82-2534 (R)

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U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
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Final Report Covering the Period
October 1, 1980 through September 30, 1981

Issued June 1982



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NBSIR 82-2534

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# I. Introduction

## A. NMR Background - The Experiment

In late 1972 and early 1973 papers appeared [1,2] describing the combined use of high power proton decoupling (HPPD) and cross-polarization (CP) techniques in order to observe $^{13}C$ spectra in organic solids. Resulting spectra were much narrower than would otherwise be observed since HPPD eliminated the strong $^{1}H$-$^{13}C$ dipolar interactions. The CP techniques, which were used to generate $^{13}C$ magnetization indirectly via the protons, resulted in a $^{13}C$ signal enhancement circumventing the problem of large $^{13}C$ relaxation time dispersions. That is to say CP techniques implied a substantial gain in sensitivity. But in return for the advantage, it was no longer necessarily true that relative $^{13}C$ intensities would be proportional to the corresponding populations of different kinds of carbons. Although this assumption often held in CP spectra, there were exceptions. Morphologically inhomogeneous systems (particularly those possessing molecules with motions in the mid-kilohertz regime [3], or those containing rubbery domains with highly mobile molecules) constituted some of these exceptions.

The $^{13}C$ spectra obtained by HPPD and CP still have strongly overlapping resonances associated with the anisotropic chemical shift (CS) interaction, which in turn is the result of the orientation dependence of the electronic shielding of the $^{13}C$ nucleus. To eliminate this anisotropic CS interaction, it was recognized [4-7] that so-called magic angle sample spinning (MAS), if fast enough, could collapse each of these broad lines to a single line located at the isotropic chemical shift position. What is meant by "fast enough" depends on the strength of the magnetic field, $B_o$, and on the size of the anistropic CS.

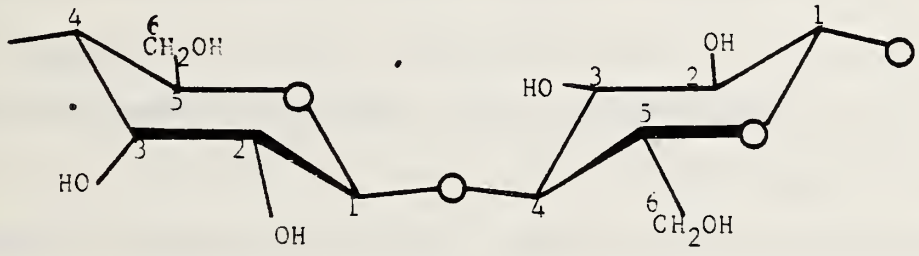
For example, in cellulose, a 1 KHz spinning rate would be more than sufficient at a magnetic field strength of 1.4T(T=Tesla), whereas 3 KHz would be an ample frequency at 4.7T. The term "magic angle" refers to the angle between the spinning axis and $B_o$ and is defined to be arccos $(\sqrt{3})^{-1}$=54.7°. Experimentally it is important to maintain the accuracy of this magic angle setting to within 0.1°.

Spectra obtained with the combined use of CP, HPPD, and MAS (CP-MAS spectra) bear a strong relationship to proton-decoupled liquid state $^{13}C$ spectra. In both kinds of spectra $^{13}C$ resonances appear at their isotropic chemical shift positions. Nevertheless a substantial difference between solid-state and liquid state spectra must be recognized. In liquids every $^{13}C$ nucleus of a given kind is likely to have the same average history of rotational motion and intermolecular interactions over the time scales(~10ms-1s) of inverse linewidths. In contrast, in solids, on time scales (3-100ms) of inverse linewidths, molecules are often confined to particular orientations, conformations, or hydrogen bonding geometries. They may also be limited by anisotropic molecular motion, and/or reside in only one region of a morphologically inhomogeneous system. These different environments produce a dispersion of isotropic CS's for a particular kind of carbon [3]. Thus, in solids, $^{13}C$ linewidths are generally broader than those observed in liquid-state $^{13}C$ NMR spectra. A systematic analysis of $^{13}C$ linewidth in CP-MAS spectra has been published [3] and provides a basis for subsequent interpretation of cellulose spectra.

B. NMR Background - General Cellulose $^{13}C$ NMR Spectra and Interpretation

A few studies applying CP-MAS $^{13}C$ NMR techniques to cellulose have appeared in the literature [8-10]. In Figure 1, CP-MAS spectra of four different

preparations of cellulose are shown, illustrating the sensitivity of the isotropic CS positions to differences in chain environment. Samples corresponding to Figures 1A and 1C are highly crystalline forms of cellulose I and II respectively. Spectrum 1B belongs to cotton which is a rather highly crystalline form of Cellulose I, except that the lateral dimensions of the cellulose crystallites are generally thought to be 3-5 times smaller in Sample B than in Sample A [10-12]. Finally, Sample D is a ball-milled sample of a Cellulose I material having a CP-MAS spectrum very similar to B. Assignments of resonance regions to particular $^{13}C$ sites in the glucose unit have been made [8,9]. The usual numbering scheme is used to designate the six different carbons, i.e.




(I)

The correspondences between carbons and resonance positions (relative to liquid tetramethylsilane) in these spectra are approximately: C6958-68ppm), C2,C3,C5 (68-79ppm), C4(77-91 ppm), and C1(96-109ppm). A small chip of linear polyethylene has been added to each of these samples to serve as a secondary chemical shift reference. Its crystalline resonance position is 33.63ppm [13].

From the spectra of Figure 1 it appears that spectral resolution is degraded significantly for the amorphous cellulose sample. This result is expected [3]. Secondly, a given carbon, say C1 of Spectrum 1C, can give rise to a multiplicity of sharp lines, thereby indicating magnetic inequivalence within the unit cell. Thirdly, in the cotton spectrum, (1B), large broad wings are associated with the C4 and C6 resonances. These wings constitute approximately 40-50% of the total intensities of these resonances, which is much higher than any x-ray estimates of amorphous cellulose in this material [10].

Based on $^{13}C$ transverse relaxation time ($T_2^C$) measurements performed in this laboratory, some of which have been published [9], the dominant broadening in the spectra of Figure 1 is dispersion of isotropic CS's. Relaxation, at most, accounts for 0.5 ppm of broadening, except in the region of the C6 wing (~63 ppm). For this wing, relaxation broadening may provide up to 1 ppm of broadening.

Broadening of resonance lines, possibly accompanied by CS displacements such as are seen in the C4 and C6 resonances of cotton, imply a dispersion of cellulose chain environments. However, we do not feel justified in interpreting the observed shifts in terms of specific models of, say, hydrogen bonding changes, distortions of bond angles, or changes in crystal packing or chain conformation. Rather, the strongest argument in interpreting the C4 and C6 wings in cotton has been made [10] based on the CP-MAS spectra of a series of native cellulose I samples having increasingly greater lateral crystalline perfection as judged by X-ray and electron microscopy studies. The series chosen was cotton, the pellicle of the bacterium, Acetobacter xylinum, and

the cell wall of the alga, Valonia ventricosa. Spectra A and B of Figure 1 correspond to the extremae in this series. In Spectrum 1A, the wings of C4 and C6, which are so prominent in Spectrum 1B, have almost vanished. Thus, it was concluded [10] that the wings of C4 and C6, appearing at approximately 85 and 63 ppm respectively, were associated with cellulose chains on the lateral crystal surfaces. In cotton, where so-called elementary fibrils of approximately 3.5 nm lateral dimension are often observed, nearly half of the cellulose chains are surface chains, consistent with the observed wing intensities for C4 and C6. Thus NMR appears to be an excellent tool for probing the integrity of the elementary fibril and/or the lateral surface area of the cellulose crystallites. This is the important observation which forms the basis for the NMR project reported herein.

Three final points can be made based on the spectra of Figure 1. First, in Spectrum 1A, resonances of C1 and C4 show emerging multiplicity (The multiplicity is more convincing for $^{13}C$ spectra taken at 50 MHz), which implies that the unit cell of cellulose I contains at least 4 glucose moieties [10]. Secondly, the shape of the resonances for C1 and C4 in the amorphous sample (Spectrum 1D) suggests that in a sample of cotton (Spectrum 1B), there is, at most, 20% of the cellulose which is amorphous in the sense of Spectrum 1D. Finally, one can easily distinguish between cellulose I and cellulose II, particularly in the C1 and C6 regions.

C. Cellulose background - Definition of the cellulose problem to be investigated by $^{13}C$ NMR.

Wetting of cellulosic materials followed by a process called wet beating, produces fibers which achieve a plasticity suitable for making paper. Without

wet beating, the fibers are too stiff and consequently do not bond to one another sufficiently to make a strong paper.

In a previous report [14], various cellulosic preparations were wetted and then beaten. Two materials in particular were investigated, Norway Spruce Kraft pulp (NSKP) and purified cotton (PC). The results of this report, in which fiber saturation points and bound (non-freezing) water fractions were measured, demonstrated a significant difference between the NSKP and the cotton. In NSKP, wet beating did not increase the fraction of bound water whereas it increased by 55% the amount of free water. (Free water plus bound water equals the amount of water measured by the fiber saturation point method.) In contrast, in cotton wet beating increased the amount of bound water by 46%; at the same time, the free water doubled. Although the absolute amount of bound and free water in NSKP was always larger than in cotton, it was an intriguing question whether the increase in bound water observed in cotton with wet beating could be related to an increase in the surface area of the elementary fibrils. The bound water, in order to be non-freezing, should interact strongly with the cellulose chains.

Therefore the objective of the $^{13}C$ NMR studies in FY 81 was to look for spectral changes between wet and wet beaten cellulose preparations as a monitor of changes in crystal surface areas accessible to water.

Three cellulose samples were chosen for this study, purified cotton, NSKP, and microcrystalline cellulose, the latter being a highly crystalline form of cellulose. The former two materials are commonly used in paper production

## II. Experimental

### A. NMR Parameters

CP-MAS spectra were obtained on a homebuilt spectrometer. The magnetic field strength is 1.4T; the corresponding $^{13}C$ radiofrequency (rf) is 15.08 MHz. Cross-polarization was performed via the spin-lock method [2]. Amplitudes of the rf field for both protons and carbons [15] corresponded to nuclear precession frequencies of 60 KHz. Contact times for cross-polarization were typically 2 ms. Proton decoupling amplitudes during $^{13}C$ signal observation were maintained at 60 KHz. The $^{13}C$ free induction decays were Fourier transformed to obtain the spectra. Signal transients were accumulated in a computer using the sequence [16] for eliminating artifacts. Under these conditions, no signals from the rotor material, polychlorotrifluoroethylene, are present.

For the wet and wet beaten cellulose samples, a specially designed rotor was used. This rotor assembly, which provided a 6.8 mm diameter sample chamber, included an O-ring seal for containing the water. The seal produced no interfering $^{13}C$ resonances. In some cases, the original amount of water was partially depleted during the several hours of spinning required for taking the spectra. In every case, the samples were unloaded, weighed, dried in a vacuum oven overnight at 100°C, and re-weighed in order to determine the final moisture contents for the wet samples. It might be expected that MAS would act as a centrifuge so that during spinning, the actual water content of the observed wet cellulosic materials would be less than that measured afterward. This possibility cannot be dismissed in principle; however, only in the case of wet beaten microcrystalline cellulose was there a noticeable radial material gradient when the sample was opened after spinning. It was in a large part concern about this centrifugation which directed us to perform all of these experiments at 1.4T even though a spectrometer operating

at 4.7 T was available. At 1.4T, rotation frequencies for the wet sample were in the range of 1500-1800 Hz. A small chip of linear polyethylene (LPE) was added to most samples as a secondary chemical shift reference. The sharp feature in its resonance arises from the crystalline regions which have a chemical shift relative to tetramethylsilane (TMS) of 33.63 ppm [13]. The linewidth of this reference ranged from 8-13 Hz (.53-.87 ppm). Variation in LPE linewidth is probably due to magnetic field drift and/or a slight misadjustment of the magic angle (less than $0.35^{o}$). Precise adjustment of the magic angle presented some problem because the wet samples spun with greater difficulty compared to the dry samples.

B. Materials and Their Preparation

Purified cotton (PC) was received from Southern Regional Research Center. The cotton was grown in the Mississippi Delta region (Delta Pine, smooth leaf variety). The cotton was purified by a modification of the Conrad method [17] with the addition of an 8 hour boil in 1% NaOH under $N_2$ atmosphere, and was washed successively with distilled water, 1% acetic acid. 1% $NH_4$ OH and finally distilled water. It was then dried in a vacuum oven at 60C. The white, finely-powered microcrystalline cellulose (MC) is a commercial product, PH-101, of the FMC Corporation [18]. It is considered to be a highly crystalline form of cellulose I. The Norway Spruce kraft pulp (NSKP) was obtained from a single log of Norway Spruce. The spruce was pulped to a yield of 47.5% and a Kappa No. of 41.8. All of the above samples of cellulose were stored in a freezer prior to use. The storage containers were polyethylene bags inside of sealed metal cans.

Other materials are mentioned in this study although they have not been studied in connection with wet beating. Spectra of two amorphous, ball-milled cellulose specimens are shown. One specimen [19] (cf. Figure 2D) was obtained by ball-milling the commercial microcrystalline cellulose, Sigmacel (American Viscose) [18], for 72 hours under argon. A second sample [20] of ball-milled cellulose (cf. Figure 1D) was prepared from Whatman CF1 powder and was preserved in a dessicated environment until after the spectrum was run. The final sample (cf. Figure 1C) is a highly crystalline, special preparation of cellulose II [20]. It is a low DP material regenerated from Whatman CF1 powder. This material should not be regarded as a typical commercial regenerated cellulose II material, since the latter materials have much less definition in their NMR spectrum.

Beating was done in a laboratory mill at a 10% consistency with distilled water. The relative velocity of roll to bedplate was 6 m/s at a force of 3.4 Kg. The beating cycle was 10000 revolutions for PC and NSKP and 5000 revolutions for MC.

## III. Results

### A. General Spectral Observations About the Dry Celluloses

Figure 2 shows CP-MAS spectra of the original materials, equilibrated at room temperature and a relative humidity of approximately 30%. The materials are identified on the Figure. The lower spectrum of the ball-milled cellulose is shown for comparison. Note the substantial intensity at 80 and 100 ppm in the amorphous cellulose spectrum. If one argues that the three upper spectra are first of all a combination of crystalline and amorphous cellulose lineshapes, then, if the lower spectrum is taken as the definition of the amorphous lineshape, upper limits on the amorphous content of the three

celluloses may be obtained by spectral subtraction. Such subtraction yields upper limits of 0.20, 0.15, and 0.30 respectively for the amorphous fraction of cellulose in PC, MC and NSKP. In all cases, further subtraction causes the region near 100 ppm to go negative. Moreover, after subtraction substantial wing intensities remain at 85 and 63 ppm which are associated with the C4 and C6 carbons respectively. The persistence of these wings even after subtraction of the amorphous lineshape fraction is further support for the interpretation that these wings originate primarily from glucose moieties on the surfaces of the cellulose crystallites.

In Figures 3 and 4 comparisons are made between the spectra of PC and MC (Figure 3) and PC and NSKP (Figure 4). The top three spectra of Figure 2 are reproduced in these Figures along with difference spectra which illustrate variations in the starting materials. After normalizing spectra to the same total intensities, differences are taken (those marked 'A-B') as well as linear combinations of the top two spectra. The linear combinations approximate the "pure component spectra" assuming that each spectrum is a different linear combination of the same two lineshapes. The 'A-rich' (Figures 3D,4C) linear combination spectra generally resemble one another and may approximate the spectrum of large cellulose crystals. If that is true, these spectra should also resemble the Valonia spectrum (Figure 1A). That agreement is pretty good with the notable exception that the splitting of the C1 resonance at 105ppm in the 'A-rich' spectra of Figures 3 and 4 is about twice that observed in Valonia. The 'B-rich' linear combination spectra (Figures 3E and 4D) crudely resemble the amorphous spectra (Figure 1D and 2D).

A notable region of difference is the C2,3,5 region (68-79 ppm) which is not split in the amorphous spectrum but has well-defined structure in the linear combination spectra. The linear combination spectra, therefore, suggest either that the cellulose lineshapes are made up of more than two component lineshapes or that mixing of the components is on such an intimate level that the component lineshapes do not apply. A three component system may indeed be indicated, i.e. amorphous, interior crystalline, and surface crystalline chains. The validity of this suggestion is discussed in the Discussion section.

The population of glucose moieties found in the interior of cellulose crystallities can be ranked from Figures 3C and 4E. Since the sharper features of the C4 and C6 resonances, at 89 and 64 ppm respectively, are believed [10] to measure the number of interior crystalline glucose moieties, it can be concluded that PC has slightly more interior crystalline chains than MC which, in turn has more than NSKP. Moreover, if the numbers for the maximum amorphous fraction, given earlier in this section, are assumed correct, it can also be concluded that the ratio of surface chains to interior chains in the cellulose crystallities increases in the same order, i.e. PC, MC, and NSKP. In other words, this would be the order of descending lateral crystallite dimensions.

A final remark is that the NSKP exhibits broad weak resonaces (not shown) which are just visible, particularly in the aromatic region (110-155 ppm). These signals are typical of lignins [21] thereby indicating that such residues remain after the pulping process. Crude intensity estimates suggest a lignin content of 10% in NSKP. However, for purposes of spectral subraction

in Figure 4, the NSKP spectrum was normalized based on the cellulose intensity fraction. Morphologically, the presence of the lignin probably increases the complexity of the cellulose spectra, particularly if lignin is a molecular dispersion as opposed to an aggregate. The presence of dispersed lignin could easily account for an increased surface to volume ratio in NSKP crystallites relative to PC and MC.

B. Spectral Effects Upon Wetting and Wet Beating Celluloses

Figures 5,6, and 7 show CP-MAS spectra of the PC, MC, and NSKP respectively. Each figure consists of five spectra which correspond to the wet beaten sample (A), the sample wet with distilled water (B), the dry sample (C), and two difference spectra (D=A-B and E=B-C). In Table I, data corresponding to these spectra are given. Included in these data are the final weight ratios of water to cellulose, following the CP-MAS runs. Similar weight ratios defining the previously measured [14] fiber saturation points and bound water fractions are also given. Included are the LPE reference linewidths and the percentages of the observed intensity relative to the total expected $^{13}C$ intensity (based on cellulose weight).

The weight ratios of water to cellulose are somewhat erratic due to the fact that the rotors were not uniformly leak-proof. The wet beaten MC sample was the least hydrated after the CP-MAS run. That was also the sample where the cellulose had centrifuged to the outer walls of the rotor cavity. The fiber saturation point, which measures[14] the sum of the "bound" (non-freezing) and 'free' (freezing) water absorbed by celluloses, corresponds to the ideal minimum weight ratio of $H_2O$ to cellulose for the CP-MAS experiments. This weight ratio was not always exceeded. However, no final weight ratio was

lower than the bound water fraction. Although the level of hydration is rather erratic no attempt was made to redo these experiments since the results, to be discussed, show no spectral evidence of free water content.

Spectra 5D, 6D, and 7D indicate that there are no significant changes in crystal surface area in going from wet to wet beaten cellulose preparations. Indeed, within the digital resolution of 0.16 ppm, there is virtually no change. The largest spectral changes are observed when one goes from dry to wet cellulose (cf. Spectra 5E, 6E, and 7E). The principal effects here consist of line sharpening. In particular, the tail of the C2,3,5 resonance line near 76-78 ppm is pulled into the main body of this line. It is difficult to say whether the fraction of surface crystalline chains, i.e. whether the total intensities of the wings of C4 and C6, have diminished slightly upon wetting since the original lineshapes cannot be deconvoluted exactly. The main conclusion, however, is that wet beating produces no observable spectral changes with respect to the wet cellulose preparations.

## IV. Discussion of the NMR Results

### A. Intensity Anomalies in CP-MAS Spectra

In terms of the stated objective of this study, the most significant conclusion of this work is that wet beating does not change crystallite structure, judging by the near superposition of the wet and wet beaten spectra of each of the celluloses studied. There is a problem, however, which needs to be addressed before this conclusion can be stated unambiguously. The problem is that the CP-MAS spectra may possess distorted relative intensities.

Table I gives the ratios of the observed to expected intensities in the CP-MAS experiments. A uniform cross polarization time of 2 ms was used in

all of these spectra. The value of unity was assigned to the dry cotton spectrum in order to establish a signal strength per unit weight of cellulose. This signal strength compared very favorably with that of LPE taking into account the different carbon densities in the two materials and the weaker intensity of the non-crystalline signal in LPE. Therefore, within experimental error in the dry cotton, all of the carbons are observed with minor, if any, intensity distortion.

The intensity ratios of Table I indicate that many samples yielded intensities less than unity which raises the possibility that relative intensities are distorted or signals are even missing. The question of intensities in CP-MAS spectra is a broad question and only a qualitative presentation will be given, starting with a brief description of the CP process itself.

The CP process can be discussed in terms of a thermal analogue [22] where the protons and the $^{13}C$ nuclei each represent respectively, a large and a small thermal mass, each initially at ambient temperature. Spin-locking of the protons is then equivalent to making the protons suddenly very cold. The CP process follows this sudden cooling by placing the $^{13}C$ nuclei in thermal contact with the cold protons. If we add to this picture that both thermal masses are imbedded in an infinitely large thermal mass (the lattice) which is maintained at ambient temperature, then we are ready to discuss the problem of intensities. The objective in this analogue is to produce cold $^{13}C$ nuclei in thermal equilibrium with the protons ($^{13}C$ signal strength is proportional to the inverse temperature).

The analogue suggests several things. First, the cold protons cannot be kept cold indefinitely since they are imbedded in the warm, 'infinite' lattice.

Thus, there is a time constant called $T_{1\rho}^{H}$ which governs the rate by which the lattice heats up the cold protons. This time constant need not be uniform, especially in a morphologically inhomogeneous solid. Secondly, there is a time constant, $T_{CH}$ which depends on the dipolar couplings among the protons and between the protons and $^{13}C$ nuclei. This time constant determines the rate of thermal transfer between the protons and the $^{13}C$ nuclei. If the objective is to produce uniformly cold $^{13}C$ nuclei, then one requires that $T_{CH} << T_{1\rho}^{H}$. Moreover, if one wishes to insure equilibrium between protons and $^{13}C$ nuclei during CP, then the time chosen for CP, $T_{CP}$, must be at least 5 $T_{CH}$. For rigid molecules and protonated $^{13}C$ nuclei, $T_{CH}$ is less than 75 μs, so $T_{CP}$ need only be 400 μs. However, as molecular motion increases, $T_{CH}$ increases with the consequence that $T_{CP}$ increases. Thus a $T_{CP}$ of 2ms was chosen in these studies to include, if possible, any partially mobile molecules. (In the extreme limit where molecules reorient isotropically and diffuse rapidly over nanometer distances, $T_{CP}$ becomes very long and the corresponding resonances do not appear.)

It is not necessarily true that relative intensities are distorted in a spectrum simply because the signal strength for a given amount of material decreases. For example, if $T_{1\rho}^{H}$ for dry cotton were 100 ms and $T_{1\rho}^{H}$ for the wet cotton were 6.4 ms then since both $T_{1\rho}^{H}$'s are still significantly longer than $5T_{CH}$ (for $T_{CH}$ less than, say, 200μs), the $^{13}C$ spectra will have proper relative intensities. Nevertheless, the total intensity of the wet cotton would only be 0.75 times that of the dry cotton (cf. Table 1).

More serious problems arise in morphologically heterogeneous systems where one region might have a shorter $T_{1\rho}^{H}$ (less than a few tens of ms) and another a longer $T_{1\rho}^{H}$. In that case, signals from the region of shorter $T_{1\rho}^{H}$ would be

preferentially suppressed.

Molecular mobility and molecular geometry usually determine $T_{1\rho}^{H}$. For the conditions of these experiments, $T_{1\rho}^{H}$ values would be minimum when the correlation time, $\tau_c$, for molecular motion peaks in the region $10^{-5}s \gtrsim \tau_c \gtrsim 10^{-6}s$. In this case, $T_{1\rho}^{H}$ can become as short as $10^{-4}$ for large amplitude motions. In principle, molecules like cellulose need not have their $T_{1\rho}^{H}$ values determined simply by cellulose chain motions. For example, in wet cellulosic systems, the surface crystalline chains as well as the amorphous chains (if the latter exist) can be in intimate contact with water. The transient interactions of cellulose and water molecules, if lifetimes in the range $10^{-4}$ - $10^{-7}$s exist, could strongly influence the $T_{1\rho}^{H}$ behavior of these chains. On the other hand, the presence of water may also result in increased molecular mobility of surface and amorphous chains, facilitated by the breaking of interchain hydrogen bonds. Therefore it is certainly possible that $T_{1\rho}^{H}$ will not be uniform throughout the cellulose system; i.e. there is little assurance at this point that relative intensites are undistorted.

There is a facet of proton spin behavior, called 'spin diffusion' [23], which tends to average out local differences in $T_{1\rho}^{H}$ behavior. This phenomenon involves the transport, i.e. the diffusion, of proton magnetization in a solid, proton-rich system. The diffusion constants are not large, however. A reasonable estimate for the diffusion constant in cellulose under proton spin locking conditions might be $2\times10^{-12}$ $cm^2/s$ [23]. Such a small diffusion constant would transport proton magnetization only about 1nm in a time of 2ms ($=T_{CP}$).

So, for a system where all inhomogeneities in structure have domain sizes larger than 1 nm, signal distortions will probably persist provided $T_{1\rho}^{H}$ is short in one of the domains. If on the other hand, the heterogeneous structures have minimum dimensions less than 1nm, $T_{1\rho}^{H}$ behavior will be quite uniform and $^{13}C$ CP signal intensities will have reasonably undistorted relative intensities.

With that introduction to signal distortions, does the data suggest anything about signal distortions in the three cellulose samples? Unfortunately the measurement of $T_{1\rho}^{H}$ was not a part of this study. For only one sample, the wet PC, $T_{1\rho}^{H}$ was crudely determined to be 31 ms based on intensities at 0.8, 2.0, and 10.0 ms for $T_{CP}$. This $T_{1\rho}^{H}$ implies that the observed intensity of the wet cotton spectrum, using 2ms = $T_{CP}$, should be no less than exp(-2/31)= 0.94. However, the observed value is 0.75. At the same time, no lineshape changes were observed in any of these spectra as a function of $T_{CP}$. Thus the stability of the lineshape for varying $T_{CP}$ suggests that relative intensities are correct; meanwhile the total intensity is much lower than the $T_{1\rho}^{H}$ would predict.

In essence, the data at this point are not sufficient to answer the question about the missing intensities. Other parameters such as the longitudinal relaxation time of the protons, $T_1^H$, could play a role although $T_1^H$ would have to exceed 2.5s in the wet materials in order to explain the observations since repetition times between 4 and 6s were used. Reported $T_1^H$ values [24] for cotton linters as a function of moisture content indicate that $T_1^H$ increases at higher moisture levels; however, these $T_1^H$ measurements were only performed up to moisture levels of 0.25 $gH_2O/g$ cellulose. Moreover, it is difficult to

imagine that $T_1^H$ would exceed the value for free water, which, especially with some dissolved oxygen present, would not be as long as 2.5s. Other possible explanations for the missing intensity could be regions which give rise to very broad lines due to large amplitude motion of the C-H bond vectors at frequencies comparable to the 60 KHz decoupling field amplitude [3]. Linewidths could become as large as 2 KHz, in an unfavorable case. Such a wide line would probably be missed completely. In addition, such motion would also cause $T_{1\rho}^H$ to be of the order of $10^{-4}$s in which case CP intensities in these regions would also be suppressed.

The experimental evidence which argues against the plausibility of such linebroadening is that in both NSKP and PC, the wet beaten samples regain most of the intensity they were missing in the wet preparations with no change in lineshape.

In summary, with respect to the question of possible distortions of relative intensities in the CP-MAS spectra, the data are not sufficient to dismiss the possibility of distortion; there is, however, strong indirect evidence that the spectra have no major distortions. Therefore the conclusion that wet beating does not increase crystallite surface area is probably valid.

One final observation which perpetuates the confusion is that a strong correlation exists between the intensity and the water content. Intensities increase monotonically for moisture contents in the range 0.48 to 0.88g $H_2O$/g cellulose. If this increase is strictly due to a dilution effect (assuming bound and free water molecules in rapid exchange [25]) then it is likely that a proton magnetization gradient would exist between surface and interior crystalline cellulose chains. Then, however, it would be difficult to justify

simultaneously both the stability of the $^{13}C$ CP-MAS lineshape as a function of cross-polarization time and the 31ms $T_{1\rho}^{H}$ observed in wet cotton. An understanding of these problems certainly awaits combined $T_1^H$, $T_{1\rho}^{H}$, and linewidth data in these systems as a function of moisture content.

B. The Sharpening of Resonances in Wet Cellulosic Materials

It has been reported [24] that cellulose proton spin-spin relaxation times $T_2^H$ in cotton linters, are 10μs at 0, 22μs at 0.06, and 32μs at 0.23g $H_2O$/g cellulose. These $T_2^H$ values, attributed solely to the cellulose protons, would therefore suggest that all of the cellulose chains were undergoing some large amplitude molecular motion on a time scale of $10^{-5}$s or less. The role of chemical exchange with the $H_2O$ protons is not known in influencing $T_2$; nevertheless, only 3 of 10 protons in the anhydroglucose unit are exchangeable protons. Therefore, it seems reasonable that some large amplitude motions are occurring.

The motion referred to above, need not be the motion of an individual molecule. Linenarrowing could also occur if, for example, an entire elementary fibril (diameter ~3.5nm) would rotate as a unit about its long axis. The observation in the $^{13}C$ CP-MAS spectra that resonances sharpen but do not shift substantially supports the idea that each chain does not move independently. Considering that $^{13}C$ isotropic chemical shift values are sensitive to hydrogen bonding configurations, any breaking of intermolecular hydrogen bonds would have to be accompanied by the rapid formation of similar bonds in order to maintain the $^{13}C$ shifts. This seems unlikely.

The sharpening of both the interior and surface crystalline resonances in wet samples could therefore be understood to arise partly from motional averaging. More important in the resonance sharpening is that water could

break up interfibrillar cellulose hydrogen bonds, thereby relieving the crystallites of possible strains. Hydrogen bonding of water to the surface cellulose chains would also improve the uniformity of their environment resulting in a sharpening of surface carbon resonances as is observed.

The claim that wet celluloses have higher crystallinity than dry preparations has been made by Morosoff [26] based on X-ray results. Although the wet/dry difference spectra (Figures 5E, 6E, and 7E) show positive intensities in the C4 and C6 interior-crystalline resonance region (66 and 90 ppm), remaining ambiguities in lineshape and relative intensities prevent a definite statement on this point. Suffice it to say that if there are not relative intensity distortions, these spectra would support the idea that there is a small increase in crystallinity upon wetting. Figure 8 shows proof that wetting is capable of producing a gain in crystallinity in an amorphous sample. In this case, after 36 hours of soaking in distilled water at ambient temperature, resonances associated with the interior regions of cellulose I crystals are evident. Moreover, just as in the other cellulosic materials, one of the principal changes in the amorphous cellulose in going from dry to wet is the pulling in of the shoulder at 77-79 ppm.

One of the explanations offered by Morosoff [26] for an increase in crystallinity upon wetting, is that drying sets up stress in cellulosic materials, mediated presumably by interchain hydrogen bonds. The immobilizing effect of these hydrogen bonds is reflected in the sudden lowering of $T_2^H$ in going from 0.06 to 0 $gH_2O/g$ cellulose [24]. With respect to our $^{13}C$ results, only two vacuum oven dried samples have been run in a desiccated condition. One is the amorphous cellulose (cf. Figure 1D); the other (not shown) is a cotton sample. In each case, the linewidths are broader and in cotton, this

is particularly true for the crystalline surface chain resonances. The broadness of these resonances does not, of itself, prove the existence of internal stress. Nevertheless, broadness (in this case it is known to be chemical shift dispersion)is an indication of non-uniformities among surface chain resonances. The idea that stress should accompany such non-uniformity is reasonable. It would also follow that in paper making, fibril damage would be minimized by mechanical deformation in the wet state.

C. The Legitimacy of Decomposing Lineshapes into Component Lineshapes.

In Figures 3 and 4 linear combinations of different cellulose spectra were taken in the hopes that a "pure component" spectrum could be constructed. A true pure component, by NMR standards, is one in which a chain is surrounded in all three directions by molecules configured in a way typical of that component. Thus it might be reasonable to isolate a spectral component corresponding to the interior crystalline chains. However, to isolate the pure surface crystalline chain lineshape makes less sense because the details of the surface and the availability and geometry of other hydrogen-bonding sites could easily influence the lineshape. Finally, the lineshape determination of the amorphous cellulose component also depends heavily on the dimensions of the amorphous region.

V. Conclusions

1. Three cellulose preparations were studied: purified cotton (PC), microcrystalline cellulose (MC), and Norway Spruce kraft pulp (NSKP). Based on the CP-MAS NMR spectra wet beating does not alter the cellulose crystal surface area in these samples, even though, in cotton, the fraction of bound water increases with beating. However, this conclusion may be misleading due to possible intensity distortions in the CP-MAS spectra. The possibility that such distortions exist accompanies the observation of deficient intensity in some spectra. Indirect evidence presented here is weighted in favor of true relative intensities.

2. On the basis of the NMR spectra of PC, MC, NSKP, and an amorphous ball-milled cellulose, it was argued that the order of decreasing crystallinity was MC≳PC>NSKP and that the order of decreasing lateral crystallite dimensions was PC>MC>NSKP.

3. Comparison of $^{13}C$ NMR spectra of wet versus dry celluloses supports the idea that wetting breaks up interfibrillar hydrogen bonds involving the surface cellulose chains. Moreover, in this process, stresses may be relieved allowing for slight increases in crystallinity. Restricted reorientation of entire elementary fibrils may also be occurring; however, the evidence for this latter claim depends solely on cellulose proton linewidth data reported in the literature [27].

4. CP-MAS spectra have been presented which confirm the utility of NMR for distinguishing between various cellulose preparations as well as distinguishing morphological features within a cellulose preparation. For example, in cellulose I, the interior crystalline chain lineshape can be isolated. It is not as easy to distinguish lineshapes arising from amorphous chains from lineshapes due to crystal surface chains, but the existence of significant numbers of crystal surface chains is not in doubt. The spectra of a highly crystalline cellulose II preparation as well as a ball-milled amorphous cellulose preparation have also been shown to give very distinct spectra.

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18. Certain commercial companies are named in order to adequately specify the experimental procedure. Such identification does not imply recommendation by the National Bureau of Standards of the U. S. Department of Commerce, nor does it imply that the equipment and material are the best available for the purpose.
19. This sample was prepared by William L. Earl at NBS.
20. This sample was prepared by R. H. Atalla of the Institute for Paper Chemistry, Appleton, Wisconsin.
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27. Note added in proof: Recent experiments performed in our laboratory discount the idea that either the chains or the fibrils undergo large amplitude motions on a timescale less than $10^{-5}$s.

TABLE I

| Sample | | Final Water Content (g $H_2O$/g Cellulose) | Fiber Saturation Point (g $H_2O$/g cellulose)†† | Bound Water (g $H_2O$/g cellulose)†† | Ratio of Observed to Expected $^{13}C$ Intensity* | LPE Reference Linewidth (Hz) |
|---|---|---|---|---|---|---|
| Microcrystalline Cellulose | As rec'd. | | | | 1.00 | 8 |
| | Wet | .88 | | | .90-.94 | |
| | Wet Beaten | .48 | | | .59 | 13 |
| Norway Spruce Kraft Pulp | As rec'd. | | | | .84† | 11 |
| | Wet | .65 | 1.33 | .45 | .65 | 10 |
| | Wet Beaten | 2.92 | 1.79 | .45 | .92 | 9 |
| Purified Cotton | As rec'd. | | | | 1.00 | 9 |
| | Wet | .71 | .53 | .23 | .75 | 8 |
| | Wet Beaten | 1.73 | .94 | .34 | .93 | 10 |
| Amorphous Cellulose | Original | | | | .61 | 9 |
| | Wet | 2.03 | | | .86 | 9 |

* $T_{1\rho}^{H}$ effects not considered

† Includes lignin intensity

†† Ref. 14.

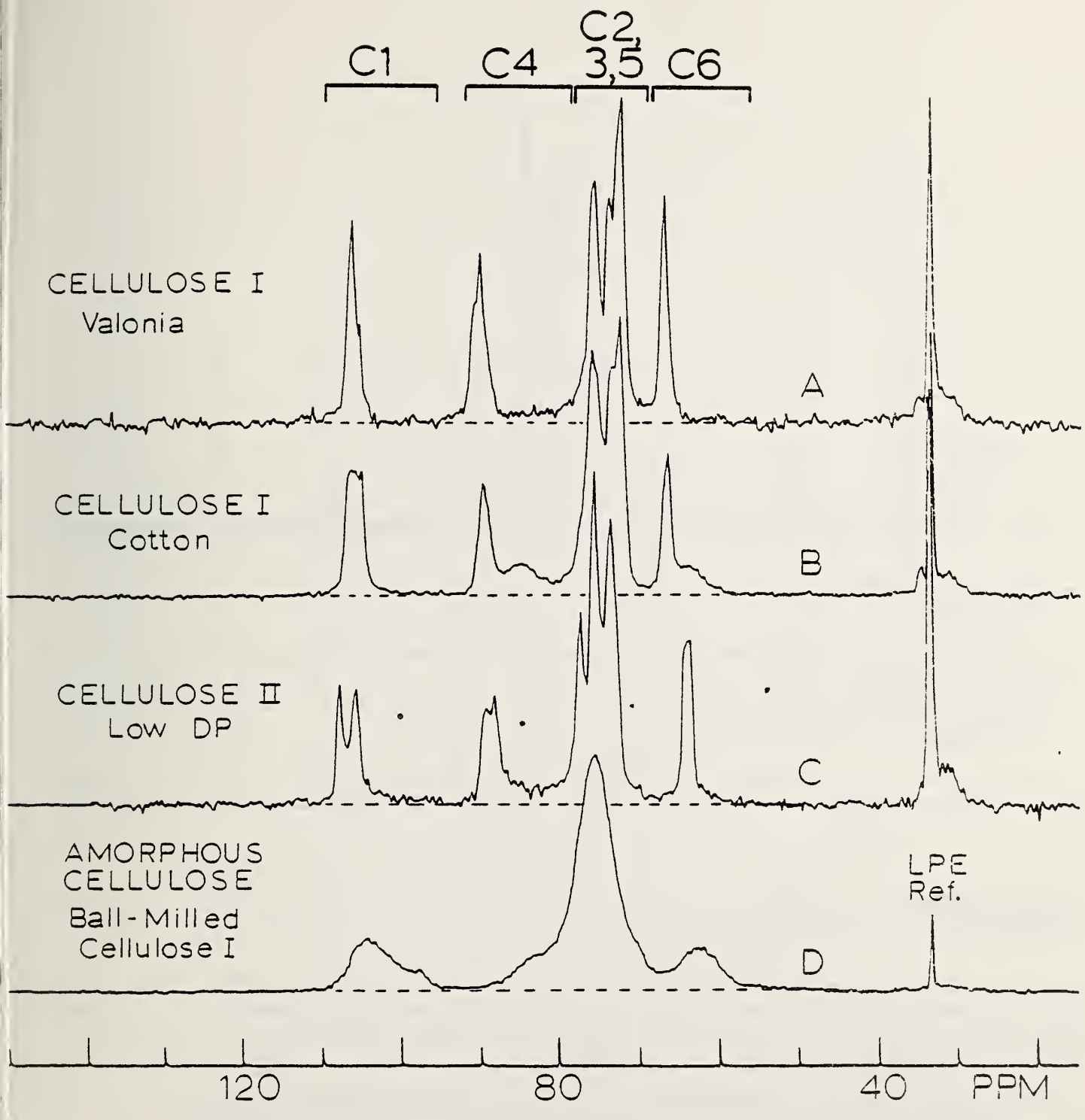


Figure 1. CP-MAS $^{13}C$ spectra of four different cellulose preparations. Samples, except for the desiccated amorphous cellulose, have been equilibrated at a RH of approximately 30%. Cross polarization times are 2ms for all spectra, and all spectra are normalized to the same total intensity. Pulse repetition times and total scans are respectively as follows: (A) 4.5s, 48K; (B) 6.05s,3.9K; (C) 7.0s, 9.7K; and (D) 6.0s, 7.2K. Linear polyethylene is used as a chemical shift reference. Baselines have been added for visual clarity. Signal to noise varies primarily because of sample quantity variations.

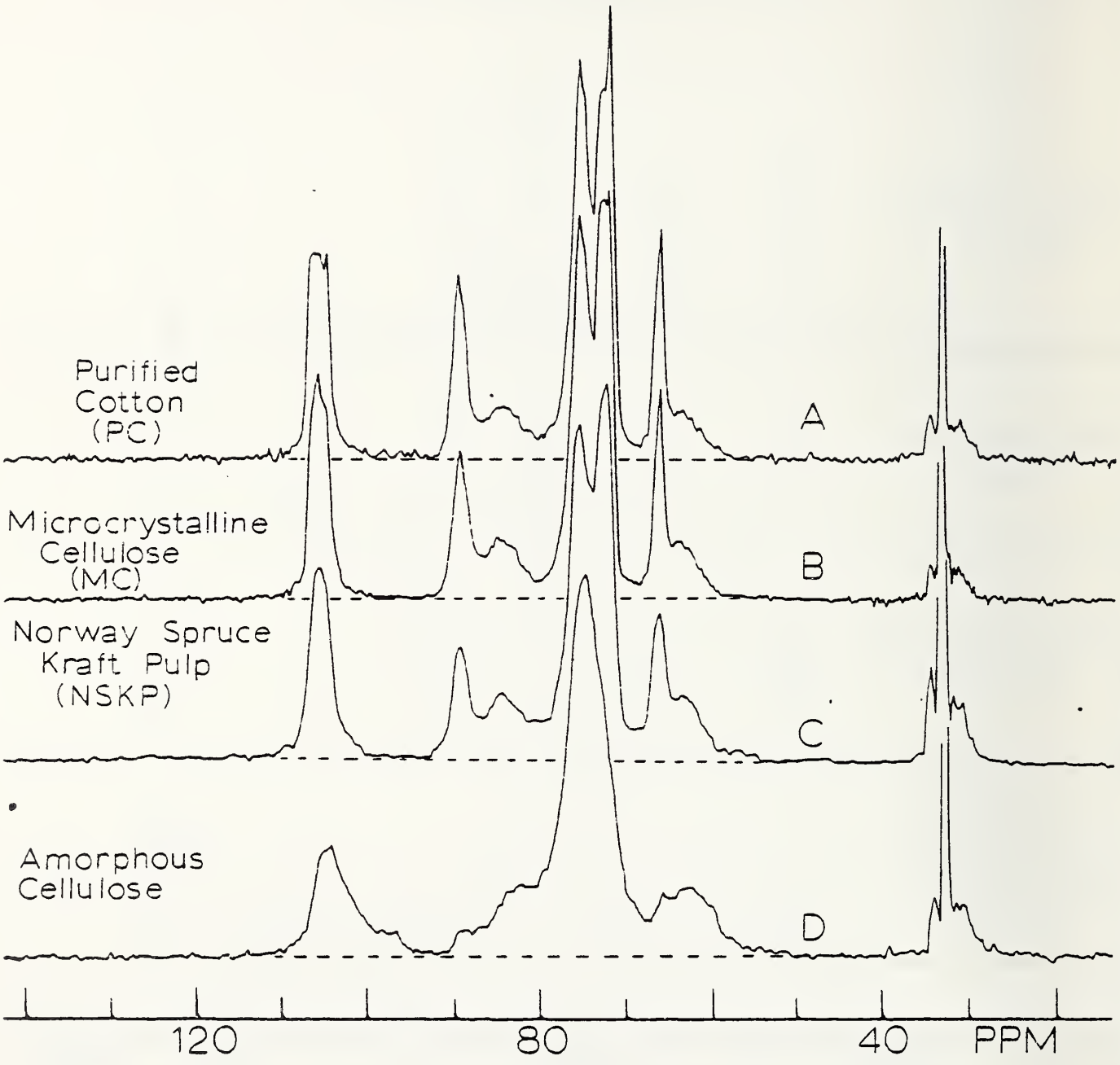


Figure 2. Normalized CP-MAS $^{13}C$ Spectra of the three samples studied in this report along with a spectrum of ball milled cellulose. All samples have equilibrated at a RH of approximately 30%. Pulse repetition times and total scans are respectively as follows: (A) 6.0s, 3.9K; (B) 6.0s, 8.0K; (C) 6.0s, 7.9K and (D) 4.0s, 15.1K. For additional explanation, see Figure 1.

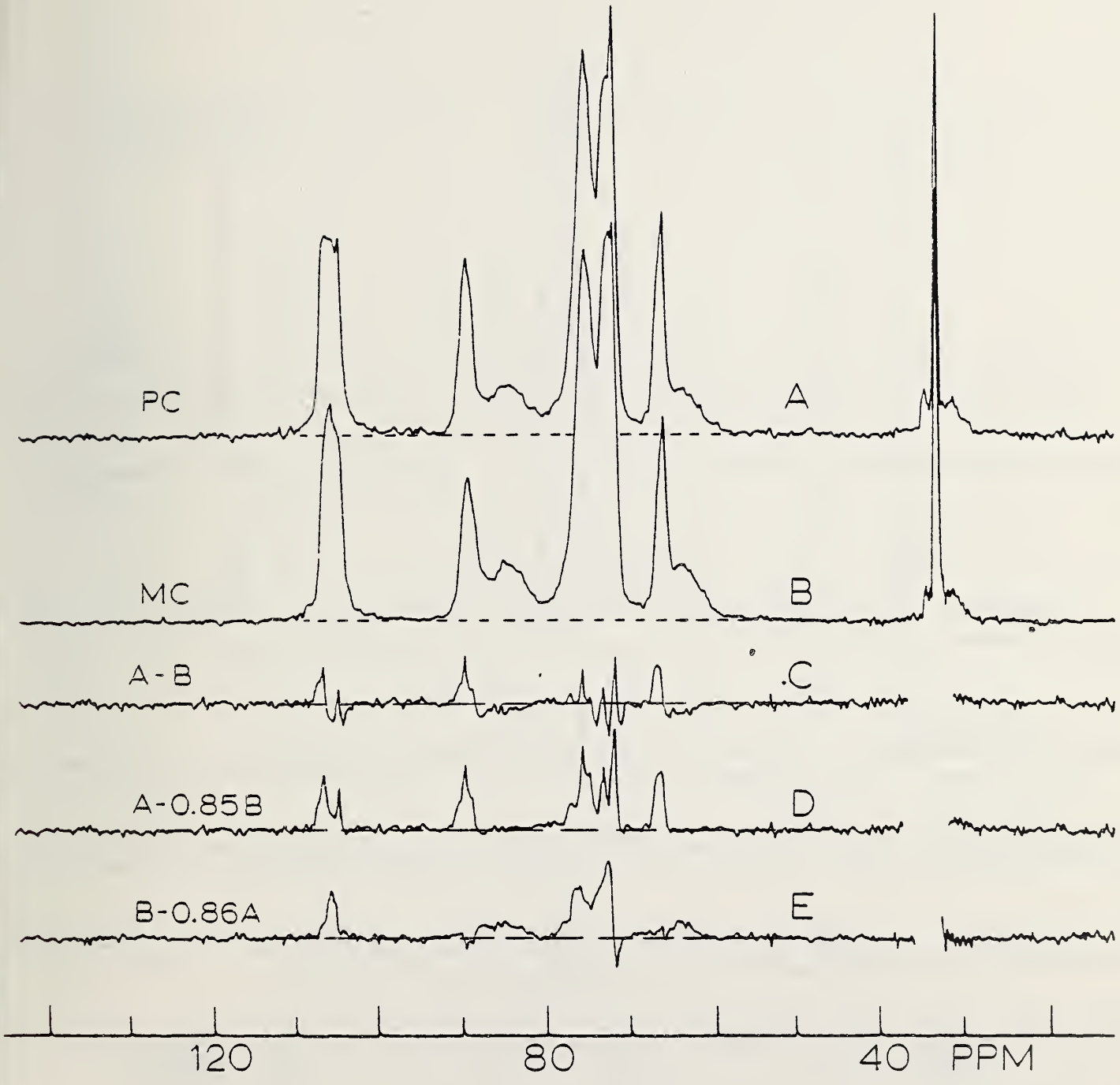


Figure 3. Comparison of normalized CP-MAS $^{13}C$ spectra of 'dry' purified cotton and microcrystalline cellulose. Upper spectra are the same as Figure 2A and 2B. Linear combination spectra (D and E) are attempts to resolve "pure component" spectra assuming a 2-component system.


Figure 4. Comparison of normalized CP-MAS $^{13}C$ spectra of 'dry' cotton and Norway Spruce kraft pulp. Upper spectra are the same as Figure 2A and 2C. Linear combination spectra (C and D) are attempts to resolve "pure component" spectra assuming a 2-component system.

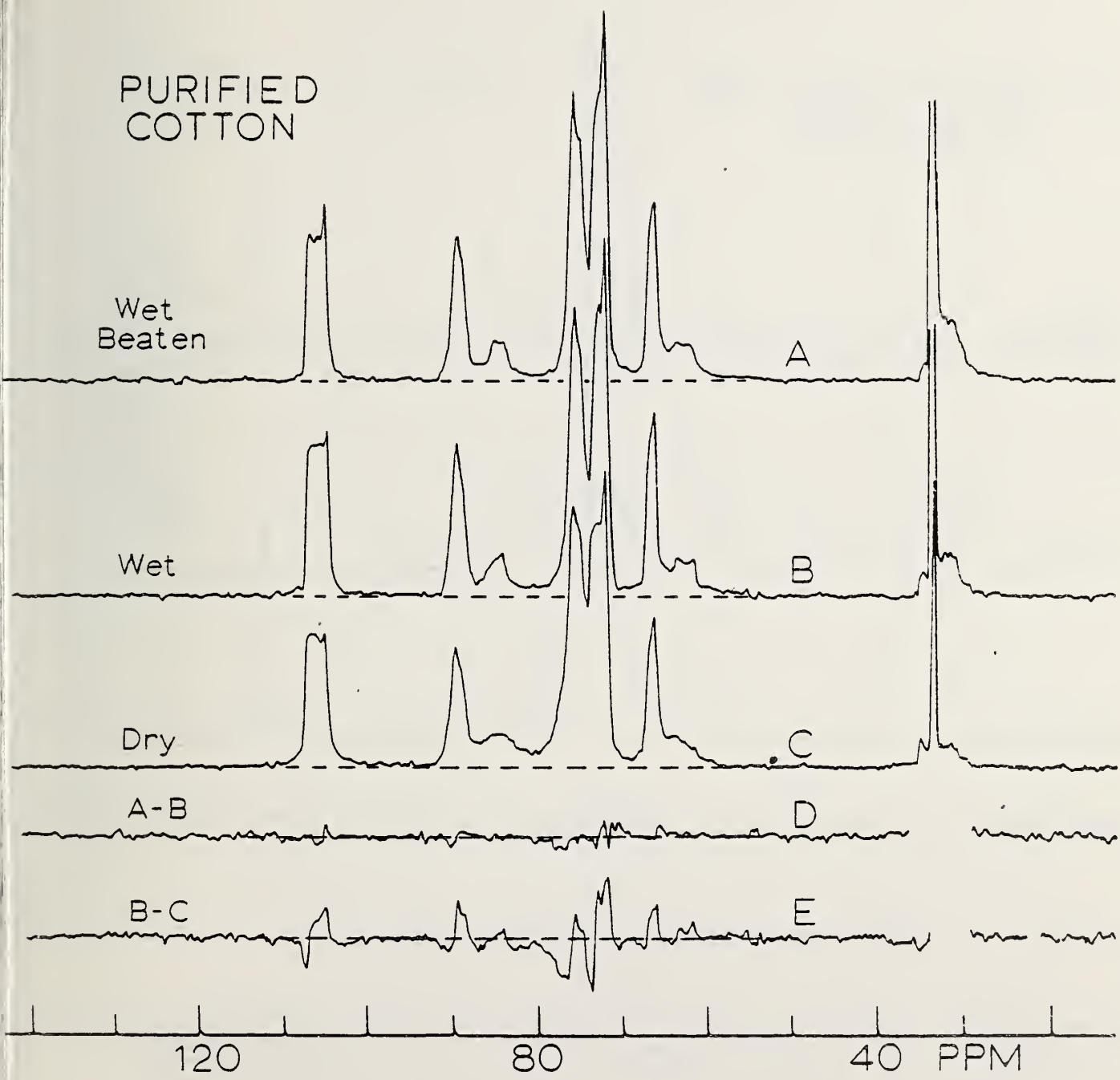


Figure 5. Comparison of normalized $^{13}C$ CP-MAS spectra of wet beaten (A), wet (B), and dry (C) cotton spectra. Difference spectra are given in (D) and (E). All cross polarization times are 2ms. Pulse repetition times and total scans are as follows: (A) 4.0s, 14.4K, (B) 4.0s, 6.8K; and (C) 6.0s, 3.9K.

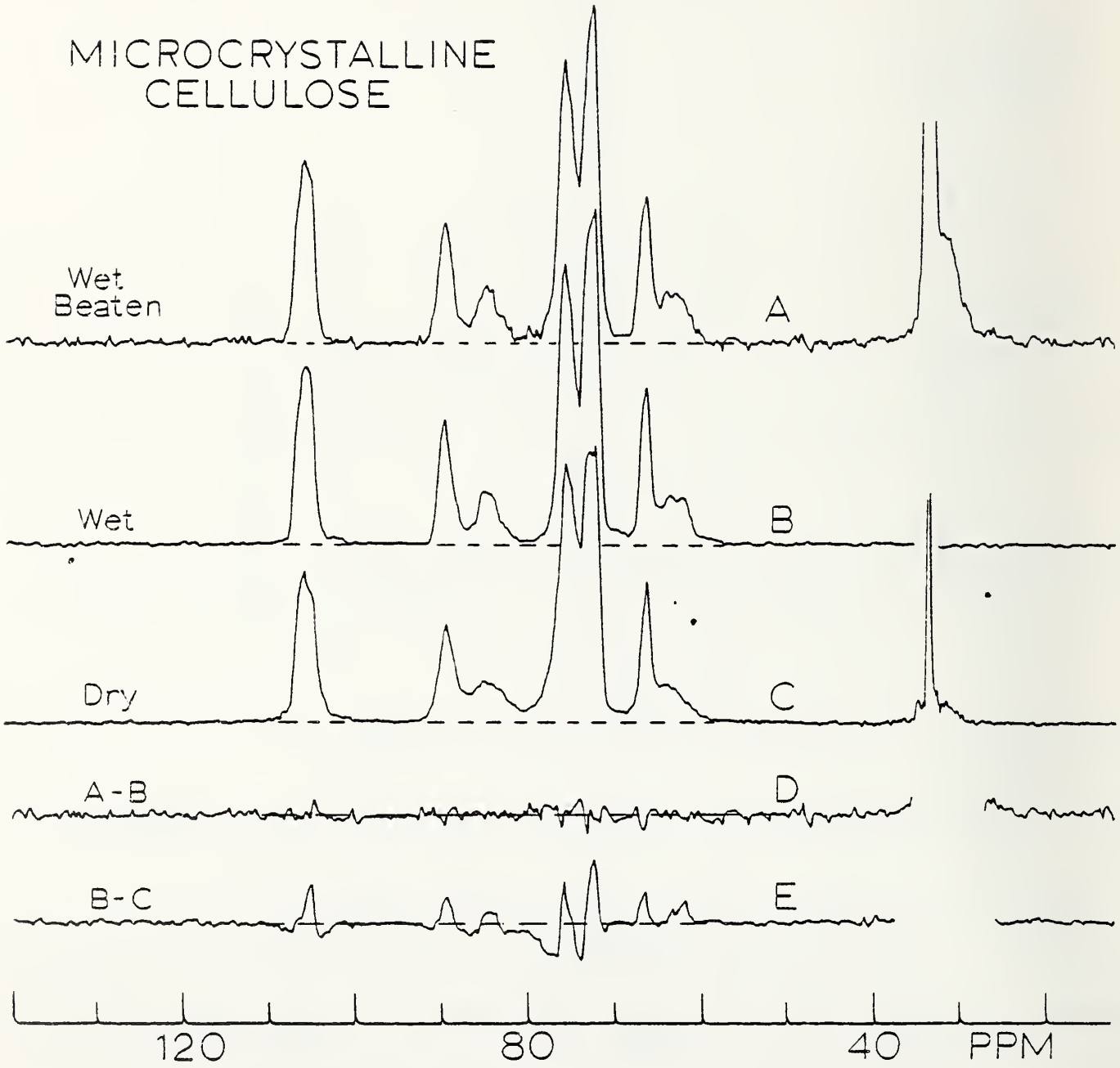


Figure 6. Spectra of microcrystalline cellulose (see explanation in Figure 5). Pulse repetition times and total scans are as follows: (A) 6.0s, 12.6K; (B) 6.0s, 8K; and (C) 6.0s,8K.

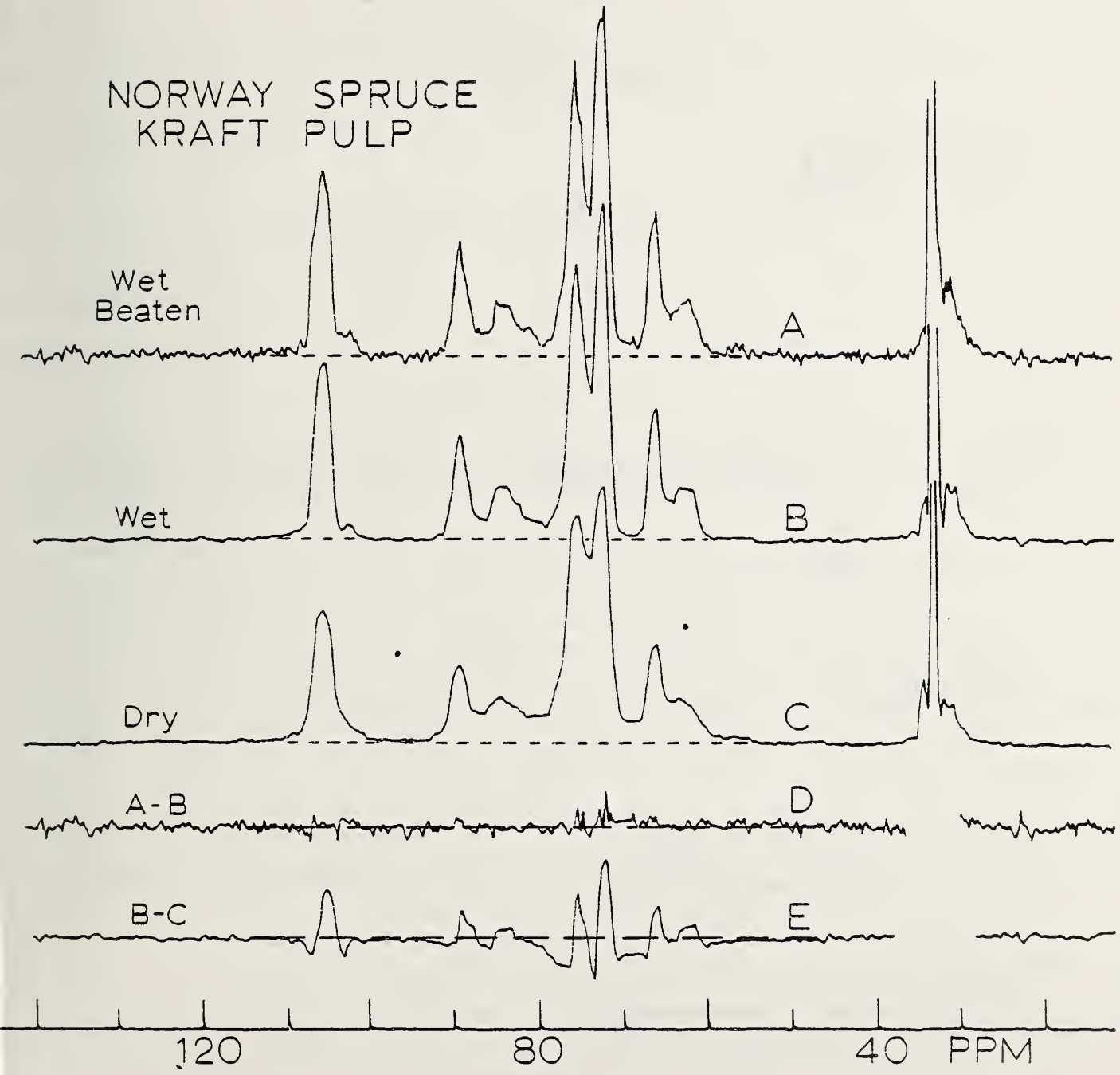


Figure 7. Spectra of Norway Spruce kraft pulp (see explanation in Figure 5). Pulse repetition times and total scans are as follows: (A) 4.0s,16K; (B) 4.0s,14.3K; and (C) 6.0s, 7.9K.

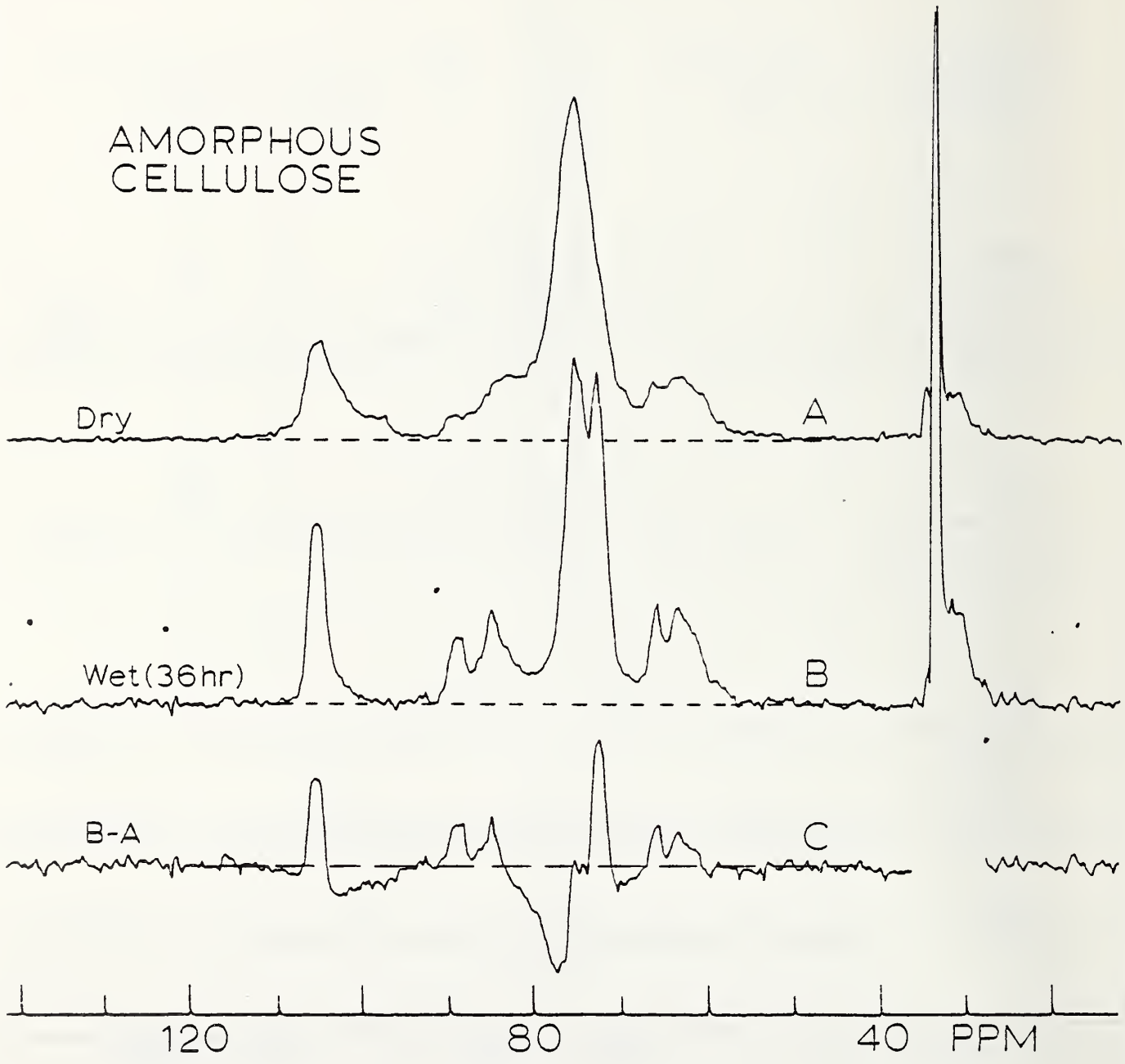


Figure 8. Normalized $^{13}C$ CP-MAS spectra of amorphous cellulose; the dry sample has been equilibrated at 30% RH and the wet sample was soaked in distilled water for 36 hours prior to taking the spectrum. The difference spectrum is also shown indicating that crystallinity has increased after wetting. Pulse repetition times and total scans are as follows: (A) 4.0s, 15.1K and (B) 4.0s, 14.3K.

| U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions) | 1. PUBLICATION OR REPORT NO. NBSIR 82-2534 | 2. Performing Organ. Report No. Nat. Bur. Stds. NBSIR 82-2534 | 3. Publication Date June 1982 |
|---|---|---|---|

4. TITLE AND SUBTITLE

Deductions about the Morphology of Wet and Wet-Beaten Celluloses from Solid State $^{13}C$ NMR.

5. AUTHOR(S)

D. L. VanderHart

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

10/1/80 - 9/30/81

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

Bureau of Engraving and Printing
Treasury Department
Washington, D.C. 20401

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

The cellulosic preparations, purified cotton (PC), microcrystalline cellulose (MC), and Norway Spruce Kraft pulp (NSKP), were examined by $^{13}C$ solid-state NMR methods. Based on previously published work, $^{13}C$ NMR spectra can indicate the fraction of anhydroglucose moieties in interior crystalline regions; moreover, the combined fraction of moieties in amorphous regions and at the surface of the crystalline regions can also be determined. In this work, changes in crystallite size resulting from wet beating (a paper-making processing step) are probed. Results show that no detectable changes occur in going from wet to wet beaten samples, although possibilities that intensity distortions may be present in the spectra cannot be entirely dismissed. Other observations made in this investigation are as follows: (1) The order of decreasing crystallinity is MC>PC>NSKP; (2) The order of decreasing lateral crystallite dimension is PC>MC>NSKP. (3) This data in conjunction with other published proton data raises the possibility that restricted reorientation of entire elementary fibrils can take place in wet samples; finally (4) Spectra of several different cellulose preparations are included in order to underscore the ability of these solid-state $^{13}C$ NMR techniques to distinguish between different crystallographic as well as different morphological preparations of cellulose.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

NMR, $^{13}C$, cellulose; wet beating; crystallinity; morphology.

13. AVAILABILITY

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☐ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES 33

15. Price $7.50