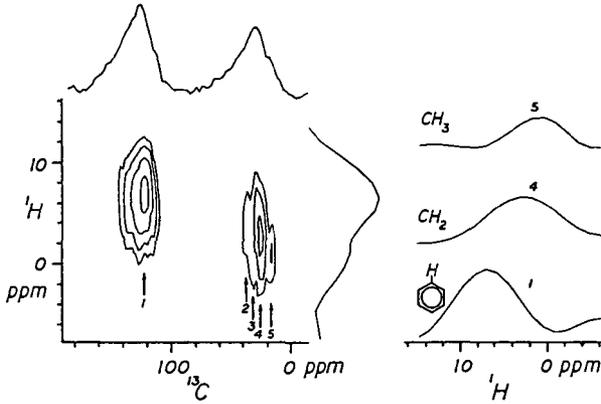


Fig. 3

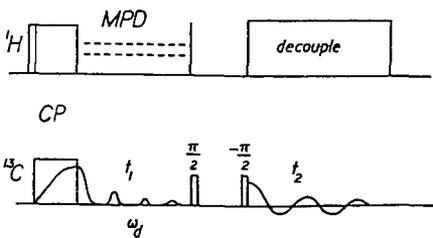


Fig. 4

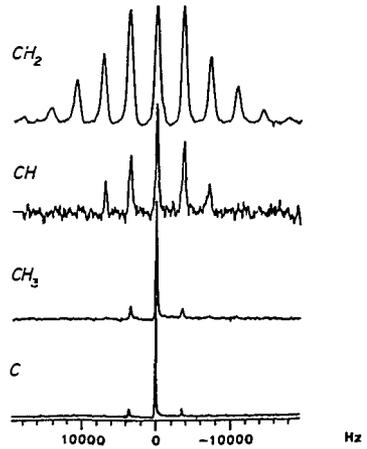


Fig. 5

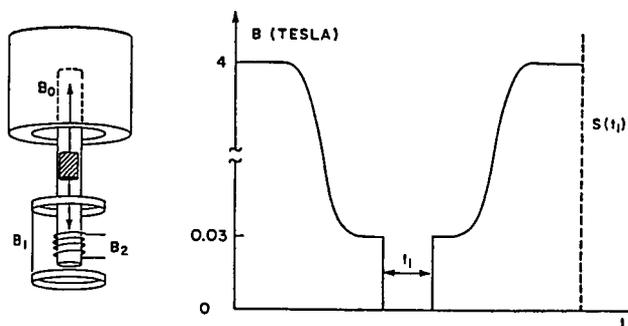


Fig. 6

