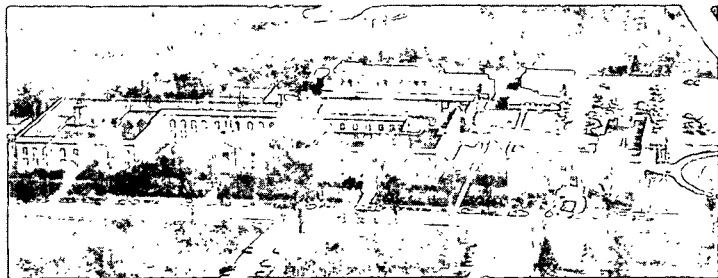


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**DIMETHYL SULFOXIDE/PARAFORMALDEHYDE: A NONDEGRADING
SOLVENT FOR CELLULOSE**

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APRIL, 1975

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SOLVENT FOR CELLULOSE

Donald C. Johnson, Myron D. Nicholson and Fred C. Haigh

INTRODUCTION

Student research at the Institute has led to the discovery of a new solvent system which will dissolve cellulose without degradation. The new solvent is dimethyl sulfoxide containing less than 1% of dissolved paraformaldehyde.

Subsequent staff and student research has established the variables which influence the dissolving process, and also the actual mechanism of dissolution. The cellulose may be recovered from solution by the addition of water.

The new solvent system may have both commercial and laboratory utility. Regeneration of the dissolved cellulose in the form of fibers and films has been demonstrated, and blends of cellulose with synthetic polymers would be expected to have novel properties. The manufacture of cellulose derivatives may be facilitated. The solvent has promise of becoming a useful analytical tool for molecular weight measurements of celluloses and hemicelluloses.

The attached paper is being presented at the Eighth Cellulose Conference at Syracuse, New York, May 19-23 (1975).

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DIMETHYL SULFOXIDE/PARAFORMALDEHYDE: A NONDEGRADING
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SYNOPSIS

Dimethyl sulfoxide (DMSO) containing the equivalent of 0.5% (w/v) of dissolved paraformaldehyde (PF) has been found to be an excellent nondegrading solvent for cellulose. Cellulosic materials successfully dissolved have had degrees of polymerization ranging from 16 to over 8,000. In addition, high-yield pulps containing substantial amounts of lignin have been partially dissolved. Regeneration of dissolved cellulose has been accomplished by dilution with water or methanol.

Evidence is presented which supports the conclusion that formation of methylol cellulose, a hemiacetal derivative, is crucial to the dissolution mechanism. Methylol cellulose was isolated and characterized by its solubility, Laser Raman spectroscopy and formaldehyde analysis. Nuclear magnetic resonance spectra showed that the DMSO/PF solvent system contains several oxymethylene chains; the major species are dimer and trimer, but significant amounts of methylene glycol and formaldehyde are also present. Addition of methanol to the system results in formation of the monomethyl ether of methylene glycol (methylol methanol).

The influence of the methylol substituent on carboxymethylation in the cellulose solvent system is briefly described.

INTRODUCTION

Cellulose solvents have long been of interest to investigators concerned with either the polymer properties of cellulose or possible routes to modification of the polysaccharide. In the late 1950's, a number of solvents were discovered by Jayme and coworkers involving relatively concentrated aqueous solutions of metal ions, alkali, and organic bases. An example is the use of sodium iron(III) tartrate in excess sodium hydroxide solution. These systems have been recently reviewed (1).

Over the last ten years, there has been increased concern with non-aqueous solvents for cellulose. Frequently, the solvent system has involved formation of a cellulose derivative. This appears to be true for the action of dinitrogen tetroxide in N,N-dialkylacylamides (2) and in DMSO (3, 4); these systems are viewed as forming soluble cellulose nitrite. Nitrosyl chloride apparently acts in the same manner (2).

In addition, reports have appeared concerning cellulose solvents containing sulfur dioxide and diethylamine in either acetonitrile or DMSO (5-8). A detailed study of the cellulose solvent DMSO/methylamine has been reported (9).

Our research in this area developed from a strong interest in the cyclic amine oxides which are known to dissolve cellulose and many other naturally occurring fibers (10-12). An important observation was that cellulose dissolved much more rapidly in N-methylmorpholine-N-oxide containing PF if DMSO was also present. This led to the finding that DMSO/PF was also capable of dissolving cellulose.

This paper presents the results of research concerning the chemical nature of the DMSO/PF system, its ability to dissolve many different cellulosic materials and the formation of methylol cellulose during the solution process. An investigation of the relationship between intrinsic viscosity and degree of polymerization and other solution properties of methylol cellulose is reported elsewhere (13).

EXPERIMENTAL

Preparation of Cellulose Solutions

A variety of related approaches have been found to successfully dissolve cellulose. A 1% solution was prepared as follows: A mixture of acetate-grade cotton linters (0.10 g) and DMSO (Eastman reagent grade, 10.0 ml) was heated with rapid stirring to 94-100°C. A stream of formaldehyde gas was bubbled into the mixture at this temperature. The formaldehyde was generated by thermal decomposition of PF (2.0 g present initially, 1.8 g decomposed) in a separate container. A clear, viscous cellulose solution resulted.

Alternatively, cellulose (0.10 g) and PF powder (Mallinckrodt, 0.50 g) were dispersed in DMSO (10.0 ml) at room temperature. The mixture was then heated with rapid stirring to 130° over a period of 6-8 minutes; evolution of formaldehyde occurred and shortly after the onset of vigorous bubbling a clear solution resulted. With a few cellulose samples, it has occasionally been necessary to use up to twice the initial amount of PF to achieve complete solution. If the solution is prepared in a closed pressure vessel, a lower initial charge of PF can be used. The water content of the PF used should not exceed 5%. The water content of the entire DMSO/PF/cellulose system should be less than 1%.

Cellulose was regenerated from solution by adding the solution to either water or methanol. The regenerated cellulose was washed several times with water and freeze-dried. Investigation by x-ray diffraction, infrared and Raman spectroscopy showed that the material was cellulose II of low crystallinity. The dissolved cellulose was also regenerated through a syringe into a tray of

methanol to give rayonlike fibers. Similarly, films of regenerated cellulose were also prepared.

Partial Dissolution of High-Yield Pulps

A kraft pulp from southern pine was used which contained 12.6% Klason lignin and had been Wiley-milled. The pulp (0.200 g) and PF powder (Mallinckrodt, 2.0 g) were dispersed in DMSO (20.0 ml), and the mixture was heated with rapid stirring to 130°C over 17 minutes. Formaldehyde was evolved. Then the system was cooled to approximately 70°, and a second charge of PF (1.0 g) was added. The system was again heated to 130° with renewed gassing of formaldehyde.

The solution was separated from undissolved residue by centrifugation. The residue was then washed with DMSO (20 ml) and the wash was combined with the prior supernatant fraction. The residue was washed twice with water and then freeze-dried (0.074 g, 37% of original pulp).

Dissolved material was regenerated by pouring the solution slowly into methanol (300 ml) containing two drops of glacial acetic acid. The resulting solid was collected on a sintered glass filter funnel and washed with water (2 x 300 ml containing two drops of glacial acetic acid). The dried regenerated material amounted to 0.116 g or 58% of the original pulp.

A neutral sulfite semichemical pulp (poplar) was partially dissolved in the above manner. The undissolved residue and the regenerated material amounted to 14% and 69% of the original pulp, respectively.

Spectroscopy

Nuclear magnetic resonance (NMR) spectra were obtained using a Varian A-60A NMR spectrometer. Spectra were run using DMSO-d₆ (minimum 99.5 atom % D) containing tetramethylsilane as internal reference. A sweep time of 250 sec was normally applied (0-1000 hz), but for clearer resolution of complex OH signals a sweep time of 500 sec was used.

Experiments designed to simulate the cellulose-dissolving system were run on a scale of 4.0 ml of DMSO-d₆ and aliquots of 0.4 ml were removed for spectral investigation.

Laser Raman spectra were recorded on a Spex Raman system in which the 5145 Å line of a Coherent Radiation 52A laser was used for excitation.

Infrared spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer using the potassium bromide pellet technique.

Isolation of Methylol Cellulose

A 3.2% (w/v) solution of cellulose (Whatman CF-1) in DMSO/PF was freeze-dried for five days. A white, fluffy, fibrous solid resulted. A sample was found to be soluble in DMSO at room temperature without need for stirring. A portion of the methylol cellulose was placed in water and tiny gas bubbles were noted at the fiber-liquid interface. Removal of the material from water followed by air-drying gave cellulose which was no longer soluble in DMSO.

The Laser Raman spectrum of the sample showed bands at 675 and 710 cm⁻¹ indicating the persistence of DMSO. Freeze-drying for longer durations up to 14 days did not appreciably reduce the level of entrapped DMSO.

The formaldehyde released from methylol cellulose was analyzed by a method involving the reaction of sodium sulfite and formaldehyde (14). Duplicate analyses indicated a mole ratio of formaldehyde:anhydroglucose of 1.15 and 1.05.

RESULTS AND DISCUSSION

Dissolving of Cellulose

Total solution of cellulose has been accomplished with the DMSO/PF system in a variety of ways. Batches of paraformaldehyde (PF) which decompose readily to formaldehyde below 130° can be used by adding the cellulose and PF to DMSO at room temperature followed by thermal decomposition of PF.

Alternatively, cellulose can be suspended in DMSO and formaldehyde gas bubbled in from external thermal decomposition of PF. In this method, the optimum temperature of the solvent for dissolution is 95-100°C. Lower temperatures can lead to the formation of polyoxymethylene, and introduction of the gas at much higher temperatures can result in too little of the gas being dissolved and/or reacted with the cellulose.

As expected cellulose can also be dissolved in a closed DMSO/PF system. The escape of formaldehyde is prevented, and solution occurs with a lower charge of PF. Solution of cellulose was achieved when the PF used amounted to 3.3% (w/v) of the DMSO/PF system whereas 5% PF was normally required in an open system. In this sealed system, it was possible by measurement of the pressure increase to estimate the amount of dissolved PF present as contrasted with gaseous formaldehyde. The equivalent of 0.5% of PF was actually in solution. The various molecular systems present in solution will be discussed subsequently.

Other approaches used to estimate the concentration of PF actually present in the dissolving system included suitable integral ratios from nuclear magnetic resonance spectra of the DMSO/PF system (no cellulose present) prepared under conditions used to dissolve cellulose. Both the DMSO solvent peak and a

methanol peak, after addition of a known amount, were used as internal standards. In various experiments using open systems which permitted escape of some formaldehyde, the dissolved PF concentration amounted to about 0.3%.

An excess of water in the system can interfere with the dissolving of cellulose. Although some water is present in the original DMSO and additional water is brought in with the PF and the cellulose, this total water concentration is not normally sufficient to prevent solution. Exposure of the solution to air for a few days will eventually cause the cellulose to come out of solution due to an increase in the water level.

The cellulose chains do not degrade (shorten) to a significant extent in the DMSO/PF solution as shown by Swenson (13). The cellulose remains in solution indefinitely as long as the container is kept closed. The nondegrading nature of the solutions and their ease of preparation have generated recent work on the macromolecular properties of cellulose in dilute solutions (13, 15).

The cellulose has been regenerated from DMSO/PF solution by dilution with either water or methanol. The x-ray diffractogram of the regenerated material was that of cellulose II, and the sample showed quite low crystallinity. The Laser Raman spectrum compared favorably with that of authentic cellulose II as shown in Fig. 1. The authentic cellulose II sample used here was of considerably higher crystallinity which accounts for the minor differences in the spectra. The region from $300-600\text{ cm}^{-1}$, in particular, has been shown to be highly sensitive to differences between cellulose polymorphs (16).

The solvent has successfully dissolved a wide variety of cellulosic materials. These have included celluloses having weight average degrees of polymerization (DPw) ranging from 16 to over 8,000, the latter extreme

representing native long fiber cotton. A holocellulose containing 18% xylan has also been dissolved. In general, concentrations of 1-2% of dissolved cellulose have been achieved. Higher concentrations can be reached with low DP samples.

Substantial proportions of high-yield pulps have also been successfully dissolved. The amounts of a kraft softwood pulp (57.5% yield, 12.6% Klason lignin) and of a NSSC pulp (poplar) which dissolved were 55% and 85%, respectively. Analysis by infrared spectroscopy showed that in both cases the dissolved and subsequently regenerated material contained very little lignin in contrast to the original pulp and the residual material. This is illustrated in Fig. 2 for the kraft pulp dissolution; the band at 1505 cm^{-1} is a good indicator of the relative amount of lignin present (17).

The DMSO/PF System

In an effort to better understand the DMSO/PF solvent system, samples were prepared for nuclear magnetic resonance (NMR) study (without cellulose) using DMSO- d_6 . Conditions such as charge of PF and temperature were maintained that were comparable to conditions used in successfully dissolving cellulose. The method of adding PF at 120° to DMSO- d_6 was employed to give the sample whose spectrum is shown in Fig. 3. Chemical shift and coupling constants are included in Table I. An identical run with cellulose present resulted in total solution.

The interpretation of spectra is aided greatly by the well-known property of DMSO to reduce the usual rate of proton exchange between hydroxyl groups so that spin-spin coupling can be observed (e). Thus, a doublet ($J = 7.5$) is seen for R-OCH₂-OH environments at δ 4.70 which was collapsed to a singlet after addition of D₂O (Fig. 3b). The corresponding -OH triplet for formaldehyde

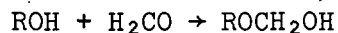
dimer is centered at δ 6.08. Since the area ratio of the CH and OH regions is less than 2.0, there must be a significant amount of formaldehyde hydrate present. The CH signal for the hydrate (monomer) is assigned as δ 4.62 on the basis of the D-exchange spectrum. Part of the hydrate triplet is visible in the original spectrum (Fig. 3a) at δ 4.49. The OH signal for the hydrate is comparable in intensity to the dimer OH signal and is a triplet centered at δ 5.73. In trimeric and longer oxymethylene chains, the internal CH_2 groups can not be coupled with other protons; these internal protons are responsible for the singlet at δ 4.80 which is, of course, unaffected by D_2O addition.

The differences noted in chemical shifts for CH protons of hydrate, methylol end groups and internal methylene groups are quite comparable to those reported earlier (19) in a deuterium oxide system.

The CH/OH ratio (and thus the average chain length) for the oxymethylene system is highly dependent on water content and the thermal history of the solution. A rather long chain system is represented in Fig. 4 by a solution of PF (added at room temperature) in DMSO which had been heated only to 110° over a 2.0 minute period. Our experience suggests that such a system would not be expected to dissolve cellulose until a higher temperature had been reached. In fact, some PF still remained undissolved at 110° . The CH/OH ratio is 5.9 and the methylene proton region is dominated by the internal CH_2 singlet at δ 4.80. The end-group OH for these longer chains is clearly visible at relatively low field as a distorted triplet. As indicated in Table 2 analogous samples heated for longer periods contained shorter oxymethylene chains. Figure 4 also shows the formaldehyde ($\text{H}_2\text{C}=\text{O}$) signal at δ 9.54 which represents about 2% of the total dissolved PF. The signals shown at δ 2.50 and 3.29 are due to the solvent (trace of $\text{C}_2\text{D}_5\text{HSO}$) and water, respectively.

The DMSO/PF/CH₃OH System

The proposed mechanism for cellulose dissolution in the DMSO/PF system is discussed more fully in a later section. In essence, however, the most prominent feature of that mechanism is the formation of methylol cellulose which can be viewed as a nucleophilic addition of an alcohol (R-OH) to formaldehyde as shown below.



Evidence was sought for this reaction in the DMSO/PF system by studying the changes induced in the NMR spectrum after addition of methanol at room temperature. After three days, an NMR spectrum showed that the oxy-methylene CH peaks had shifted upfield clearly indicating a change in the molecular species. Ultimately, the spectrum was that shown in Fig. 5. The spectrum is in agreement with the structural assignment of methylol methanol, the hemiacetal formed from formaldehyde and methanol. The methylene doublet at δ 4.53 is shifted upfield somewhat compared to its position in the original DMSO/PF system.

The OH signal is a clear triplet at δ 6.08. The area ratio of the signals was 2.0 favoring the CH doublet. Addition of D₂O collapsed the doublet to a singlet and removed the methylol OH signal entirely. After deuterium exchange, two methyl singlets were clearly evident at δ 3.22 and 3.17 and are assigned to the methyl protons of the hemiacetal and excess methanol, respectively.

These results clearly demonstrate the formation and stability of a hemiacetal system in DMSO solution.

Other DMSO/PF Systems

It was highly desirable to obtain evidence that the DMSO/PF system containing dissolved cellulose was indeed similar to the system containing methanol. Dissolving experiments were carried out using two cellulose samples of very low degrees of polymerization (DP) which had been prepared by graded acetolysis followed by deacetylation (20). The average DP values of the samples were 16.7 and 30.9. Comparison between runs using DMSO/PF and DMSO alone showed that the former system was a greatly superior solvent. The lower DP cellulose dissolved in DMSO alone at 130° (0.5% w/v solution) but precipitated on cooling.

The NMR spectrum of the DMSO-d₆/PF solution of the lower DP cellulose is shown in Fig. 6. The major features of the spectrum are like those previously discussed. The signal for molecular formaldehyde at δ 9.54 is again clearly evident and represents approximately 2% of the total oxymethylene system. The oxymethylene chains are still rather long as indicated by both the integral ratio and the intense singlet for internal CH₂ protons at δ 4.80. Here, the spin-spin coupling of the terminal methylol groups has been obliterated so that the CH protons give a broad singlet at δ 4.70 and the OH protons give a broad signal at δ 6.25. The cellulose -OH protons do not contribute to this latter signal but may contribute somewhat in the region 4.0 to 5.0 ppm (21). The cellulose CH protons are responsible for the broad signal in the region 3.2-3.9 ppm. Water is partly responsible for the peak at δ 3.27.

Methyl β -D-glucopyranoside was also examined by NMR using the DMSO-d₆/PF solvent system (Fig. 7). The C₆-OH triplet signal is seen in DMSO alone at δ 4.50 (21); the spectrum in DMSO/PF shows that the carbohydrate hydroxyl region has been changed. The change is attributed to partial addition of methylol units.

Mechanism of Cellulose Dissolution in DMSO/PF

The mechanism by which cellulose dissolves in the DMSO/PF system is dependent, in part, on the formation of methylol cellulose as shown in Fig. 8. As formaldehyde is generated in the system, a portion of it reacts with cellulose hydroxyl groups with the primary C₆-OH group being the favored reaction site. DMSO serves at least two key roles; first, it promotes swelling of the cellulose so that reaction with formaldehyde is reasonably uniform and second, it stabilizes the hemiacetal units (-OCH₂OH) through hydrogen-bonding association after they have been formed. Thus, the resulting solutions are stable for many months as long as they are protected from an increase in water content. The strong methylol-DMSO association prevents the cellulose chains from aggregating together and precipitating from solution. The solvent association undoubtedly helps to prevent cross-linking.

The strongest evidence for the actual formation of a cellulose derivative in the DMSO/PF system came from the isolation of methylol cellulose. It was found that when a solution of cellulose was freeze-dried a white solid resulted. This solid was easily soluble in DMSO at room temperature. Prior treatment of the freeze-dried solid with water rendered it insoluble in DMSO. Analysis of the methylol cellulose for formaldehyde content (14), after addition of water, showed that the average degree of substitution was 1.1.

The Raman spectrum of methylol cellulose (Fig. 9) contains two bands near 900 cm⁻¹ (910 and 950 cm⁻¹) which are characteristic of substituted celluloses (22); the cellulose spectrum has only one band in this region at 900 cm⁻¹. A spectrum of methyl cellulose is included for comparison.

Reactions in DMSO/PF/Cellulose System

Carboxymethylation of cellulose in solution has been studied. Initially, it was found that carboxymethylation with chloroacetic acid had apparently produced carboxymethyl cellulose according to the water solubility and the infrared spectrum of the product. Acid-catalyzed hydrolysis, however, yielded only glucose with no appreciable amount of the O-carboxymethyl glucose derivatives. It was concluded that carboxymethylation had occurred at the methylol hydroxyl groups, and acid hydrolysis simply cleaved the acetal linkages along with the glucoside links to produce only glucose.

When sodium hydride was used in the system, the methylol groups were more readily removed prior to the etherification reaction. The gas-liquid chromatogram for such a run at 20° is shown in Fig. 10. The substituent distribution for the 2, 3, and 6 hydroxyls was 1.7:1.5:1, respectively. A run at 50° gave a substituent distribution of 1:1:1.2. Apparently, the methylol group has preferentially blocked the 6-position from etherification, but a higher temperature reduces the influence of the methylol groups by removing a portion of them.

Further work is in progress on etherification reactions of cellulose in DMSO/PF and will be reported later.

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TABLE I
 ASSIGNMENT OF PROTON NMR SIGNALS
 FOR DMSO-d₆/PF₆ SYSTEM

Molecular Unit	δ CH ^a	δ OH ^a	\underline{J} , hz
H ₂ CO	9.54s	--	--
H ₂ C(OH) ₂	4.62t	5.73t	7.0
O(CH ₂ OH) ₂	4.70d	6.08t	7.5
ROCH ₂ OH ^b	4.70d	6.34t	7.5
(CH ₂ O) _n	4.80s	--	--

^as = Singlet, d = doublet, t = triplet.

^bEnd-groups of trimeric and higher oxymethylene chains.

TABLE II

EFFECT OF TEMPERATURE ON CHAIN LENGTH IN
DMSO/PF DETERMINED BY NMR

Heating Time, min	Maximum Temperature, °C	Integral Ratio ^a CH/OH
2.0	110	5.9
3.0	119	4.9
4.2	130	3.0

^aThe CH and OH signals are in the ranges δ 4.5-5.0 and δ 5.9-6.6, respectively. The average oxymethylene chain length is equivalent to the integral ratio.

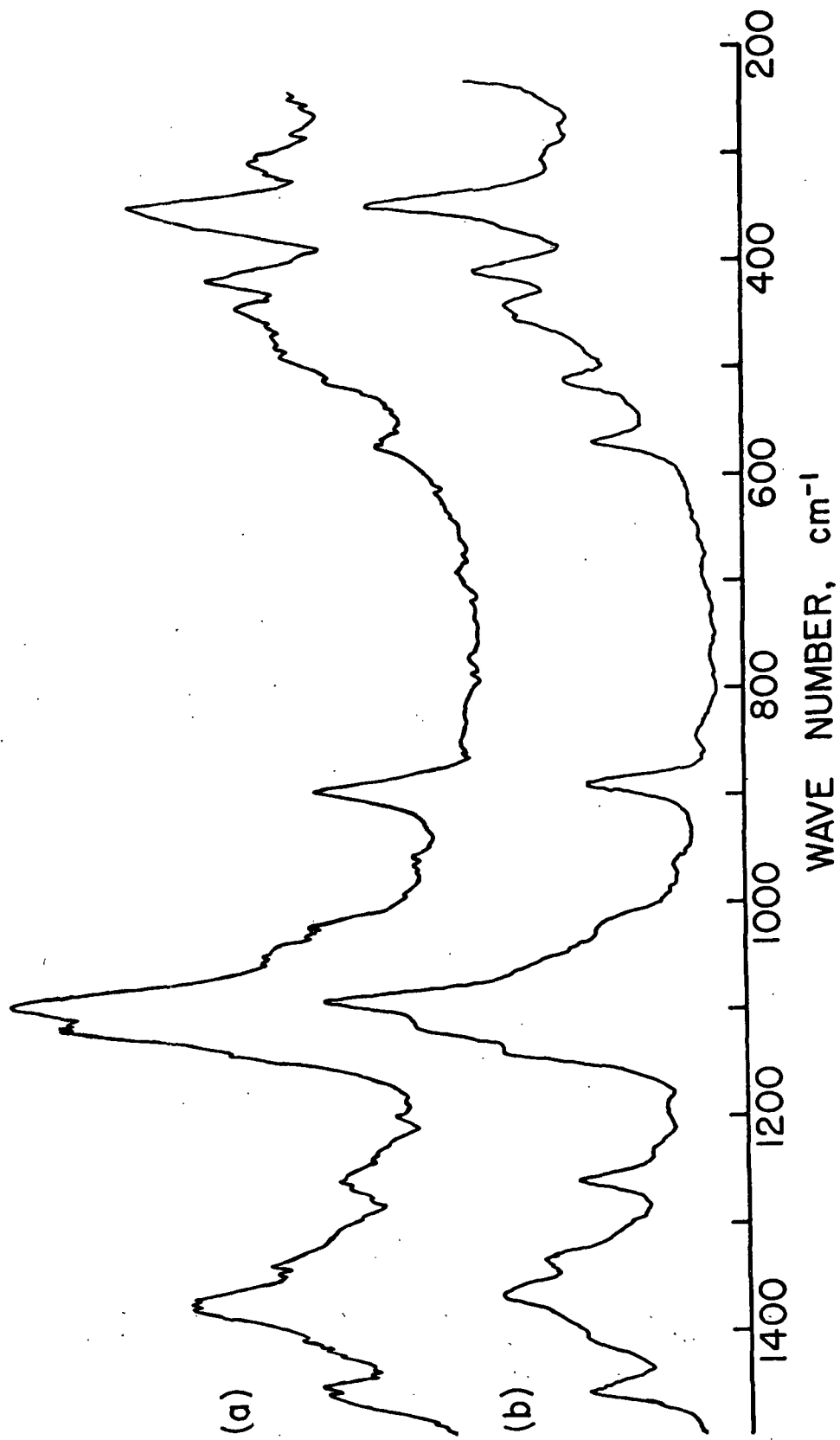


Figure 1. Laser Raman spectra of (a) regenerated cellulose from DMSO/PF solvent and (b) a highly crystalline cellulose II.

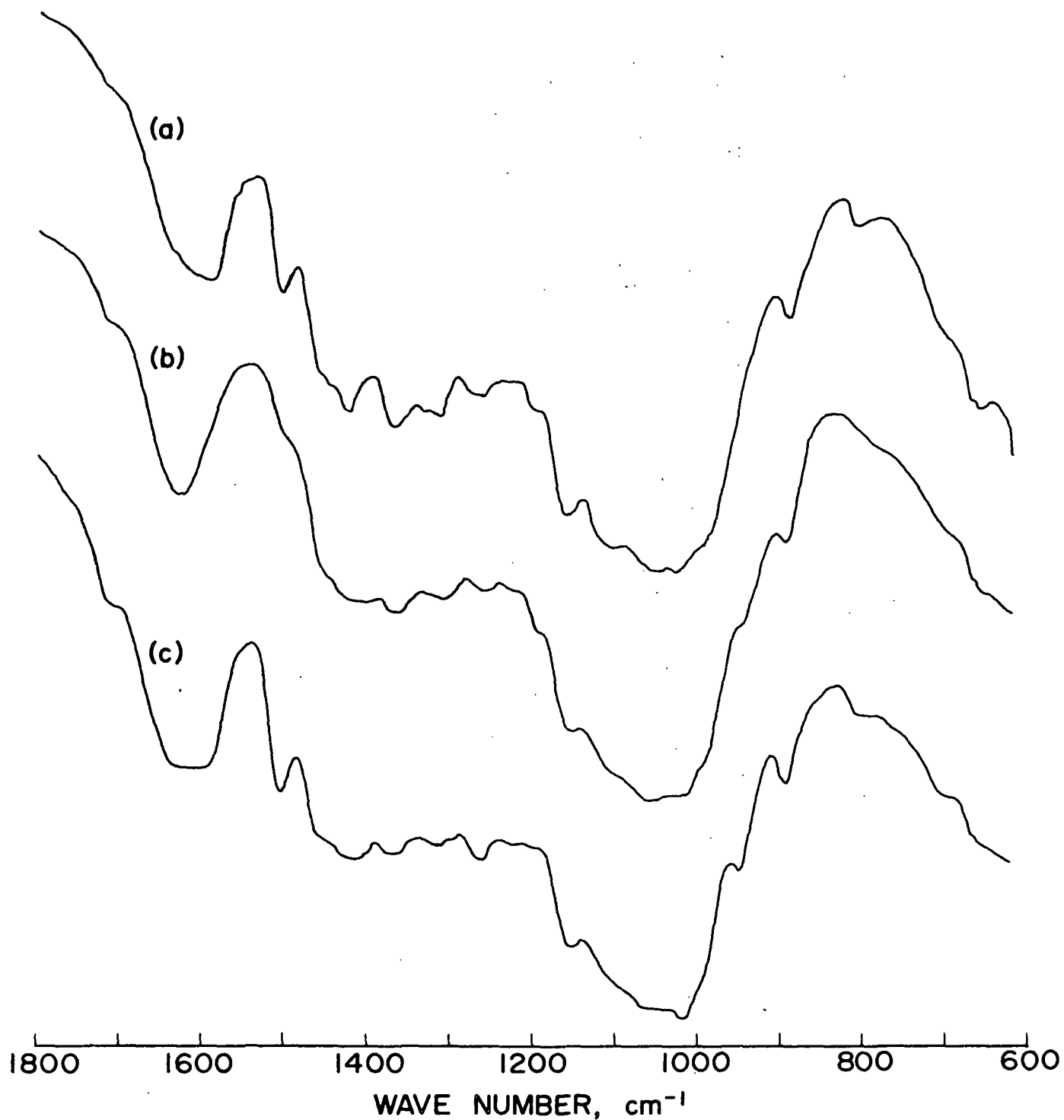


Figure 2. Infrared spectra (1800-600 cm⁻¹) of (a) kraft pulp, 12.6% Klason lignin, (b) regenerated portion after partial pulp dissolution by DMSO/PF, and (c) undissolved material.

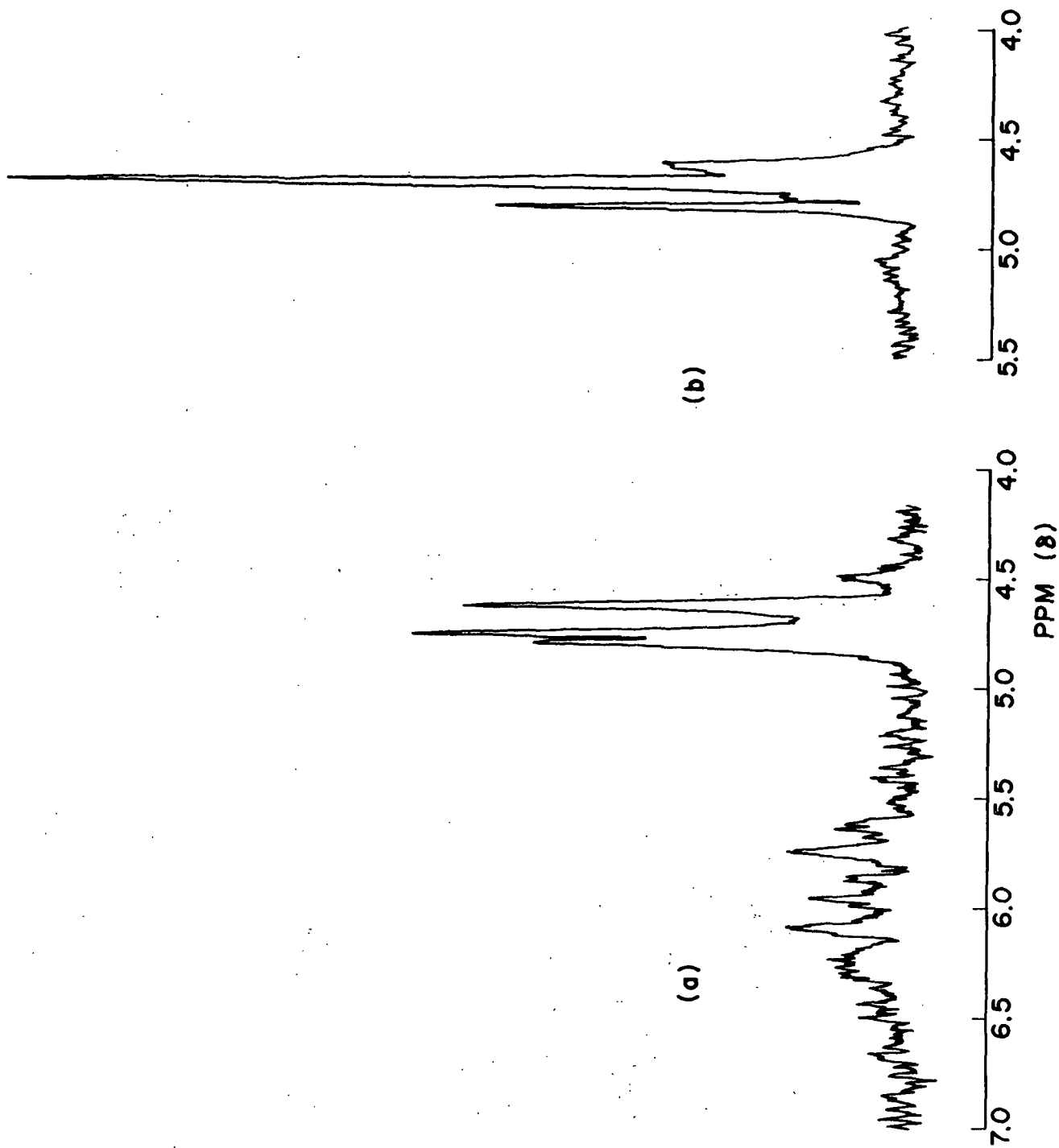


Figure 3. Nuclear magnetic resonance spectra of DMSO-d₆/PF system (a) before and (b) after addition of D₂O.

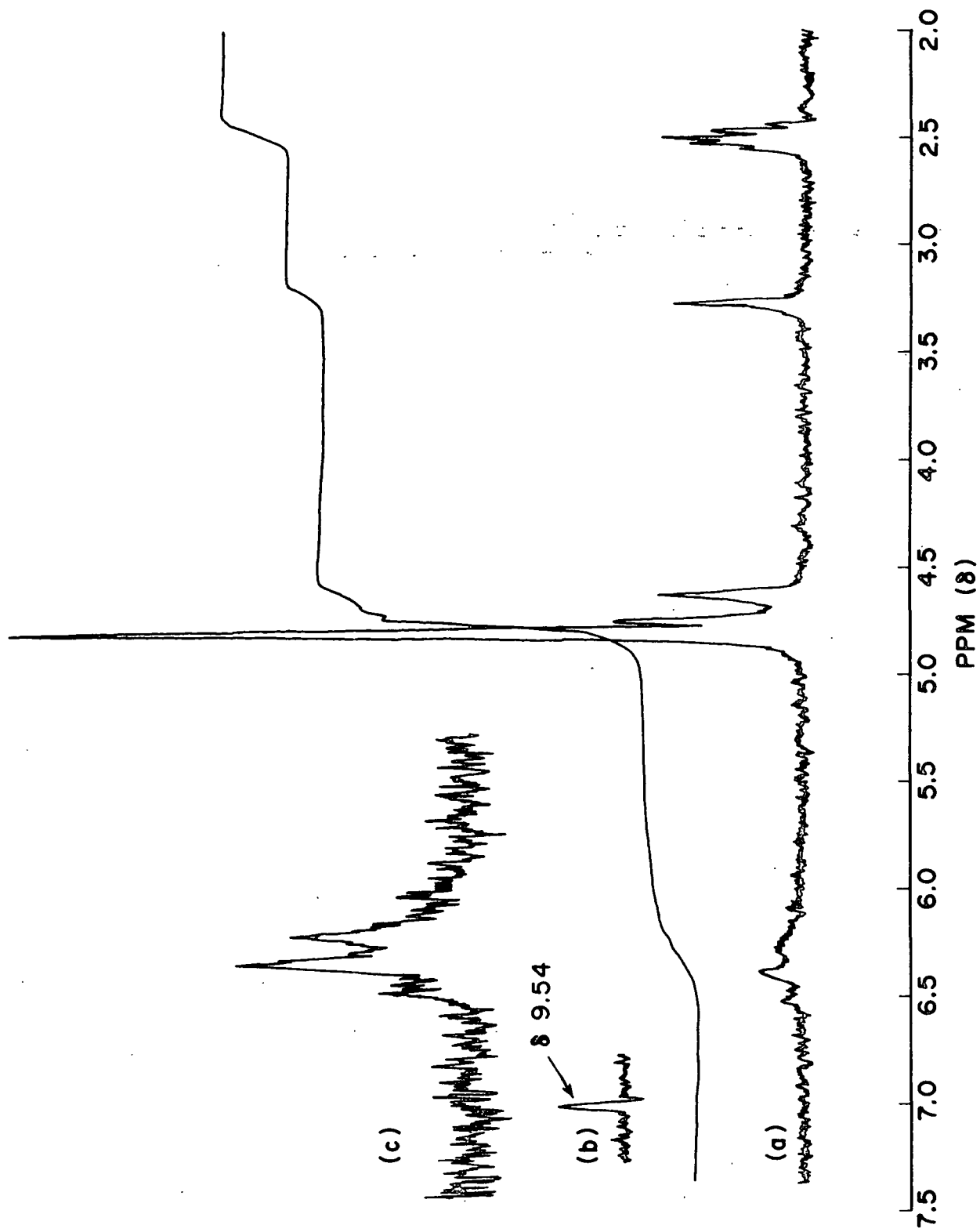


Figure 4. Nuclear magnetic resonance spectra of DMSO- d_6 /PF system after heating 2.0 min. to 110°C: (a) normal spectrum, amplitude 32 and sweep time 250 sec, (b) H_2CO signal, and (c) OH region at amplitude 200 and sweep time 500 sec.

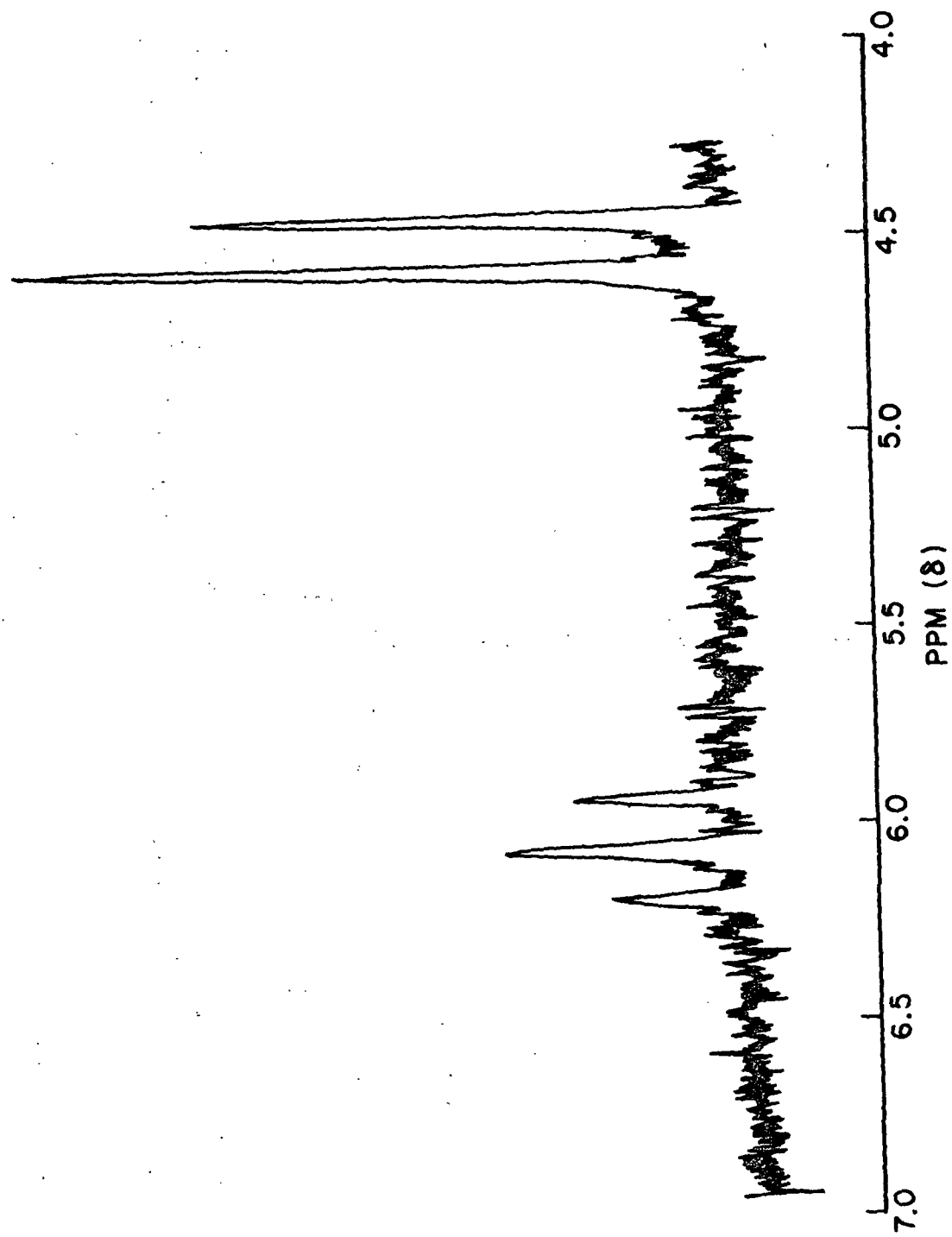


Figure 5. Nuclear magnetic resonance spectrum of DMSO-d₆/PP system after reaction with methanol.

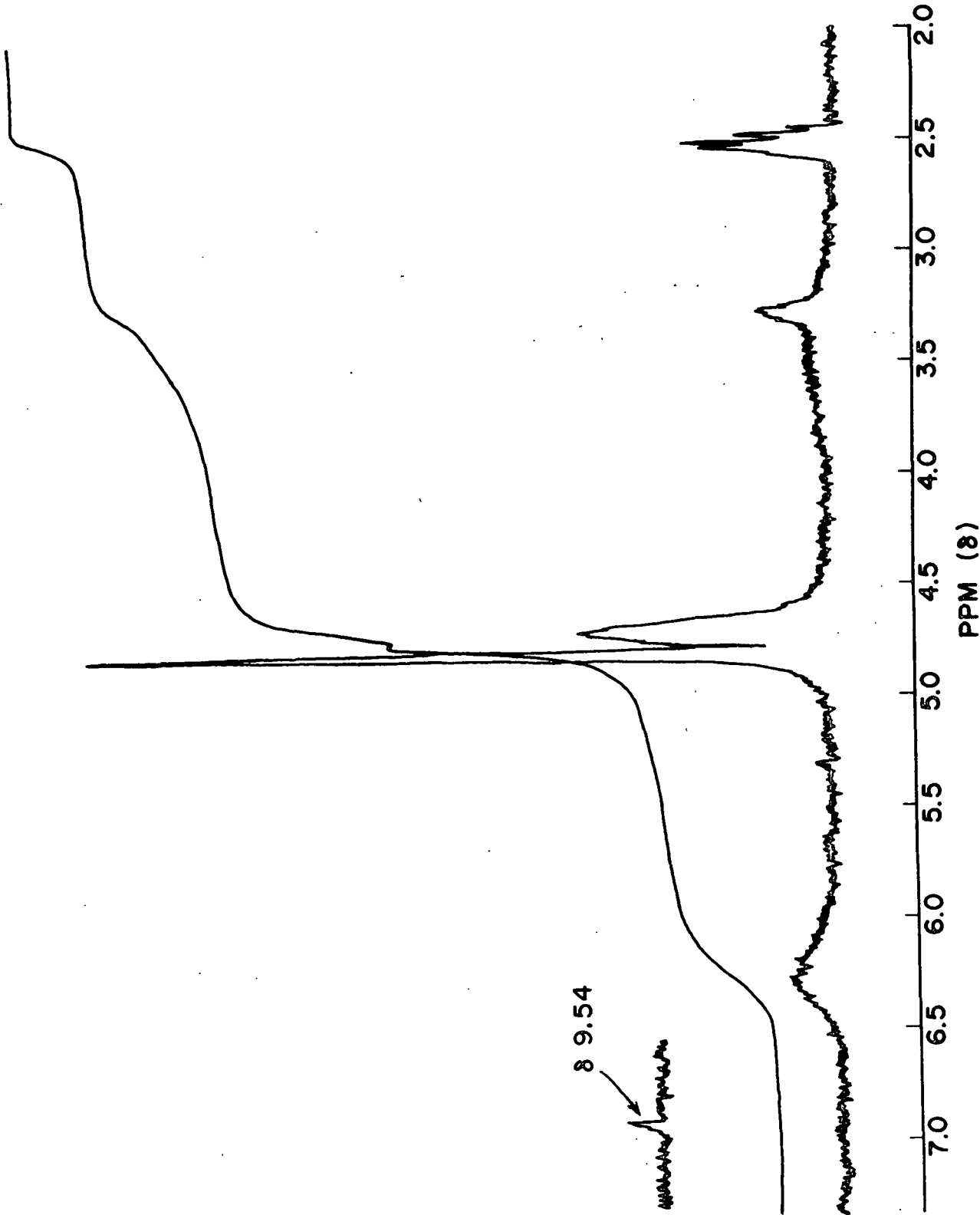


Figure 6. Nuclear magnetic resonance spectrum of DMSO- d_6 /PF solution of cellulose (average DP 16.7).

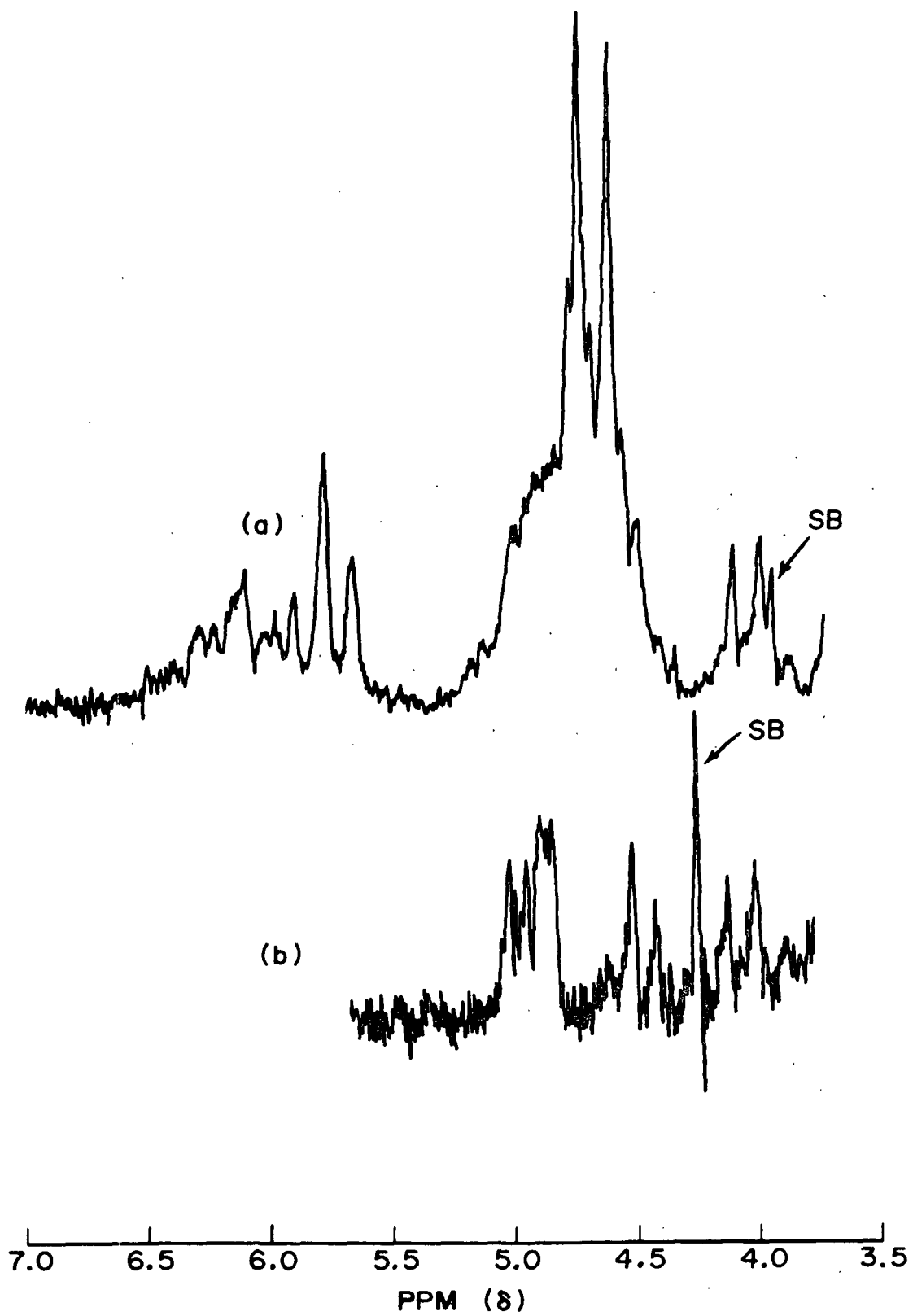


Figure 7. Nuclear magnetic resonance spectrum of solutions of methyl β-D-glucopyranoside in (a) DMSO-d₆/PF and (b) DMSO-d₆.

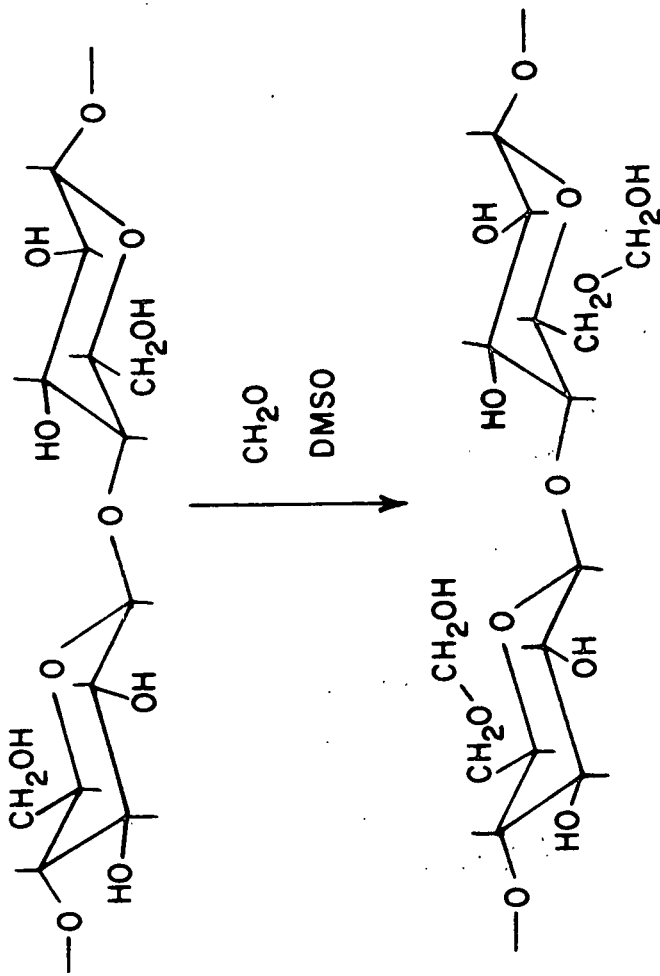


Figure 8. Mechanism of cellulose dissolution in DMSO/PF: formation of methylol cellulose.

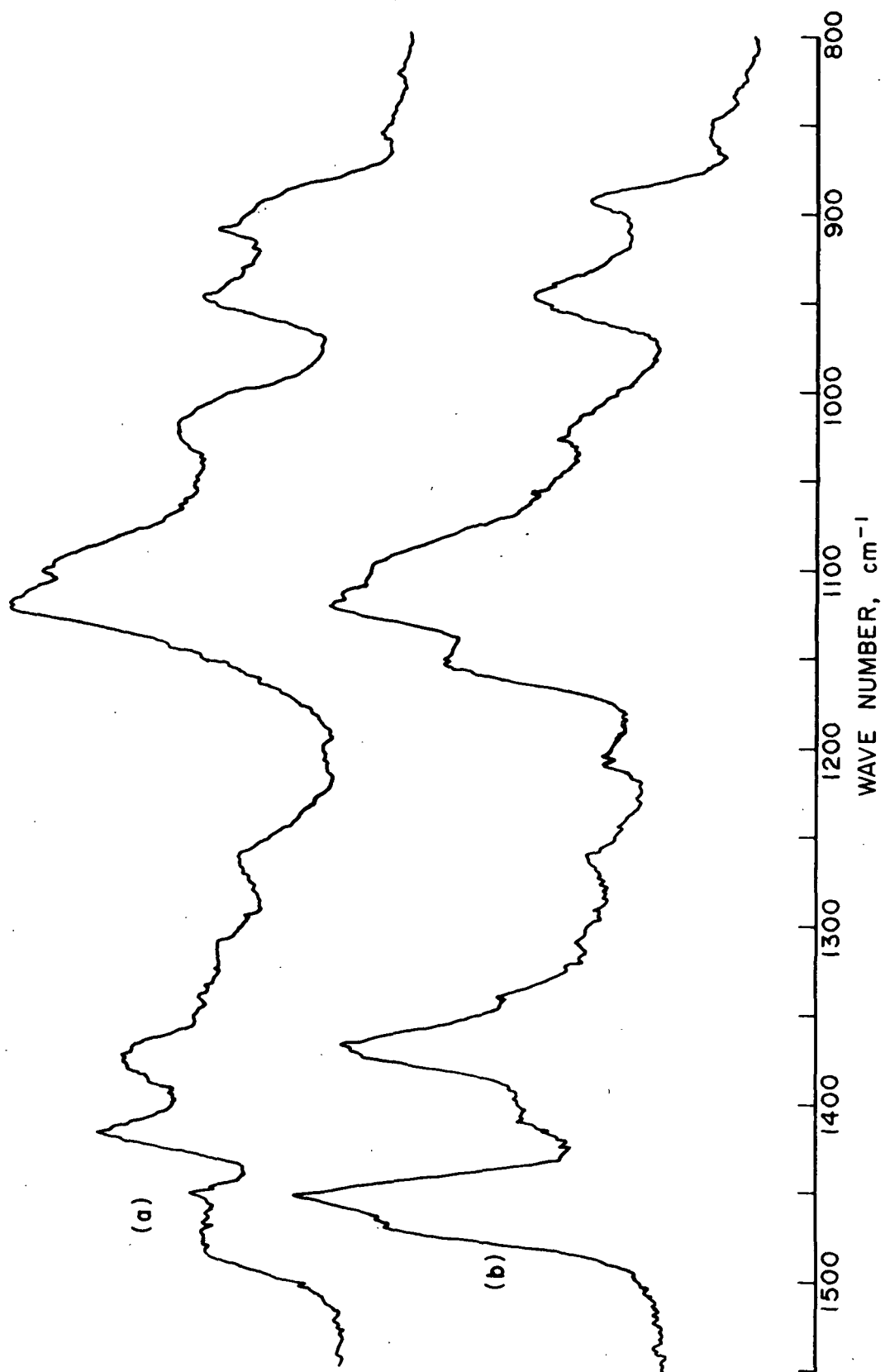


Figure 9. Laser Raman spectra (1550-800 cm⁻¹) of (a) methylol cellulose and (b) methyl cellulose.

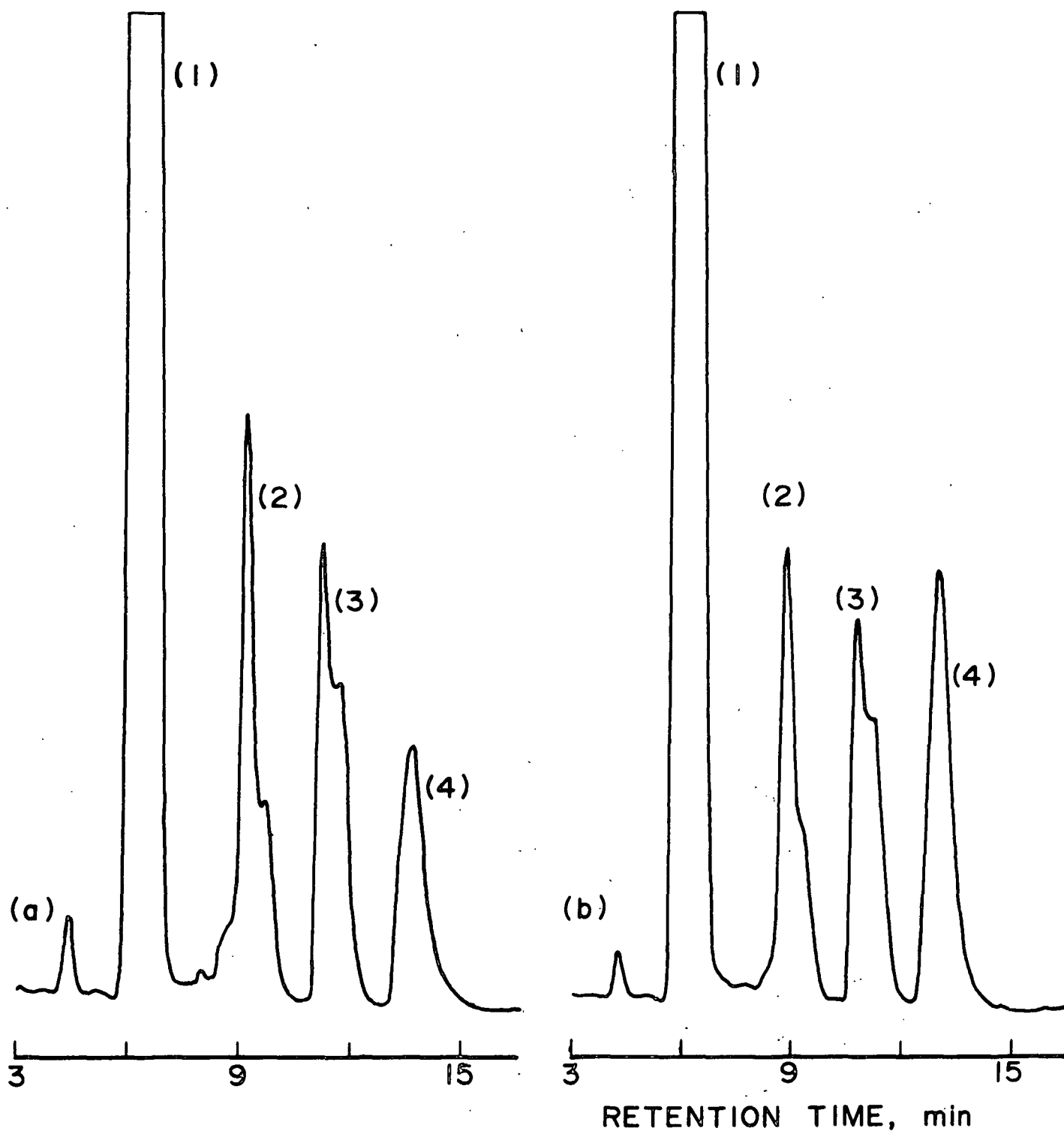


Figure 10. Gas chromatograms after hydrolysis of carboxymethyl cellulose prepared in DMSO/PF at (a) 20°C and (b) 50°C. Peaks shown represent (1) glucose, (2) 3-O-carboxymethyl glucose, (3) 2-O-carboxymethyl glucose, and (4) 6-O-carboxymethyl glucose, all as TMS derivatives.