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^{1}H and ^{13}C Solid-state NMR of *Gossypium barbadense* (Pima) Cotton

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Abstract:

The interaction of water with cellulose and its influence on the nuclear spin dynamics in *Gossypium barbadense* (Pima) cotton were investigated by ^{1}H and ^{13}C solid-state NMR techniques. ^{1}H spin diffusion results from a Goldman-Shen experiment indicate that the water is multilayered. ^{1}H MAS experiments provide evidence of a range of correlation times for the water, indicative of molecular motion ranging from restricted to relatively mobile. The ^{1}H spin-lattice relaxation time varies with water content and is different for static and MAS conditions. By coupling the Goldman-Shen sequence with ^{13}C CP/MAS, cross-polarization from the molecularly mobile water protons distributes magnetization throughout the cellulose (as opposed to enhancing ^{13}C resonances from only the crystalline or the amorphous domains or from only the surface of the cellulose). However, spatial localization of the combined Goldman-Shen-^{13}C CP/MAS experiment using both short mixing and contact times yields a spectrum consistent with predominantly the I_β polymorph of cellulose. Longer mixing times and the same, short contact time yield a spectrum that is indicative of an increased I_α polymorph content in the crystallite interiors relative to the smaller values found with short mixing times.

Key Words:

NMR; ^{1}H NMR; ^{13}C CP/MAS; spin diffusion; Goldman-Shen; spin-lattice relaxation; T_1; cellulose; moisture; water; cotton; *G. barbadense*.

Introduction

Cotton is a commercially important crop grown throughout the world. Its fiber is mostly cellulose, a natural polymer with widespread applications in the textile, chemical, and pharmaceutical industries [1]. Diffraction studies have provided structures for a number of polymorphs, designated I_α, I_β, II, III_I, and IV_I [2-6]. Many spectroscopic studies of the chemical and physical properties of cellulose [1,7-12], not only from plants but also from algae and bacteria, have examined the structure, morphology, and interactions with water. Often these studies have focused on processed samples of exceptional crystallinity, rather than on cellulose in its native form.

In this study, ^{1}H and ^{13}C solid-state nuclear magnetic resonance (NMR) techniques are applied to raw cotton fibers to characterize both the structure of the cellulose and its interaction with water. The absorption of water drastically influences the physical properties of cellulose [13-15]. Interaction between water and cotton is of special interest because moisture strengthens the cotton fiber in practical situations, but the mechanism is unknown. Fiber strength is a major factor in the speed at which the fiber can be spun into yarn, so it is economically important. The comfortable traits of cotton fabrics are due, in large part, to their ability to absorb moisture, but they require large energy inputs to dry. To better capitalize on the advantages of cotton, and diminish the impact of the negative traits, it should be useful to have a better understanding of moisture-cotton interaction at the molecular level. The effect of water on the ^{1}H nuclear spin-dynamics is investigated through ^{1}H spin diffusion with a Goldman-Shen [16] sequence. Coupling the Goldman-Shen sequence with ^{13}C cross-polarization/magic angle spinning (CP/MAS) [17] provides further insight into spatial arrangement of the various components.

Experimental

Spectra were acquired with a Bruker Avance 300 spectrometer. Proton NMR data were obtained from static samples using a standard Bruker ^{1}H wideline probe with a 5-mm solenoid coil. The ^{1}H $\pi/2$ pulse width was 1 μs. The ^{1}H spin-lattice relaxation (T_1) data were acquired with an inversion recovery sequence (π - tau - $\pi/2$ - acquire) [18].

A standard Bruker MAS probe with a 4-mm (outside diameter) zirconia rotor was used to acquire ^{13}C CP/MAS data and ^{1}H data in both static and MAS experiments. The ^{13}C CP/MAS spectra were acquired with a ^{1}H $\pi/2$ pulse width of 4 μs, a contact time of 0.8 ms, a data acquisition time of 65 ms, and a recycle delay of 15 s. Sample spin rates of 5 and 10 kHz were used for MAS.

All samples were *Gossypium barbadense* (Pima) cotton. In addition to samples of the raw stock, other samples were extracted with ethanol to remove surface waxes. For NMR measurements on static samples, the 5-mm glass NMR tube was flame-sealed. For MAS measurements, the seal of the rotor was inspected periodically by ^{1}H MAS NMR to check for any change in moisture content.

Results and Discussion

Cotton is an example of cellulose that occurs in a relatively pure form in its native state. The ^{13}C CP/MAS spectrum of an 81.7 mg sample of raw stock of *G. barbadense* (Pima) cotton is shown in Figure 1A, along with a vertical expansion (Figure 1B) to show the smaller peaks in the spectrum arising from various minor components. As per Attala and VanderHart [7,19], the cellulose resonances are assigned as follows: C-1, the anomeric carbon, ranges from 102 to 108 ppm; C-4 has a relatively large resonance at ~89 ppm with a smaller one upfield at ~84 ppm; C-2,3,5, the remaining ring carbons, appear at ~75 ppm and ~72 ppm; and finally C-6, the primary alcohol, has a relatively large resonance at ~65 ppm (*tg* orientation of O-6 according to Horii [9], in agreement with the diffraction studies) with a smaller resonance upfield at ~63 ppm (*gt* orientation). C-1 and C-4 provide the linkages in the cellulose chains.

The assignment of multiple resonances (*e.g.*, the smaller upfield resonances) indicates that NMR distinguishes cellulose chains in multiple environments. In particular, the presence of the additional, smaller upfield resonances for C-4 and C-6 is indicative of cellulose chains in "less ordered environments" [7]. For the other sites, the signal contributions from the less ordered chains are assumed to be present beneath the more prominent resonances of the crystalline components. The "less ordered environments" consist of an amorphous part, *i.e.,* from regions where there is a loss of order in three dimensions, as well as cellulose chains at the surfaces of the crystalline region. Cellulose in these two environments may differ in molecular mobility and in conformation, the result of disordered hydrogen bonding of the primary alcohol groups.

In addition to the cellulose resonances, several small resonances are observed in the spectrum. The broad resonance around 175 ppm is a carboxyl resonance arising from carboxylic acids present in the sample. The resonances around 210 and -60 ppm are spinning sidebands from the large resonance around 74 ppm. The sharp resonance around 33 ppm is from the wax, identified by comparison with an ethanol-washed sample from which the wax has been removed. There is also a rather broad resonance beneath the wax that extends upfield to about 20 ppm. This resonance is of approximately the same intensity as the carbonyl peak at 175 ppm and arises from various proteins in the raw material.

Figure 2A shows the ^{1}H wideline NMR spectrum of a static, 70-mg sample of the Pima cotton. This sample was conditioned at a laboratory temperature of 22° C and a relative humidity of 33%. The sample was then flame-sealed in a 5 mm NMR tube with two solid glass rod inserts to confine the sample inside the radiofrequency coil of the probe. Sealing the sample proved necessary to prevent changes in moisture content over the course of the NMR experiments. A single ^{1}H spin-lattice relaxation time, T_1, of 1.1 s was measured at ambient temperature for this static sample. Measurements on other samples packed at different humidity levels indicate that the ^{1}H T_1 changes with humidity [15]. To avoid complications due to the humidity dependence of the relaxation rate, all subsequent NMR measurements were made on samples packed at the stated temperature and relative humidity.

The ^{1}H wideline NMR spectrum of the static sample in Figure 2A exhibits a narrow peak with a full width at half maximum (FWHM) of 2.2 kHz on top of a broad component with a FWHM of 46 kHz. That the narrow peak observed in the ^{1}H wideline

spectrum and in the ^{1}H MAS spectrum [v*ide infra*] is indeed moisture was verified by blowing other Pima samples with dry compressed air and observing the disappearance of the narrow peak from the proton spectra. After exposing these samples to the atmosphere (humidity), this narrow peak was again observed in both the static and MAS ^{1}H spectra. The broad component arises from the protons of cellulose and the other minor components observed in the ^{13}C CP/MAS spectrum.

^{1}H wideline NMR spectra are usually broad and featureless as a result of homonuclear dipolar interactions. However, such spectra are sensitive to the presence of molecular motion, which may result in a narrowing of the resonance [20]. Occasionally differences in molecular mobility lead to two-component spectra, *i.e.*, those showing a narrow peak superimposed on a broad peak. Alternatively, in the time domain, such spectra are characterized by an initial fast decay followed by a slower decay. One explanation for such two-component behavior, often invoked in polymer studies, utilizes a two-region model in which hard (crystalline) domains yield a fast decay and soft (mobile) domains yield a slow decay [21]. An alternative explanation is that a very wide range of correlation times produces such an observed decay without the existence of separate phases or components, as might be found for adsorbates on surfaces [22].

These two situations can be distinguished by the application of the three-pulse Goldman-Shen sequence. After the application of the first $\pi/2$ degree pulse, a delay of sufficient length allows the fast-decaying component to effectively go to zero. The second $\pi/2$ degree pulse of opposite phase stores the remaining magnetization of the slowly decaying component along the static magnetic field. After a mixing time, a third $\pi/2$ degree pulse is used to record the NMR signal. If there is a transfer of nuclei or nuclear magnetization between the groups of nuclei showing fast and slow decays, then the original two-component signal will be observed. If no such transfer occurs, then the original two-component signal is restored only with sufficient spin-lattice relaxation.

Figure 3 shows a series of ^{1}H wideline spectra of Pima cotton acquired with the three-pulse Goldman-Shen sequence. An initial delay of 200 μs allows the broad component to completely disappear before returning the magnetization back to the Z axis in order to observe the effect of ^{1}H spin diffusion from the protons of the remaining moisture and wax. The spectra shown in Figure 3 were acquired with mixing times of 0.003, 0.010, 0.5, 1, 10, 25, 50, and 100 ms to examine the possibility of spin diffusion. These spectra exhibit the loss of relative intensity of the narrow peak and an increase in relative intensity of the broad component. The mixing times are short compared with the measured ^{1}H spin-lattice relaxation time of 1.1 s. The increase in the broad component is, therefore, not due simply to relaxation recovery. The recovery of the broad component plotted against the square root of the mixing time (Figure 4) is linear within experimental uncertainty. This behavior is indicative of proton spin diffusion [21].

To illustrate that the initial delay of 200 μs in the Goldman-Shen sequence is sufficient to allow the loss of the broad component, the ^{1}H wideline spectrum resulting from a delayed acquisition (with a delay of 200 μs) is shown in Figure 2B. The resulting spectrum shows the broad resonance suppressed.

Similar effects are also apparent in a ^{13}C CP/MAS ^{1}H wideline separation (WISE) [23] experiment on the cotton sample. The basic WISE spectrum (Figure 5A) shows that all ^{13}C cellulose resonances are correlated with the broad ^{1}H resonance. This confirms the assignment of the broad component in the ^{1}H wideline spectrum to include the protons on

the cellulose polymer. The use of very short contact times suppresses polarization transfer from any protons not directly bonded to the carbon atoms. In contrast, the broad resonance observed in the wideline ^{1}H experiment will include not only the protons of the cellulose but also protons from any strongly bound water that is molecularly rigid [13].

A WISE experiment that includes a 500 μs mixing time before data acquisition (Figure 5B) shows that, under these conditions, the narrow ^{1}H resonance is also correlated with the ^{13}C cellulose resonances through ^{1}H spin diffusion. The fact that no ^{13}C CP/MAS spectrum was obtained when a 200 μs delay was inserted into the normal cross-polarization sequence after the initial ^{1}H $\pi/2$ degree pulse (data not shown) demonstrates that direct cross-polarization from the narrow moisture peak to the cellulose does not occur under these conditions. The conclusion is that this transfer results from spin diffusion among the mobile water protons and the rigid cellulose protons, followed by cross-polarization only from the cellulose protons.

The absence of any direct cross-polarization from the narrow moisture peak to the cellulose after allowing the broad component to dephase rules out any fast molecular exchange for water between the molecularly mobile water and that rigidly bound to the cellulose. Such exchange can be investigated with D_2O [24]. A recent infrared spectroscopic study of the H/D exchange in the I_β polymorph of cellulose [11] indicates that water does not penetrate the hydrogen bond network except at the crystalline surfaces. For exchange that does occur, ^{2}H NMR spectroscopy of cellulose [13] has indicated three types of water bound to the cellulose, as classified by dynamic behavior. The first is non-freezable, strongly bound, rigid water whose ^{2}H lineshape shows no temperature dependence. The second is water undergoing 180º flips about the molecular bisector due to anisotropic constraints. The third type is mobile and exhibits isotropic motion. The presence of three types of water is consistent with the results from thermal analysis [25]. Exchange on the microsecond time scale would be expected to significantly alter the observed ^{2}H lineshape.

Figure 6 shows the ^{1}H wideline spectrum acquired with a Goldman-Shen sequence using a 200-μs delay and a 3-μs mixing time. In addition to a small amount of the broad component observed in this spectrum, there is a second, intermediate component that is much narrower than the broad component (although broader than the narrow component due to the protons in the water).

The results of the Goldman-Shen experiments on Pima cotton plotted in Figure 4 are unusual in comparison with typical results observed in polymers [21] or in biological samples, such as proteins in hydrated lipid bilayers [26] and suberin found in wounded potato tissues [27]. The difference is that the recovered fraction of the broad component does not extrapolate to zero at a mixing time of zero. Approximately 30% of the total recovered broad component is observed for mixing times as short as 3 to 10 μs. This quick recovery of the magnetization of the broad component is a result of the range of correlation times displayed by the moisture; this reflects increasingly stronger homonuclear dipolar interactions. These strong dipolar interactions facilitate the transfer of magnetization into the broad component even for very short mixing times. The diffusive behavior of the spin magnetization from the narrow component to the broad component is then demonstrated by the linear dependence upon the square root of the mixing time (Figure 4). The observed ^{2}H spectroscopic results [13] rule out this recovery occurring by molecular exchange on this time scale of 3 to 10 μs.

The length scale $\langle x \rangle$ covered by spin diffusion during the mixing time τ can be estimated [23] from the spin diffusion coefficient *D* by equation (1):

$$\langle x \rangle = \sqrt{4D\tau/\pi} \qquad (1)$$

Using the reported spin diffusion coefficient of 0.15 nm^2/ms for the mobile ^1H component [13], the length scale over which spin diffusion is occurring may be specified. Diffusive behavior is still observed at mixing times up to 100 ms, corresponding to $\langle x \rangle$ = 4.4 nm. A monolayer of ordered water has a thickness of 0.25 nm and a monolayer of ordinary water has a thickness of 0.31 nm [14]. This indicates that the moisture is present as multiple layers, in the range of 14-17 monolayers.

Using the same diffusion coefficient in equation (1) with the cross-polarization contact time of 0.8 ms, an upper limit of 0.4 nm can be established for spin diffusion during the cross-polarization. This upper limit is determined by the fact that MAS narrows the observed line width of the mobile moisture, hence reducing the homonuclear dipolar interactions necessary for spin diffusion, and spin locking during the cross-polarization limits the homonuclear dipolar interactions [28].

The Goldman-Shen data indicate that the spectrum of a narrow component on top of a broad component results from mobile (moisture) and rigid (cellulose) domains. Nevertheless, there is also experimental evidence for the moisture having differing correlation times. Rather than relying on the reappearance of the two-component behavior as a function of spin-lattice-relaxation recovery, evidence for this range of correlation times appears in the ^1H MAS spectrum of the Pima cotton. The ^1H MAS spectrum acquired with a sample spin rate of 5 kHz is shown in Figure 7. Its features are similar to those of the spectrum of the static sample shown in Figure 2A. There are, however, several differences. The line width of the narrow moisture peak is reduced upon MAS to a FWHM of 1 kHz. This narrowing reveals a smaller upfield peak from the wax. While the line width of the broad component is essentially unchanged, a small portion of the broad component is narrowed by the magic angle spinning, as indicated by the appearance of spinning sidebands at ±5 kHz about the narrow moisture peak. The ^1H spin-lattice relaxation time increases with MAS to 2.4 s. The observation of differing correlation times is consistent with the report of three distinct types of water observed in ^2H NMR experiments [13] in which water was exchanged with D_2O. In short, the two-component behavior observed in the wideline proton spectra of Pima cotton results from both reasons discussed above: a) regions consisting of rigid cellulose and relatively mobile water, and b) water that exhibits differing correlation times for various molecular motions. Some of the broad component in the ^1H spectrum results from immobile water.

The Goldman-Shen sequence applied to protons with MAS (spectra not shown) yields results similar to those described above for the static sample. That is, a 200-μs delay still allows the broad component to dephase with a short mixing time of 10 μs showing the reappearance of the broad component.

Finally the Goldman-Shen sequence on protons can be combined with ^{13}C CP/MAS to investigate how moisture is distributed about the cellulose. The Goldman-Shen delay time of 200 μs ensures that the only remaining ^1H magnetization is from the mobile moisture. The use of a short mixing time of 5 μs in the Goldman-Shen sequence ensures

that the biggest contribution to spin diffusion occurs during the contact time of the cross-polarization sequence. In the wideline ^{1}H spectrum, the broad component is primarily from the rigid cellulose. The increased line width observed indicates much stronger homonucelar dipolar interactions. As a result, the spin diffusion coefficient within the cellulose will be substantially larger than the 0.15 nm^2/ms used for the mobile moisture. As an approximation, a spin diffusion coefficient of 0.77 nm^2/ms for the rigid methylene protons in crystalline α-glycine [29] can be used with equation (1) to estimate that a 0.9-nm layer of the cellulose, in terms of location from the interface with the mobile water, is observed in the ^{13}C CP/MAS spectrum.

The results of the combination of the Goldman-Shen sequence with ^{13}C CP/MAS are shown in Figure 8. As per the ^{13}C CP/MAS spectral assignments for the I_α and I_β polymorphs of Atalla and VanderHart [7], the C-1 I_β resonance appears as a doublet while the I_α resonance appears as a singlet (between the two I_β resonances). Attala and VanderHart also note that in "higher plant celluloses" such as cotton, the downfield shoulder of the C-4 resonance, "a feature associated exclusively with the I_α component", always appears to be about half as intense as the upfield shoulder of the C-4 resonance.

The expanded ^{13}C CP/MAS spectra of the C-1 and C-4 resonances are shown in Figure 9. The normal ^{13}C CP/MAS spectrum (Figure 9C) indicates that cellulose in the Pima cotton is predominantly in the I_β form, with the I_α form estimated to be about 1/3 that of the I_β form, based on spectral deconvolution of the lineshape. Others have reported the I_α/I_β ratios obtained by various methods that range from 0.15 to 0.61 in cotton linters and cotton [7]. Attala and VanderHart [7] have pointed out that this wide variation in results raises questions about "the degree of confidence" in the assumptions necessary for the analyses, especially those related to lineshape analysis. In particular, they specifically state that "it is very dangerous to use the normal C-1 lineshape to analyze for the I_α/I_β ratio", though they do suggest that such techniques can be useful in looking for trends. The numerical result given here is simply for comparison.

Figure 8A shows that with a short mixing time of 5 μs for the Goldman-Shen sequence, the I_α content is reduced (or possibly absent) while both amorphous and I_β resonances are observed. A mixing time of 500 μs (Figure 8B) shows an increased I_α content relative to that of the I_β. This is apparent in both the C-1 and C-4 resonance lineshapes shown in Figure 9. This is particularly interesting for the C-4 resonance. According to Attala and VanderHart [7], "the question remains open as to whether the downfield shoulder of C-4 in the higher plant celluloses could be a 'near-surface' contribution associated with imperfect I_β crystallites or whether it indicates a true mixture of the I_α and I_β forms". The fact that these signals are enhanced with a 500-μs mixing time would suggest that these signals are further away from surfaces where water is located. A mixing time of 50 ms yields a spectrum (not shown) virtually identical to the normal ^{13}C CP/MAS spectrum. The Goldman-Shen spectra show a loss in sensitivity relative to that of the normal ^{13}C CP/MAS spectrum because only the remaining ^{1}H magnetization from the narrow component is utilized and allowed to diffuse to the rest of the sample.

The ^{13}C spin-lattice relaxation (T_1) times were also measured. The spectrally resolved C-4 amorphous resonance around ~84 ppm had a relaxation time of 22 s while the crystalline resonance around ~89 ppm had a relaxation time 58 s. The C-1 resonance around ~105 ppm had a relaxation time of 73 s when fit with a single exponential. No

evidence of any significant difference in the relaxation times of the I_α and I_β polymorphs was observed. These results are similar to those reported for cotton linters [30], though those samples were subjected to both acid hydrolysis and solvent exchange to improve spectral resolution.

In the ^{13}C CP/MAS sequence with a Gold-Shen preparation, the use of both short mixing and contact times results in the observation of ^{13}C spectral resonances associated with crystalline and amorphous domains as well as with surfaces, indicating that a significant amount of the cellulose is in contact with the water. This result is similar to that found with the J-WISE NMR experiment for the water-cellulose interaction in hydrated onion cell wall [31]. In particular, this result is also in agreement with the suggestion that C-4 carbon resonances in the less ordered environments are not localized in some limited area, such as on surfaces, but are distributed throughout the fibrils, as was found for a bacterial cellulose sample [32]. The results reported here show water to be more widely adsorbed than the simple two-component analysis of infrared spectra by Jefferies [33] indicating the amorphous fractions to be linearly related to moisture uptake.

The raw stock of Pima cotton also contains wax that is molecularly mobile, though ^{1}H-^{13}C cross-polarization still occurs (as indicated by the small resonance at 33 ppm shown in Figure 1). This raises the possibility that the ^{1}H spin diffusion observed in the Goldman-Shen sequence that leads to the actual cross-polarization of the carbon nuclei of the cellulose may come from the wax. However, virtually identical results are obtained on the ethanol-washed Pima sample in which the wax was removed.

Conclusions

^{1}H and ^{13}C solid-state NMR techniques were used to investigate the interaction of moisture with cellulose and its influence on the nuclear spin dynamics in *G. barbadense* (Pima) cotton. The ^{1}H spin-lattice relaxation time, T_1, was adequately fit by a single exponential function and was found to vary with moisture content. For samples packed and sealed at the same temperature and relative humidity, the proton T_1 was shown to increase upon magic-angle spinning from that measured for the static sample.

The ^{1}H wideline spectrum showed two components, as indicated by the presence of a narrow peak on top of a broad peak. The Goldman-Shen experiment showed substantial recovery of the broad component at very short mixing times of 3 to 10 μs. This arises from the range of correlation times of moisture on the cellulose. This variation of correlation times for water protons allows very efficient transfer of magnetization from the narrow moisture peak to the broad cellulose peak. The diffusive behavior of the ^{1}H spin magnetization from the narrow, mobile moisture peak to the broad cellulose peak, as indicated by the linear dependence on the square root of the mixing times, is observed at longer mixing times of up to 100 ms. These mixing times are all short compared to the ^{1}H spin-lattice relaxation time of 1.1 s. This diffusive behavior indicates that the moisture is present as multiple layers, in the range of 14-17 monolayers.

Combining the Goldman-Shen experiment using very short mixing times of 3 to 10 μs with ^{13}C CP/MAS with a short contact time yields a ^{13}C CP/MAS spectrum of cellulose that is physically near the interface with the moisture. The spectrum from this portion of the sample indicates predominantly the I_β polymorph of cellulose. A longer

mixing time of 500 μs yields a ^{13}C CP/MAS spectrum in which the I_α polymorph is increased relative to that of the I_β polymorph. The use of a longer mixing time yields a ^{13}C CP/MAS spectrum similar to that of the normal ^{13}C CP/MAS spectrum of the whole sample. Cross-polarization from the moisture does not preferentially enhance ^{13}C resonances assigned to the crystalline and amorphous domains or to the surfaces.

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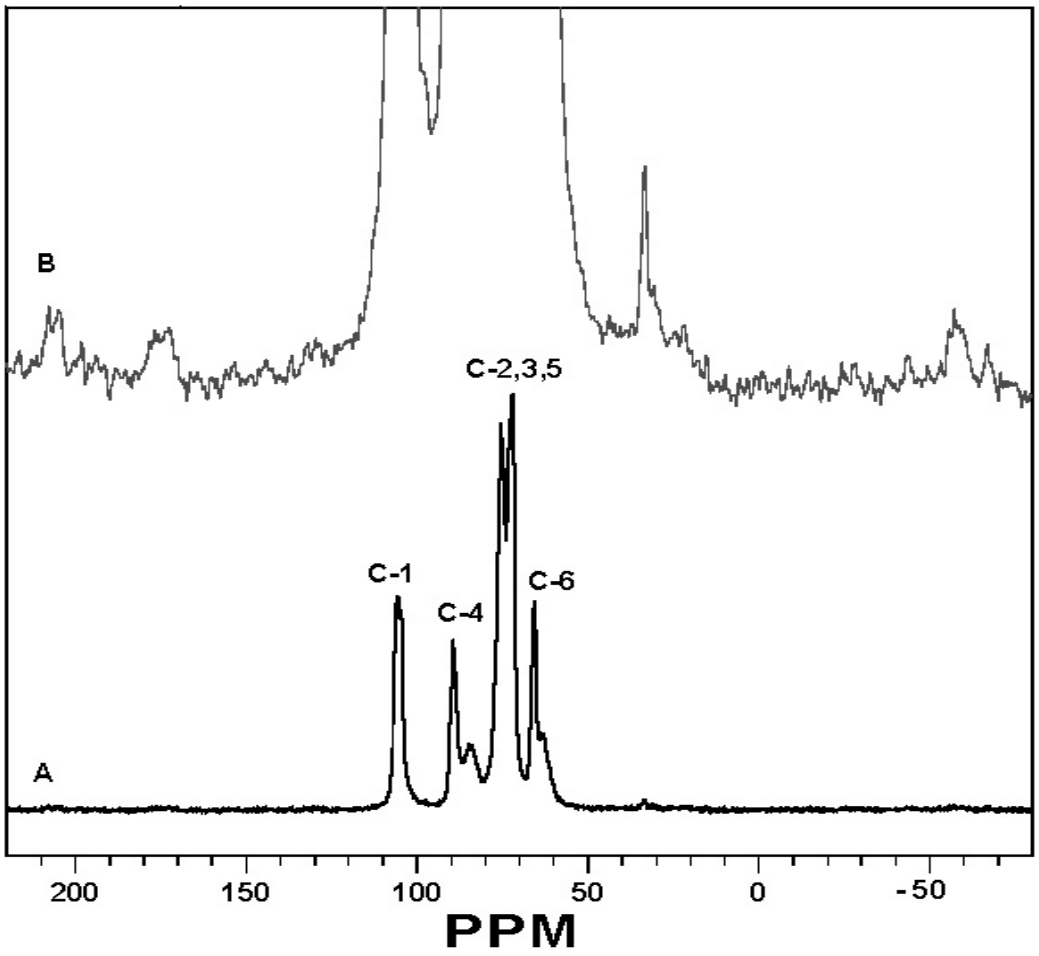

Figure 1: ^{13}C CP/MAS spectrum of Pima cotton (A) with a vertical expansion (B) to show minor components.

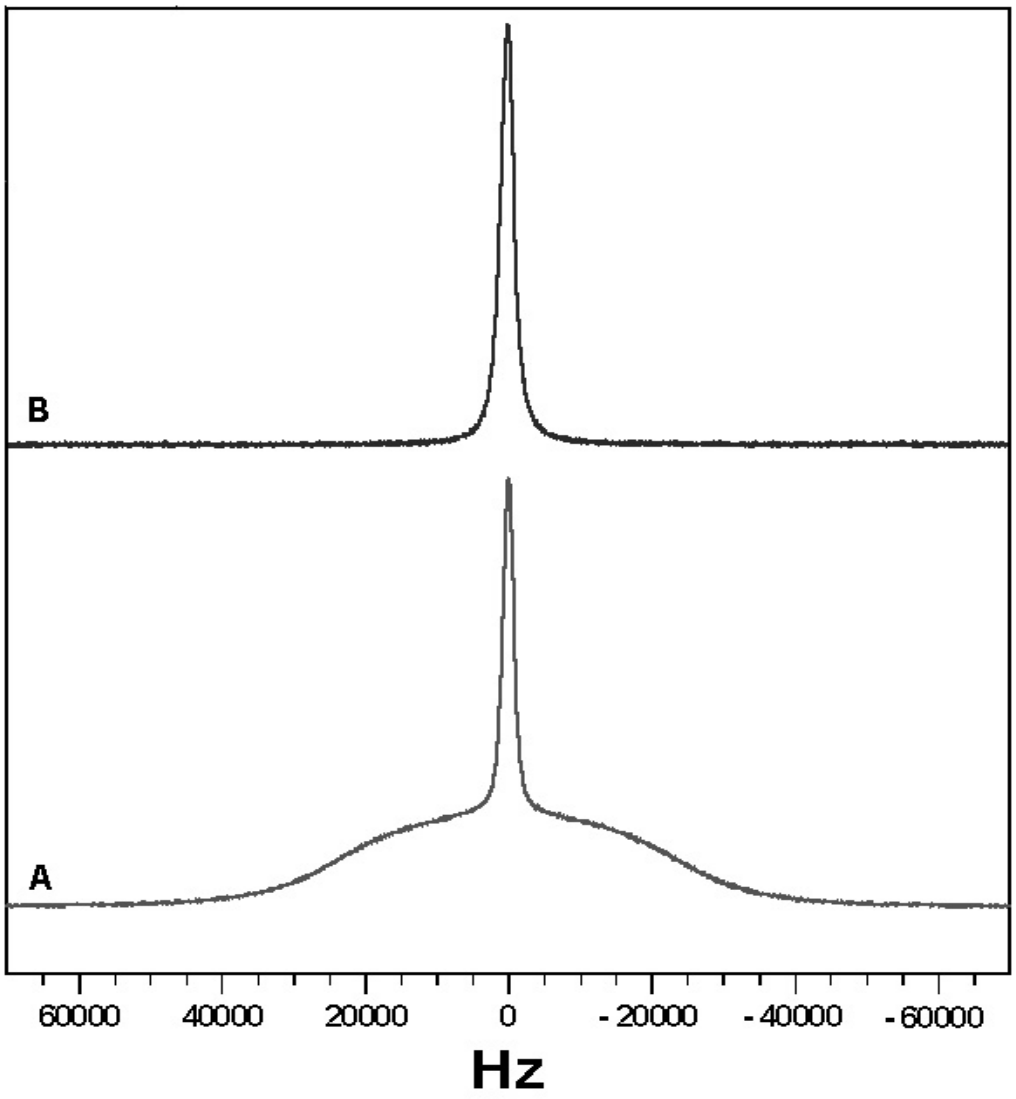

Figure 2: ^{1}H wideline NMR spectrum (A) and the ^{1}H wideline spectrum using a delayed acquisition time of 200 μs after the radiofrequency pulse (B) from the static Pima cotton sample. With delayed acquisition, only the narrow component is observed.

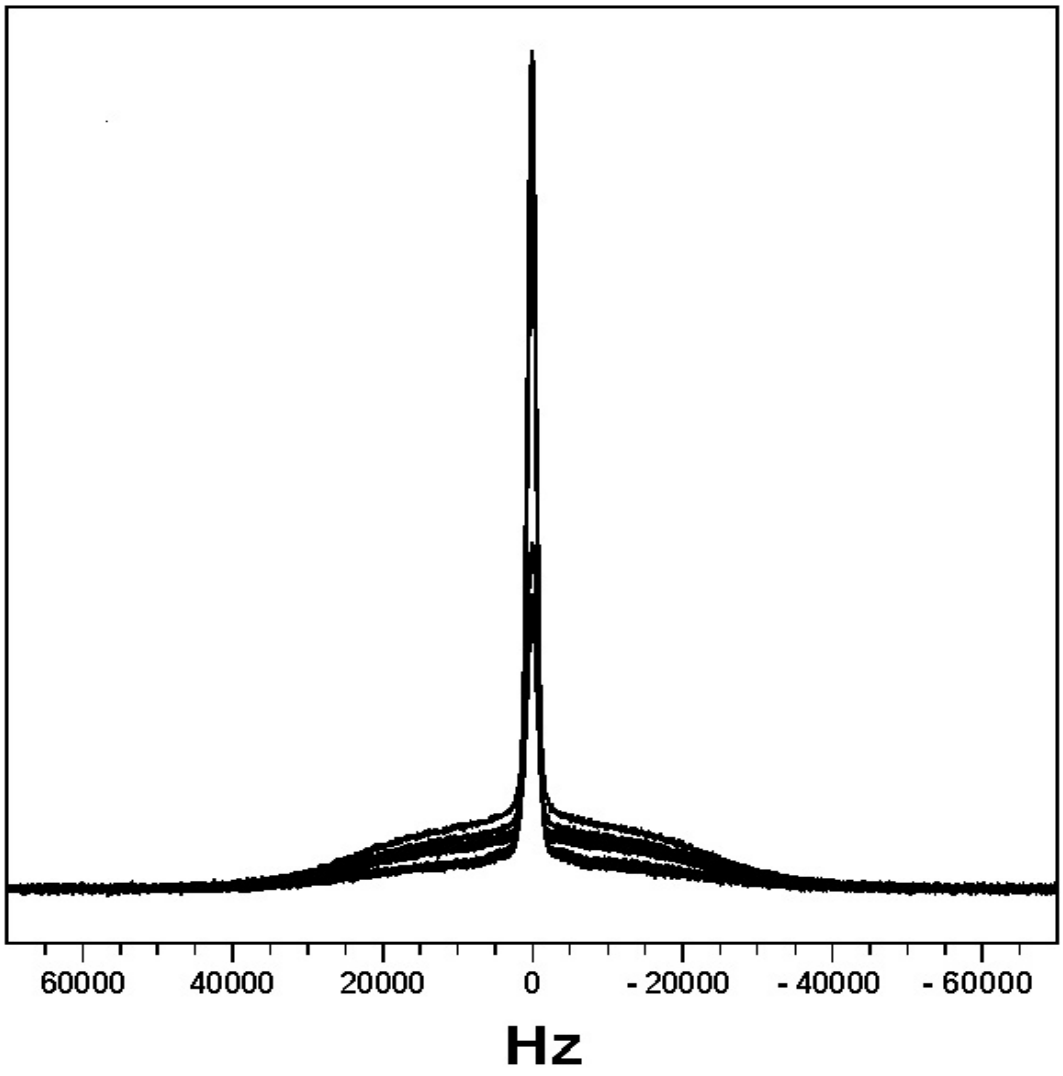

Figure 3: The ^{1}H wideline spectra from the Pima cotton sample acquired with a Goldman-Shen pulse sequence. A delay of 200 μs after the first pulse allowed the broad component to completely disappear before the second pulse returned the magnetization to the Z axis. Mixing times of 0.003, 0.010, 0.5, 1, 10, 25, 50, and 100 ms allowed ^{1}H spin diffusion to occur prior to the acquisition of the spectrum. The narrow peak in the center loses intensity while the broad component gains intensity as a function of mixing time.

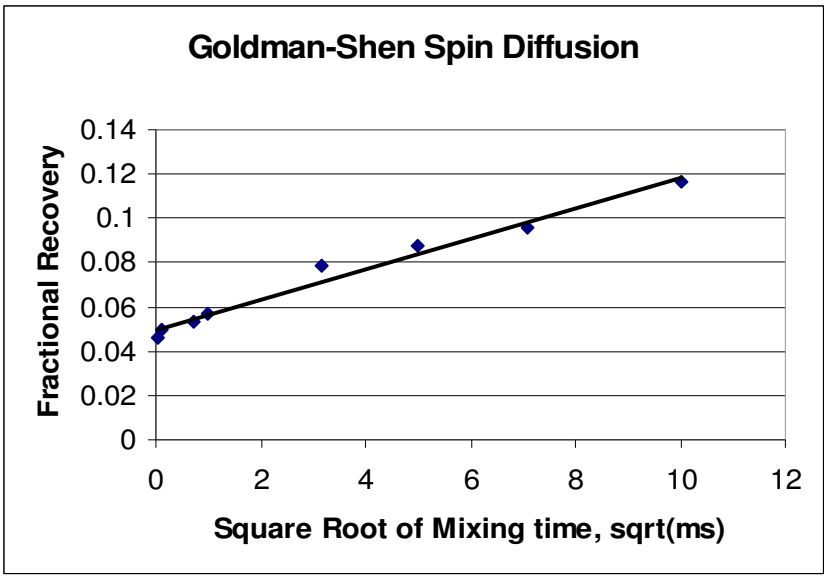

Figure 4: The fractional recovery of the broad component versus the square root of the mixing time for the ^{1}H Goldman-Shen spectra shown in Figure 3.

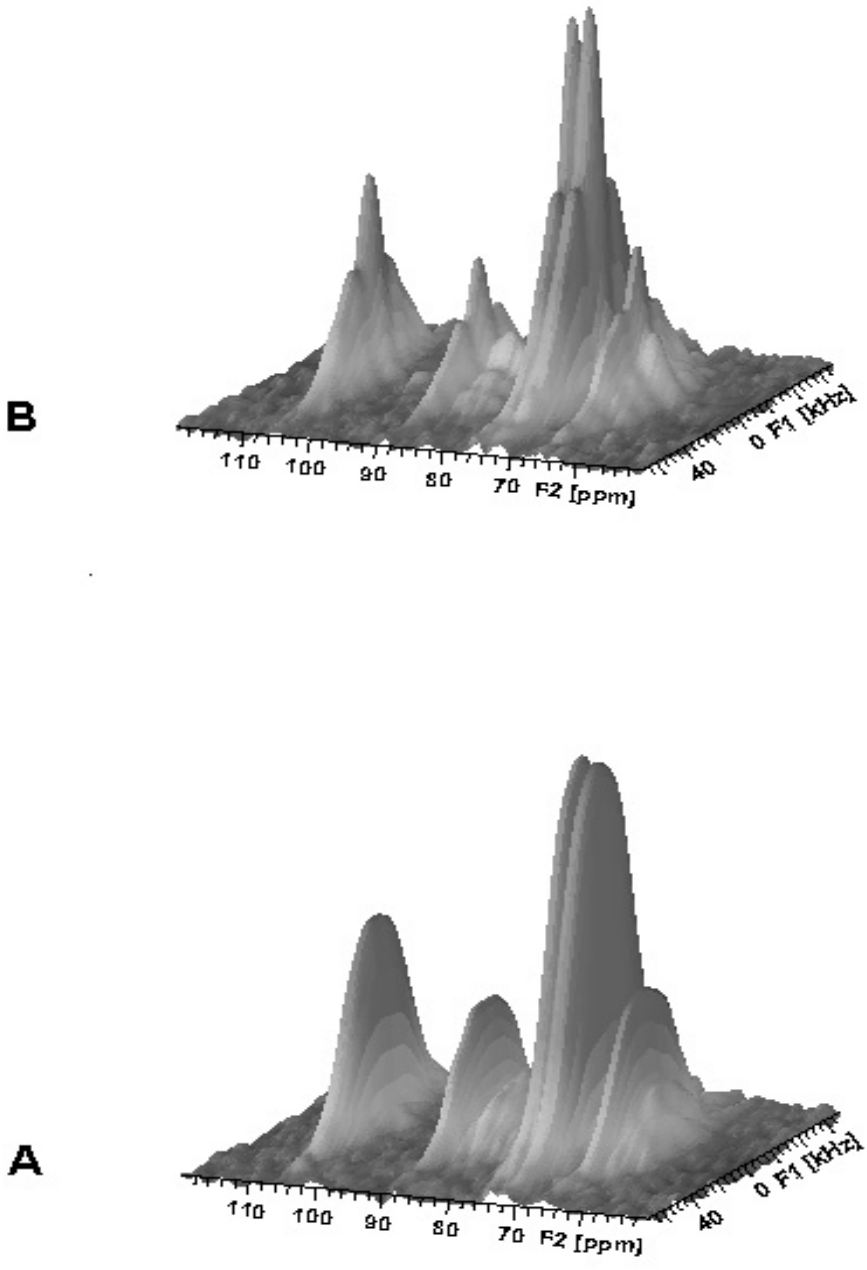

Figure 5: ^{13}C CP/MAS WISE spectra of Pima cotton. Spectrum A is the basic WISE experiment. Spectrum B is an extension of the WISE experiment that includes a 500 µs mixing time before data acquisition.

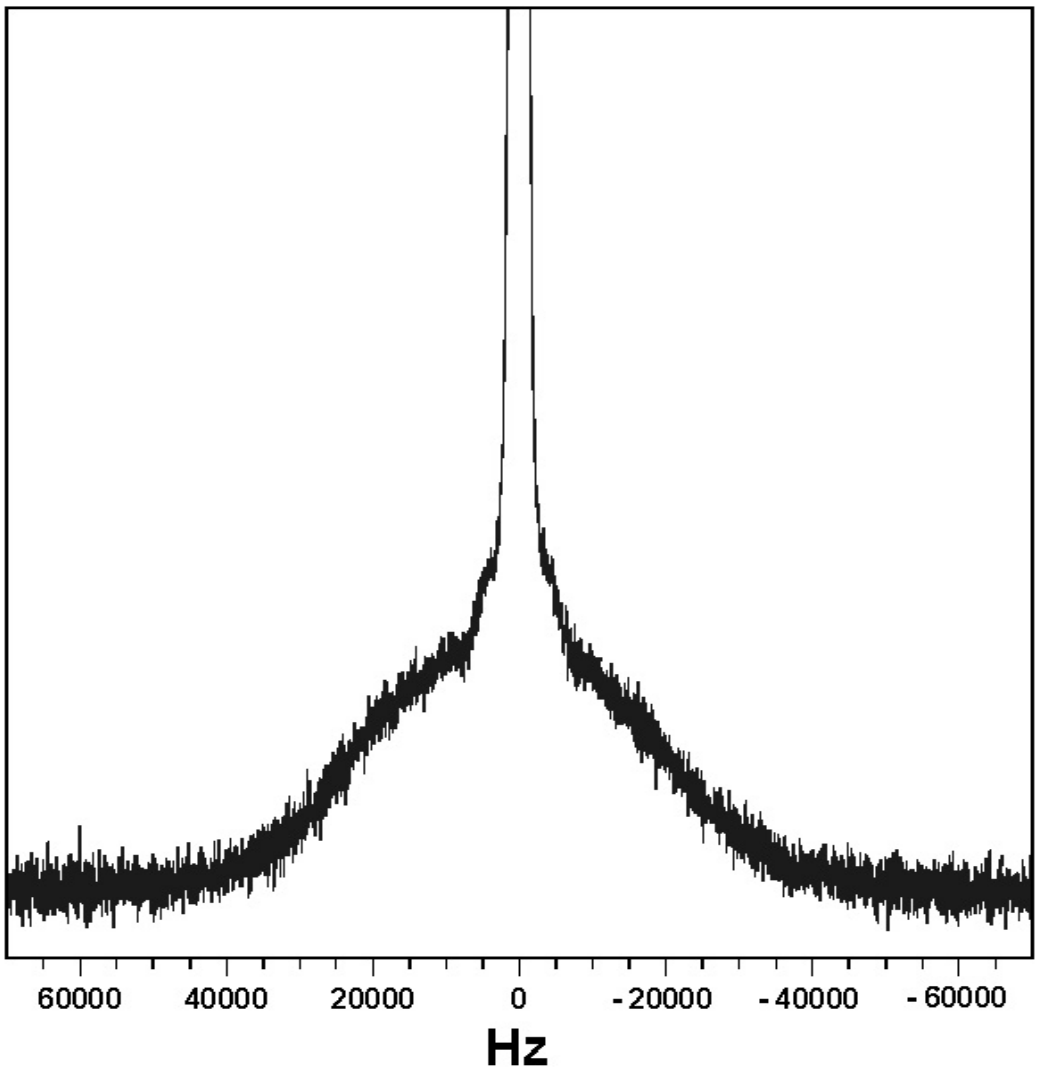

Figure 6: The ^{1}H wideline spectrum acquired with a Goldman-Shen sequence using a 200 μs delay and a 3 μs mixing time. In addition to a small amount of the broad component, there is second component that is much narrower (though broader than the narrow moisture component) which appears on top of the broad component.

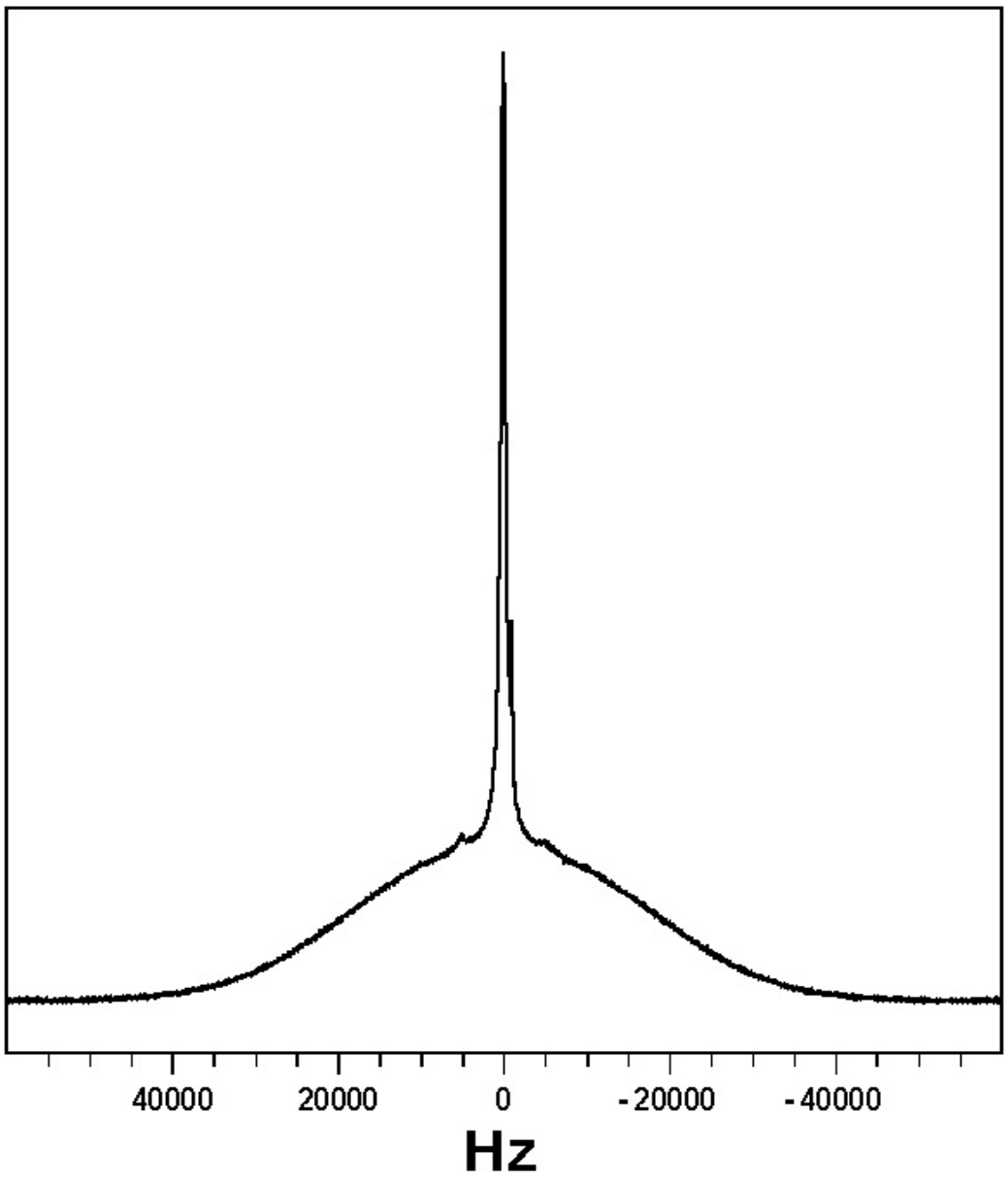

Figure 7: ^{1}H MAS NMR spectrum of the Pima cotton sample. Spectral features include the narrow (moisture) and broad (cellulose) components. The smaller sharp peak upfield of the moisture is from the wax. In addition, two spinning sidebands appear at ± 5 kHz of the moisture peak.

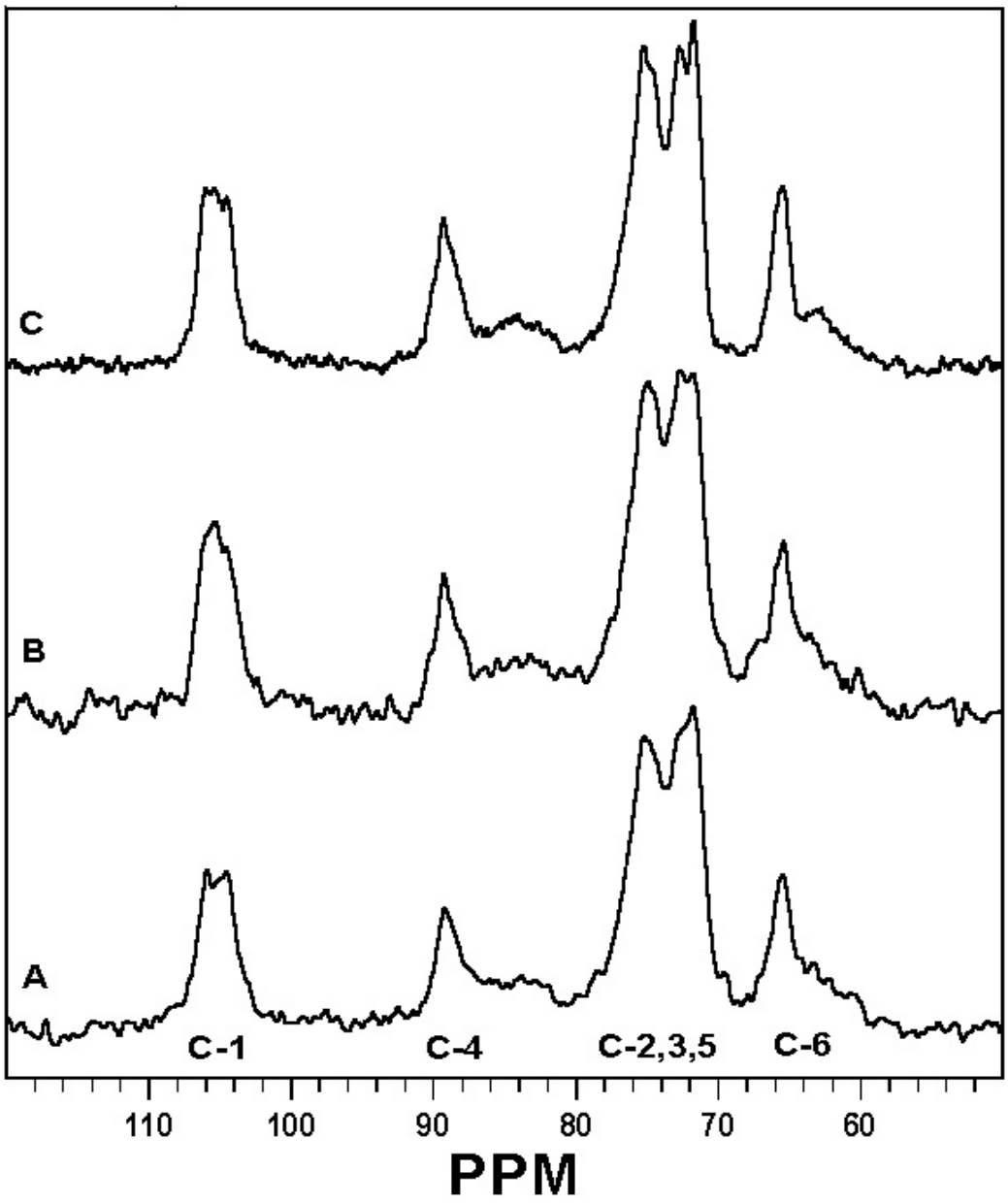

Figure 8: ^{13}C CP/MAS spectra from a Pima sample. Spectrum A was acquired by using a Goldman-Shen sequence (200 µs delay for dephasing and 5 µs mixing time) prior to the cross-polarization. Spectrum B is from the same experiment but with a 500 µs mixing time. Spectrum C is from the normal ^{13}C CP/MAS experiment.

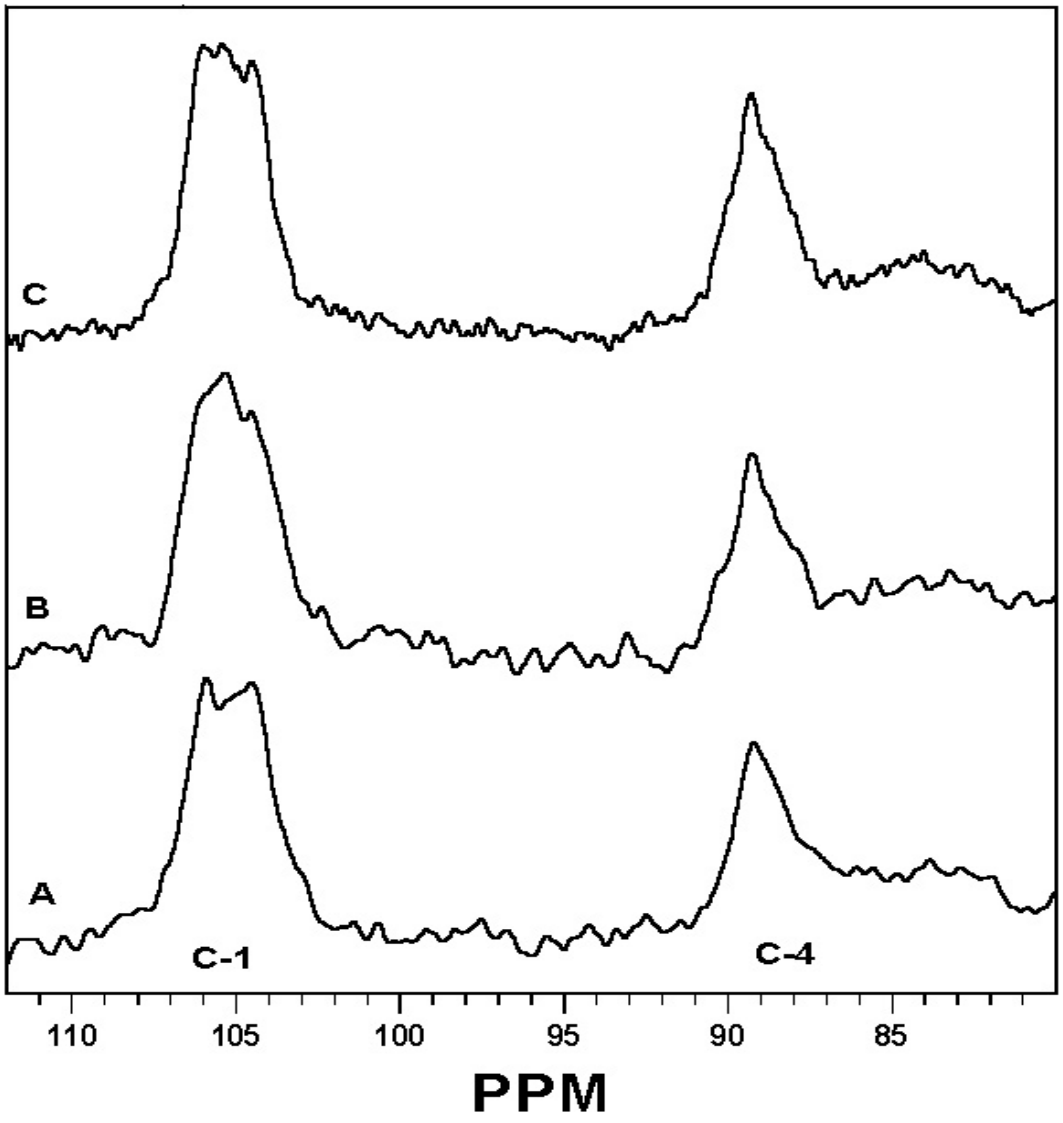

Figure 9: An expansion of the C-1 (105 ppm) and C-4 (89 ppm) resonances from the three data sets in Figure 8.