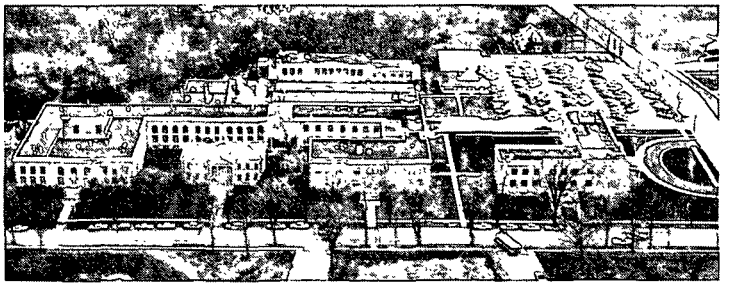

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RAMAN SPECTRA OF CELLULOSES

JAMES H. WILEY AND RAJAI H. ATALLA

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James H. Wiley and Rajai H. Atalla

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Raman Spectra of Celluloses

James H. Wiley and Rajai H. Atalla

The Institute of Paper Chemistry
Appleton, Wisconsin 54912

An investigation to study molecular orientation and polymorphy in cellulose fibers, and to further assign the bands in the vibrational spectrum of cellulose was conducted utilizing the Raman microprobe. The microprobe allows spectra to be recorded from domains as small as 1 micrometer and thereby greatly increases the potential of Raman spectroscopy as a tool for studying the structure of cellulose fibers. In the band assignment work, spectra were recorded from oriented fibers by varying the polarization of the incident light relative to the fiber axis. Analysis of the band intensities revealed new information about the directional character of the vibrational displacements. This information was used in conjunction with the spectra of deuterated celluloses and normal coordinate analyses of cellulose model compounds to make assignments.

Cellulose polymorphy was studied by comparing the spectra of Valonia, ramie, and mercerized ramie. It appears that the conformation of the cellulose backbone is the same in Valonia and ramie celluloses, but that the hydrogen bonding patterns are different. Mercerized cellulose and native celluloses differ in both their backbone conformations and hydrogen bonding patterns.

Cellulose orientation in the plane perpendicular to the chain axis was studied by recording spectra of ramie cross sections with different polarizations of the incident light relative to the cell wall surface. The intensities are consistent with random cellulose orientation. It appears, however, that the sample preparation techniques can influence the cellulose orientation. Therefore, further studies will be necessary to understand the molecular orientation in cellulose fibers.

Many questions about the molecular organization in plant cell walls remain unanswered. A new instrument, the Raman microprobe, has

provided a novel method for investigating plant cell wall structure. The objective in this work was to study the structure of the principal cell wall component, cellulose, using the Raman microprobe's unique capabilities. The investigation had two phases. In the first phase, the information made acessible by the microprobe was used to advance the assignment of the Raman spectrum of cellulose. In the second phase, the microprobe was used to study molecular orientation and polymorphy in cellulose fibers. The major results from both phases of this investigation will be discussed in this report.

Background

Raman Spectra of Cellulose. In laser excited Raman spectroscopy, a sample is exposed to monochromatic light, and the scattered light is analyzed. The frequency of a small fraction of the scattered light is shifted relative to the exciting light. The magnitude of the frequency shift corresponds to the vibrational frequencies of the molecules in the sample. Therefore, Raman spectroscopy provides information similar to that provided by infrared spectroscopy.

Both Raman and infrared spectroscopy yield information about chemical functionality, molecular conformation, and hydrogen bonding. Raman spectroscopy, however, has some important advantages. Highly polar bond systems, which result in intense infrared bands, have relatively low polarizabilities and, hence, weak Raman intensities. Water, therefore has very weak Raman bands and does not interfere with the spectrum of cellulose. In the Raman technique, control of the polarization of the exciting light coupled with analysis of the polarization of the scattered light can facilitate assignment of the spectra and provide information about molecular orientation. In infrared spectra, the attenuation of the incident beam is measured. This means that any processes other than absorption which cause attenuation of the incident beam are problematic. Since the refractive index of the sample will often go through large excursions in the neighborhood of absorption bands, the scattering losses will vary greatly with frequency over the infrared region. The variations in the refractive index can cause anomalous features in infrared spectra. In Raman spectroscopy, refractive index variations are not a problem, since the excitation frequency is far removed from any absorption bands. Therefore, it is easier to record Raman rather than infrared spectra from samples such as cellulose which scatter light strongly.

Raman Microprobe. A recent innovation in Raman spectroscopy was the development of the Raman microprobe. The microprobe is a specially designed optical microscope coupled with a conventional Raman spectrometer. The microscope performs two key functions. It focuses the exciting light on the sample down to a diameter of one micrometer; then it gathers the scattered light and transmits it to the entrance slit of the spectrometer. Since the microprobe acquires spectra from such small domains, the structural heterogeneity of the domains is greatly reduced relative to the domains examined in conventional Raman spectroscopy. The microprobe makes it possible to identify the morphological features from which

spectra are recorded so that orientation, composition, and structure can be studied as a function of morphology.

The special attributes of the microprobe make new information available. This investigation utilized the ability of the microprobe to record spectra from morphologically homogeneous domains, using polarized light to derive new information for assigning the Raman spectrum of cellulose. These assignments along with other spectral information obtained with the microprobe were then used to study polymorphy within the cellulose I family and cellulose orientation as a function of morphology.

Band Assignments. In order for Raman spectroscopy to provide structural information, the assignment of the spectra must be understood. The large number of vibrational degrees of freedom and low symmetry possessed by the cellulose molecule have made interpretation of the spectrum difficult. Given the complexity of the problem, a series of detailed normal coordinate analyses of model compounds were conducted in our laboratory to provide a basis for interpreting the vibrational spectrum of cellulose (1-8). The calculations showed that, except for the internal vibrations of the methylene groups, the modes below 1500 cm^{-1} are delocalized motions which are not adequately described by the group frequency approximation in which modes are assumed to be localized within certain chemical groups in the molecule.

Polymorphy. The two major allomorphs of cellulose, cellulose I and cellulose II, have been studied extensively. The question of polymorphy within the cellulose I (native cellulose) family has not received as much attention. Evidence has been reported, however, that the structure of native cellulose varies depending on the source. Early x-ray studies of cotton, ramie, linen, algal cellulose, and bacterial cellulose detected significant differences in the unit cell parameters (9). Based on electron diffractograms, Honjo and Watanabe (10) and others (11-13) concluded that the unit cell of algal cellulose is larger and has lower symmetry than the commonly accepted cell for cellulose I. Marrinan and Mann (14-15) and later Liang and Marchessault (16) observed that the infrared spectra of algal and bacterial cellulose differ from the spectra of ramie.

More recently, Atalla and VanderHart (17-18) have studied the solid-state ^{13}C NMR spectra of several forms of native cellulose. They concluded that native celluloses appear to be composites of two distinct crystalline forms of cellulose called I_α and I_β. The proportions of I_α and I_β in the composite varies depending on the source of the cellulose. In algal and bacterial cellulose, the I_α form dominates, whereas the I_β form dominates in ramie, cotton, and wood pulp. These results are consistent with the data from diffractometry and infrared spectroscopy in that algal and bacterial cellulose are similar to each other but different from other native celluloses.

The structural differences between I_α and I_β are not understood yet. Atalla (18) compared the Raman spectra of various native celluloses with different I_α to I_β ratios. He also compared the native cellulose spectra with the spectrum of cellulose II. The spectra of

the native celluloses are all similar to each other in the region most sensitive to cellulose conformation. The spectrum of cellulose II is quite different in this region. Therefore Atalla concluded that celluloses I_α and I_β have similar conformations but are packed in different lattices. In cellulose II, both the conformation and lattice are different from that of cellulose I.

Other workers (19-20) have interpreted these differences in the NMR spectra and other data in alternative ways. They believe that celluloses I and II have the same skeletal conformation but are packed in different lattices. In this theory, the differences within the cellulose I family are derived from the size of the unit cells. Valonia contains a larger 8 chain unit cell, whereas ramie contains a mixture of the 8 chain unit cell and the smaller Meyer and Misch unit cell. Therefore the interpretation of the NMR spectra remains controversial.

Orientation. The orientation of the cellulose chain axis in a number of different fibers has been studied in detail (21-22). Much less is known about the cellulose orientation in the plane perpendicular to the chain axis. The orientation in this plane is determined by the lateral arrangement of the microfibrils relative to each other. In algal celluloses, the evidence from x-ray and electron diffraction indicates that the microfibrils are arranged nonrandomly in the plane perpendicular to the chain axis (21-29). Preston (22) proposed the model shown in Figure 1 to explain his x-ray data. There are two different orientations of the microfibrils. The 002 planes in one set of microfibrils are approximately perpendicular to the 002 planes in the second set. In both sets of microfibrils, the 101 planes are oriented parallel to the cell wall surface (refer to Figure 1). Preston's model has been confirmed in more recent studies (29). In the remainder of this report, the type of orientation shown in Figure 1 will be referred to as alternating orientation.

Direct measurements of cellulose orientation in fibers have yielded conflicting results. Evidence from x-ray diffraction studies of wood samples suggested that the cellulose crystallites are arranged randomly in the plane perpendicular to the fiber axis (30-33). Raman spectroscopic studies of cotton fibers dried under tension, however, demonstrated that the methine C-H bonds are oriented preferentially perpendicular to the surface of the cell wall (34). Since the C-H bonds are perpendicular to the 002 plane, the orientation suggested by the Raman evidence differs from the alternating orientation in algal celluloses.

Overview of Experimental Method

In the spectra of nonrandomly oriented polymers, the intensity and polarization of the Raman scattered light are dependent on the polarization of the exciting light relative to the orientation of the molecules (35). If the orientation of the molecules is known, comparison of spectra recorded with different polarizations of the exciting light yields useful information about the directionality of the vibrational motions. Conversely, information about molecular orientation can be gained if the directionality of the vibrations is

known. In the present work, the major technique employed in the experiments was to compare spectra recorded with different polarizations of the incident laser beam relative to the morphology of the samples.

In all spectra recorded, precautions were taken to avoid complications associated with the dichroism inherent in the optics of the microscope and the monochromator. First, a polarization scrambler was inserted in the path of the Raman scattered light at the coupling between the microscope and the monochromator. Second, we did not change the polarization of the incident light directly but instead used a rotating stage to rotate the sample relative to the plane of polarization of the incident light.

Two classes of experiments were conducted. In both sets of experiments, fibers in which the cellulose chains are oriented parallel to the fiber axis were used. In the first class of experiments, the plane of polarization of the incident light was changed relative to the axis of the fibers by rotating the fibers around the optical axis of the microscope (see Figure 2a). The dependence of the band intensities on the polarization of the incident light was studied to determine the directional character of the vibrational motions. This information was used to advance the assignment of the Raman spectrum of cellulose. Spectra from Valonia, ramie, and mercerized ramie fibers, which have different allomorphic compositions, were compared to study the structural differences between the allomorphs.

In the second class of experiments, spectra were recorded from ramie fiber cross-sections. The plane of polarization of the incident light was changed relative to plane of the cell wall by rotating the cross-sections around the optical axis of the microscope axis (see Figure 2b). The information from these spectra was used to study the orientation of the cellulose in the plane perpendicular to the chain axis.

Results and Discussion

Assignment of the Vibrational Spectrum of Cellulose. Sets of spectra in which the orientation of the electric vector of the incident light was varied in 15 degree increments relative to the fiber axis were recorded. Figure 3 shows the set recorded from a fibrillar aggregate of Valonia macrophysa cellulose. Scanning electron micrographs showed that the aggregates are highly oriented bundles of fibrils. Therefore, the cellulose chains are parallel to the axis of the bundle. A set of spectra recorded from a ramie fiber is shown in Figure 4. In ramie, the cellulose chains are also approximately parallel to the fiber axis (21-22).

From the figures it is clear that the band intensities are strongly dependent on the polarization of the light. The intensities are related to the orientation of the electric vector by the following equation:

$$I = a + b\,(\cos^2\theta) + c\,(\cos^4\theta) \qquad (1)$$

where a, b, and c are constants related to scattering activities, and θ is the angle between the electric vector of the incident light

and the fiber axis. Equation 1 was derived by following Snyder's treatment (35) and assuming that the cellulose chains are parallel to the fiber axis, and that the chains are oriented randomly around their axes. Equation 1 was fitted to the data in Figure 3 and 4 by a linear regression technique. Equation 1 adequately described the observed data for bands which were well resolved. An example of the fit which could be achieved by this analysis is shown in Figure 5, where the observed and predicted peak heights are plotted against θ for the intense band at 1095 cm^{-1}. Bands which were weak and/or poorly resolved could not be fitted as well.

Based on the number and location of the maxima and minima in the intensity vs. θ curves, the bands in the Raman spectrum of native cellulose were divided into four categories. Table 1 summarizes the band classifications for those bands which were resolved well enough to be analyzed. The classifications provide information about the directional character of the vibrations. The four categories are described as follows:

1) A_0 bands are most intense when the incident electric vector is parallel to the cellulose chain axis. Therefore, the maximum change in polarizability associated with the vibrations is parallel to the chain axis. The intensity vs. θ curves contain a single maximum and minimum.
2) A_{90} bands are most intense when the incident electric vector is perpendicular to the chain axis. The maximum change polarizability is perpendicular to the chain axis. These bands also exhibit a single maximum and minimum in the intensity vs. θ curves.
3) B_0 bands are most intense when the incident electric vector is parallel to the chain axis. As was the case with A_0 bands, the maximum change in polarizability is parallel to the chain axis. In the intensity vs. θ curves, however, these bands exhibit two maxima and a single minimum. The multiple maxima may result from accidentally degenerate modes which have maxima at 0 and 90° or from modes in which some of elements of the polarizability decrease during the vibration.
4) B_{90} bands are most intense when the incident electric vector is perpendicular to the chain axis. The maximum change in polarizability is perpendicular to the chain axis. These bands also exhibit two maxima and a single minima in the intensity vs. polarization curves.

As a supplement to the intensity work, the nature of the vibrations was also studied by recording spectra from deuterated celluloses. By comparing the spectrum of fully deuterated cellulose with that of normal cellulose, the vibrations involving the hydrogen atoms can be separated from the pure skeletal motions. Figure 6 is the spectrum of carbon-deuterated bacterial cellulose. This sample was kindly provided by Dr. H. L. Crespi. It was prepared by growing Acetobacter xylinum in deuterated growth media (36). The residual intensity in the O-H and C-H stretching regions indicates that the cellulose is not fully deuterated. We also recorded Raman spectra

of oriented samples of partially deuterated cellulose with the electric vector both parallel and perpendicular to the chain axis. Based on these studies, the deuteration sensitivity for several of the bands was determined. This information is also listed in Table I.

Based on the intensity studies, deuterated cellulose spectra, and normal coordinate analyses of model compounds (7-8), the assignment of the bands in the vibrational spectrum of cellulose was advanced. The information is summarized in Table 1. A detailed discussion of the band assignments is beyond the scope of this report and will be given elsewhere (37). A brief overview of the assignments will be given here. The frequency region between 600 and 250 cm^{-1} is dominated by bending motions of the cellulose skeleton. These are complex modes which are very delocalized and often involve motion at the glycosidic linkage. The frequencies, especially between 400 and 300 cm^{-1}, are sensitive to the conformation of the anhydroglucose residues about the linkage (8). In the modes between 900 and 1200 cm^{-1}, CC and CO stretching motions are dominant. This region contains very intense bands. The modes between 1200 and 1500 cm^{-1} involve methylene, methine, and hydroxyl bending motions. Although the modes in this region are generally delocalized motions, the HCH bending motion is isolated and behaves as a group mode. In the regions between 2700 and 3000 cm^{-1} and 3200 and 3500 cm^{-1}, the C-H and O-H stretching motions occur. These motions behave as pure group vibrations. Although the assignments do not provide a complete description of the vibrational motions, they serve to increase our understanding of the cellulose vibrational spectrum.

Polymorphy. Cellulose polymorphy within the cellulose I family was studied by comparing the Raman spectra of Valonia and ramie cellulose. Solid state NMR spectra indicate that the I_α form predominates in Valonia while the I_β form predominates in ramie (17-18). The cellulose I spectra were also compared with spectra of cellulose II recorded from a mercerized ramie fiber. Figures 7 and 8 show the Raman spectra of these three celluloses. Spectra were recorded with the electric vector of the incident light parallel and perpendicular to the chain axis. These spectra can be divided into two regions. The region below 1600 cm^{-1} (Figure 7) is most sensitive to the conformation of the cellulose backbone (especially below 700 cm^{-1}). The higher frequency region, above 2700 cm^{-1} (Figure 8), is more sensitive to hydrogen bonding.

In the low frequency region (Figure 7), there are only minor differences between the spectra of native ramie and Valonia. The peaks in the Valonia spectra are narrower and better resolved. The reason for this is probably the larger size of the crystallites in Valonia cellulose (38-39). When the crystallites are larger, the environment of the molecules is more homogeneous. Therefore, the vibrational energy of the molecules is more uniform, resulting in narrower bands.

The most significant difference between the two native cellulose spectra in the low frequency region is that the intensity of the peak at 913 cm^{-1} is greater in the ramie spectra. This peak is also more intense in the spectrum of bacterial cellulose than in the

Valonia spectra. Since bacterial cellulose has approximately the same I_α to I_β ratio as Valonia (17-18), the intensity of this peak does not appear to be related to structural differences between I_α and I_β. Instead, the intensity of this peak appears to be inversely correlated with the size of the crystallites. It is very weak in the spectra of Valonia which has very large crystallites, but it is stronger in the spectra of ramie and bacterial cellulose which both have smaller crystallites (38-39).

The differences between the spectra of ramie and Valonia are quite small compared to the differences between native cellulose and cellulose II (see Figure 7). In the spectra of ramie and Valonia, the different peak widths and relative intensities can be attributed to the difference in the crystallite sizes. In the spectrum of cellulose II, however, the frequency and number of peaks is significantly different. In previous publications, the differences between the spectra of celluloses I and II have been interpreted as evidence for different conformations in celluloses I and II (40-41). The spectral differences which are indicative of conformational change are not observed in the spectra of ramie and Valonia. Since ramie and Valonia have different I_α to I_β ratios, it would appear that celluloses I_α and I_β must have similar molecular conformations.

In the C-H stretching region (Figure 8, 2700-3000 cm^{-1}), the primary difference between the spectra of ramie and Valonia is the broadness of the peaks. The peaks in the ramie spectra are broader as was the case in the low frequency region presumably due to the smaller crystallite size. In the spectra of mercerized ramie, the C-H stretching region differs slightly from that in the native celluloses but the differences are not as large as those in the low frequency region.

In the O-H stretching region (3200-3600 cm^{-1}), however, significant differences are observed between all three celluloses. These differences are most prominent in the spectra recorded with the electric vector parallel to the fiber axis (Figure 8a-c). The frequency as well as the broadness of the peaks varies in this region. The spectra of Valonia cellulose have a peak at 3231 cm^{-1} that is not observed in the ramie spectra. The spectra of native ramie on the other hand, have a peak at 3429 cm^{-1} that is not observed in Valonia. The spectrum of mercerized ramie recorded with the electric vector parallel has two sharp peaks at frequencies above those observed in the native celluloses. The differences in the O-H region between Valonia, ramie, and mercerized ramie suggest that the hydrogen bonding patterns are different in each of these celluloses. In summary, the Raman spectra indicate that celluloses I_α and I_β exhibit different hydrogen bonding patterns but have similar molecular conformations. Celluloses I and II have different molecular conformations as well as different hydrogen bonding patterns.

Cellulose Orientation. The orientation of the cellulose molecules in the plane perpendicular to the chain axis was studied by using the microprobe to record spectra of ramie fiber cross sections. Figure 9 shows spectra recorded with the electric vector of the exciting light tangential, perpendicular, and at 45° to the cell wall surface. If the cellulose orientation in the plane perpendicular to the fiber axis is anisotropic, then the intensities

should differ in the cross-section spectra recorded with different orientations of the incident electric vector. With the exception of the peaks at 1095 and 1123 cm^{-1}, the relative peak intensities in the cross-section spectra did not vary noticeably as the polarization of the incident light was changed (see Figure 9). The insensitivity of the majority of the bands to the orientation of incident electric vector is not consistent with either a preferential orientation of the methines perpendicular to the cell wall surface or the alternating type of orientation found in algal celluloses.

The variation in the relative intensities of the 1095 and 1123 cm^{-1} bands between the 0° and 45° spectra suggests anisotropy in the cellulose orientation. Table I shows that these peaks are skeletal stretching modes that are most intense when the electric vector of the incident light is parallel to the chain axis. Since the 1095 cm^{-1} peak is very sensitive to the orientation of the incident electric vector relative to the chain axis, the intensity variation suggests that the plane of sectioning was not exactly perpendicular to the cellulose chain axes so that the chains are tilted relative to the plane of sectioning.

If the cellulose is oriented randomly in the plane perpendicular to the chain axis, then the band intensities would be the same regardless of whether the incident electric vector was parallel, perpendicular, or 45° to the cell wall surface. The cross-section spectra, therefore, are consistent with random cellulose orientation in the plane perpendicular to the chain axis. These results conflict with our earlier spectra of tension dried cotton fibers (34) that indicated the methines were oriented preferentially perpendicular to the cell wall surface. More recent spectra of cotton fibers have shown that if the fibers are not dried under tension, the methine orientation is random in the plane perpendicular to the chain axis. Therefore, it appears the cellulose orientation can be influenced by the sample preparation methods. Since microtoming exerts large forces on the fibers, it is also possible that the cellulose orientation could have been disrupted during the preparation of the cross-sections. Further experiments will be necessary to understand the factors which influence the cellulose orientation.

Conclusions

Based on the number and location of the maxima and minima in the relationship between the band intensities and the polarization of the incident light relative to the chain axis, the bands in the Raman spectrum of cellulose could be divided into four groups. The about the direction of the vibrational motions in cellulose. The directions of the vibrations are such that the major change in polarizability associated with the motions is either parallel or perpendicular to the chain axis. Raman spectra recorded from deuterated celluloses allowed the vibrational modes involving C-H and O-H motions to be identified. These spectra demonstrated that most of the modes are complex coupled vibrations. Normal coordinate analyses of cellulose model compounds were done to determine the types of motion most likely to occur in each region of the spectrum. The calculations also suggested that the vibrational motions are very complex. The information from the normal coordinate calculations,

intensity studies, and spectra of deuterated celluloses was used to advance the assignment of the cellulose vibrational spectrum.

Comparison of the Raman spectra of Valonia, ramie, and mercerized ramie indicates that the conformation of the cellulose backbone is similar in Valonia and native ramie but different in mercerized ramie. The hydrogen bonding patterns, however, are different in Valonia and native ramie as well as in mercerized ramie.

Spectra recorded from ramie cross-sections suggest that the cellulose is oriented randomly in the plane perpendicular to the chain axis. It appears, however, that the sample preparation methods can influence the cellulose orientation. Therefore, further studies will be necessary to characterize the molecular orientation in cellulose fibers.

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Figure 1. The cellulose orientation in the plane perpendicular to the chain axis found in algal celluloses.

Figure 2. Microprobe experiments in which the polarization of the exciting light was varied relative to the geometry of the samples.

Figure 3. Polarized Raman spectra from a fibrillar aggregate of Valonia cellulose. The angle between the electric vector and the chain axis was varied from 0° to 90°.

Figure 4. Polarized Raman spectra from a ramie fiber. The angle between the electric vector and the chain axis was varied from 0° to 90°.

Figure 5. The dependence of intensity on the polarization of the incident light for the band at 1095 cm^{-1} in the spectra of Valonia.

Figure 6. Raman spectrum of deuterated bacterial cellulose.

Figure 7. Comparison of the Raman spectra from Valonia, ramie, and mercerized ramie (low frequency region). Spectra were recorded with the electric vector at both 0° and 90°.

Figure 8. Comparison of the Raman spectra from Valonia, ramie, and mercerized ramie (high frequency region). Spectra were recorded with the electric vector at both 0° and 90°.

Figure 9. Polarized Raman spectra of a ramie cross section. The angle between the electric vector and the cell wall surface was varied from 0° to 90°.

Table 1. Summary of intensity maxima, deuteration sensitivities, and band assignments for the Raman spectra of Valonia and ramie.

Band Frequency[a] (cm^{-1})		Intensity Classification	Deuteration Sensitivity	Assignment
Valonia	Ramie			
331	331	A_0	weak	heavy atom bending, some
344	344	$B_?$	"	heavy atom stretching
381	380	$B_?$	"	"
437	437	$B_?$	"	"
459	458	B_0	"	"
520	519	A_{90}	"	"
913	910	B_0	?	HCC and HCO bending at C6
968	969	B_{90}	?	heavy atom (CC and CO)
997	995	A_0	?	stretching
1034	1035	A_0	?	"
1057	1057	A_0	?	"
1095	1095	A_0	weak	"
1118	1117	B_0	"	"
1123	1121	A_0	"	"
1152	1151	$B_?$	?	heavy atom stretching plus HCC and HCO bending
1279	1275	A_0	?	HCC and HCO bending
1292	1291	?	?	"
1334	1331	A_0	strong	"
1337	1337	A_0	"	HCC, HCO, and HOC bending
1378	1378	$B_?$	"	"
1406	1407	A_0	"	"
1455	1456	B_{90}	"	HCH and HOC bending
1477	1475	A_{90}	"	"
2868	2866	B_{90}	"	C-H and CH2 stretching
2885	2889	B_{90}	"	"
2941	2943	$B_?$	"	"
2965	2963	B_0	"	"
3291	3286	B_0	"	O-H stretching
3334	3335	$?_0$	"	"
3261	3363	$?_0$	"	"
3395	3402	B_0	"	"

[a]Only the bands resolved in both the Valonia and ramie are included in the table.

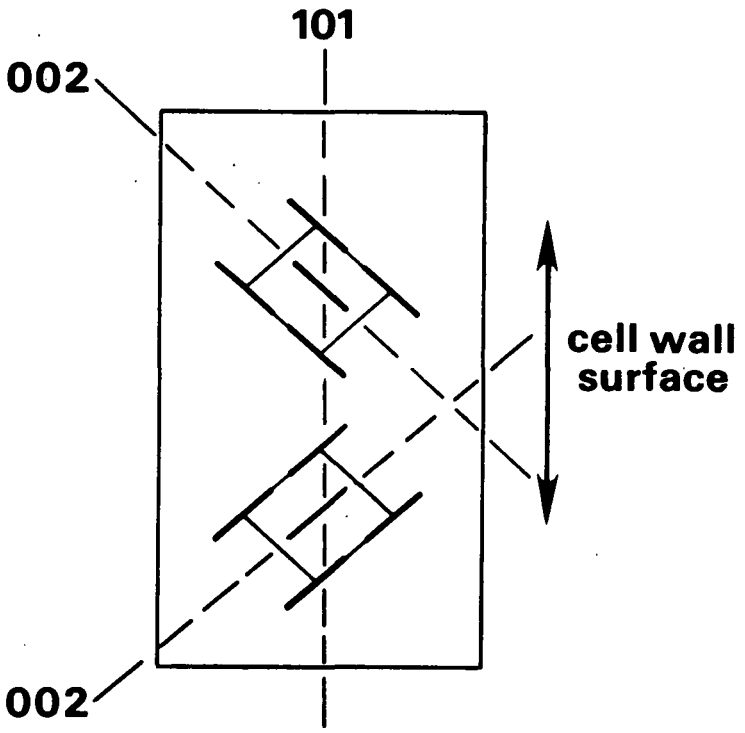

Figure 1. The cellulose orientation in the plane perpendicular to the chain axis found in algal celluloses.

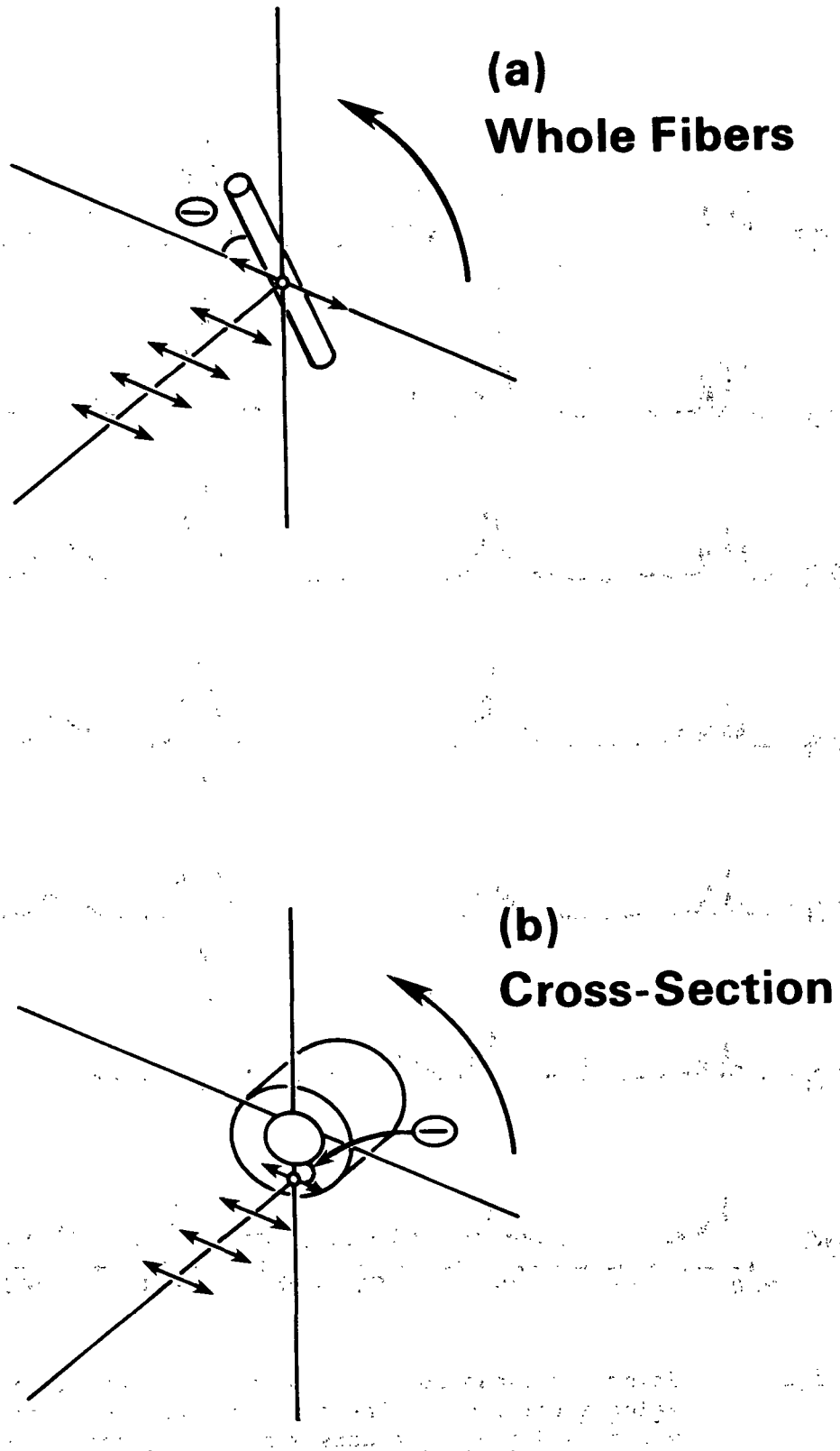

Figure 2. Microprobe experiments in which the polarization of the exciting light was varied relative to the geometry of the samples.

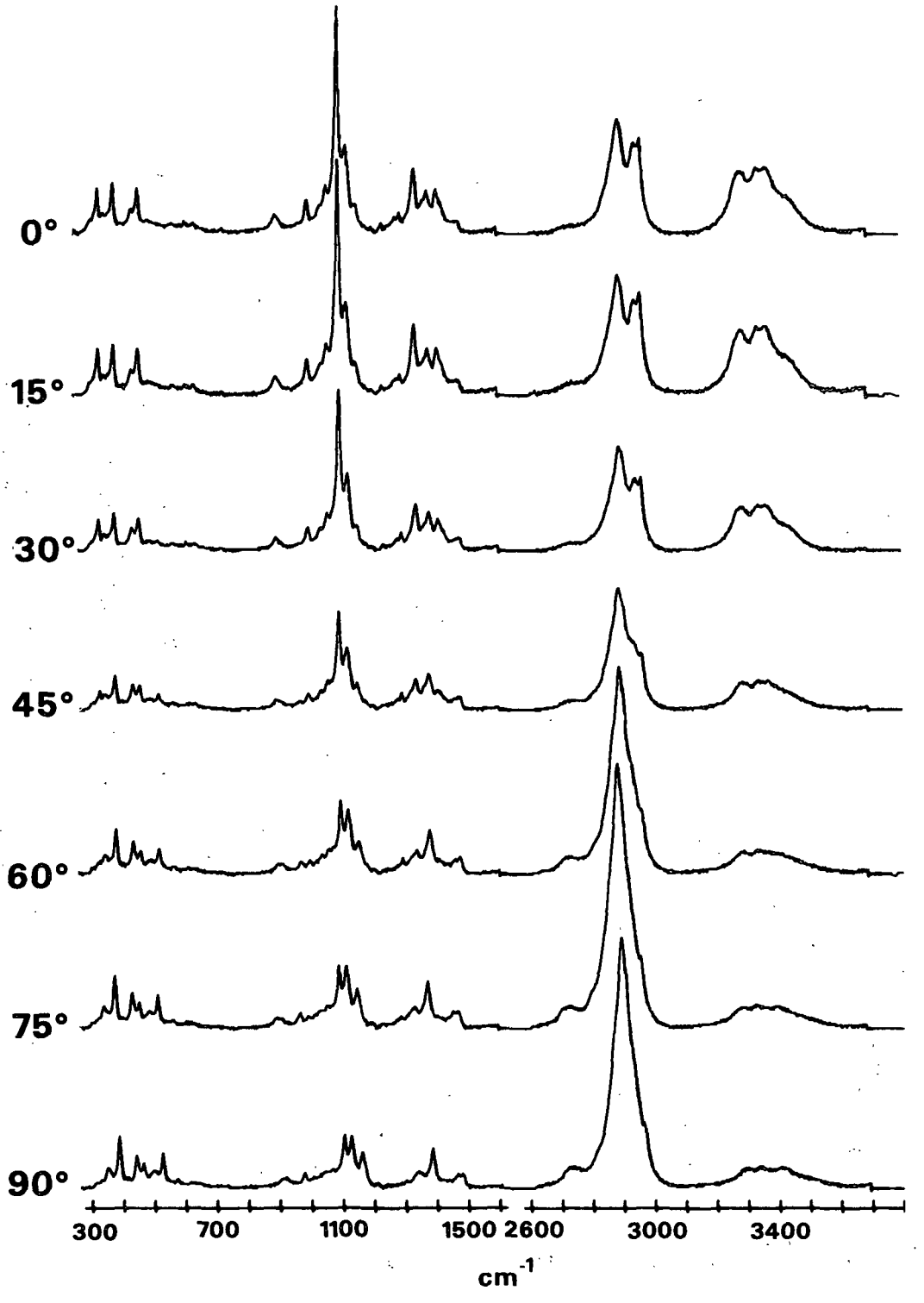

Figure 4. Polarized Raman spectra from a ramie fiber. The angle between the electric vector and the chain axis was varied from 0° to 90°.

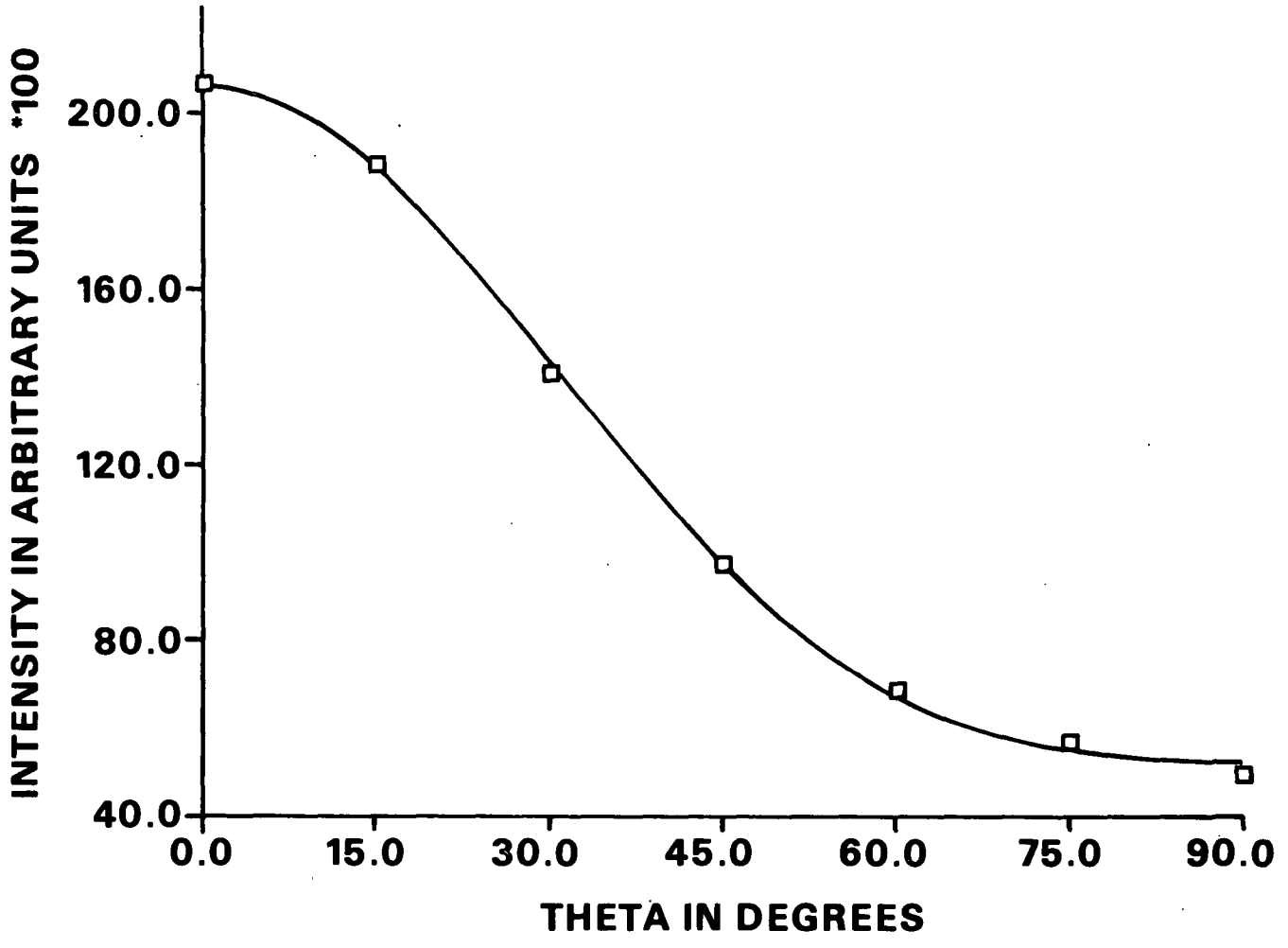

Figure 5. The dependence of intensity on the polarization of the incident light for the band at 1095 cm^{-1} in the spectra of Valonia.

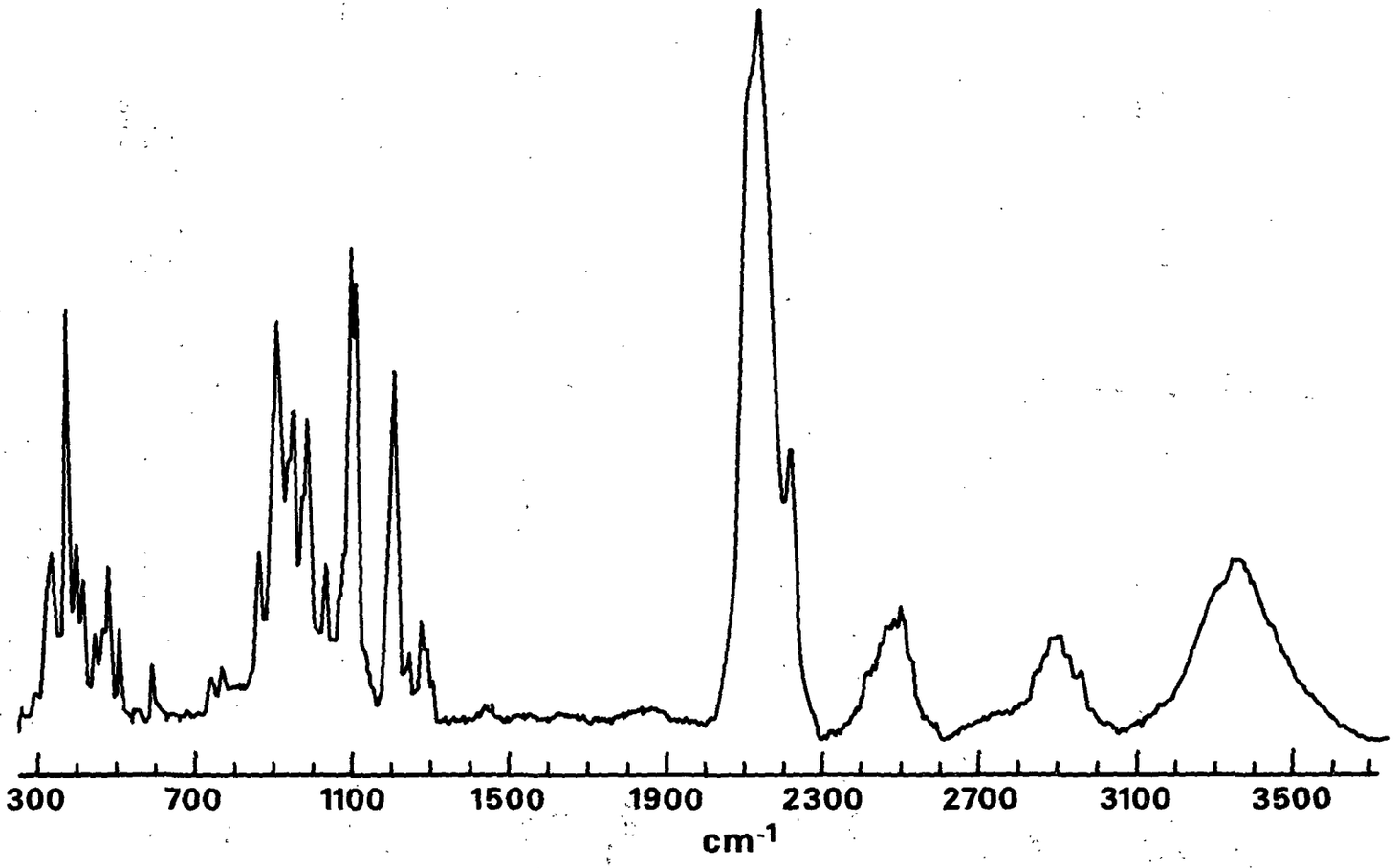

Figure 6. Raman spectrum of deuterated bacterial cellulose.

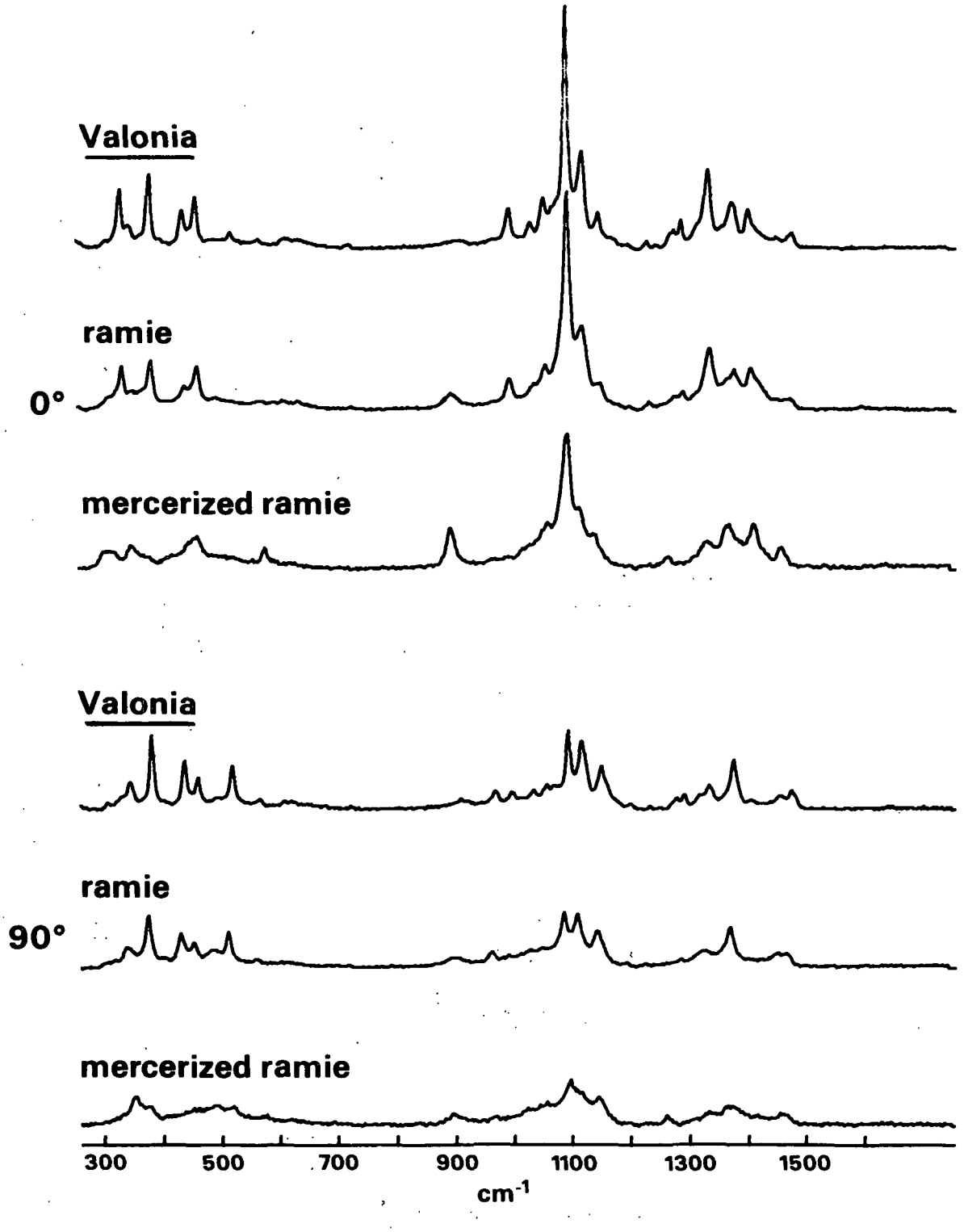

Figure 7. Comparison of the Raman spectra from Valonia, ramie, and mercerized ramie (low frequency region). Spectra were recorded with the electric vector at both 0° and 90°.

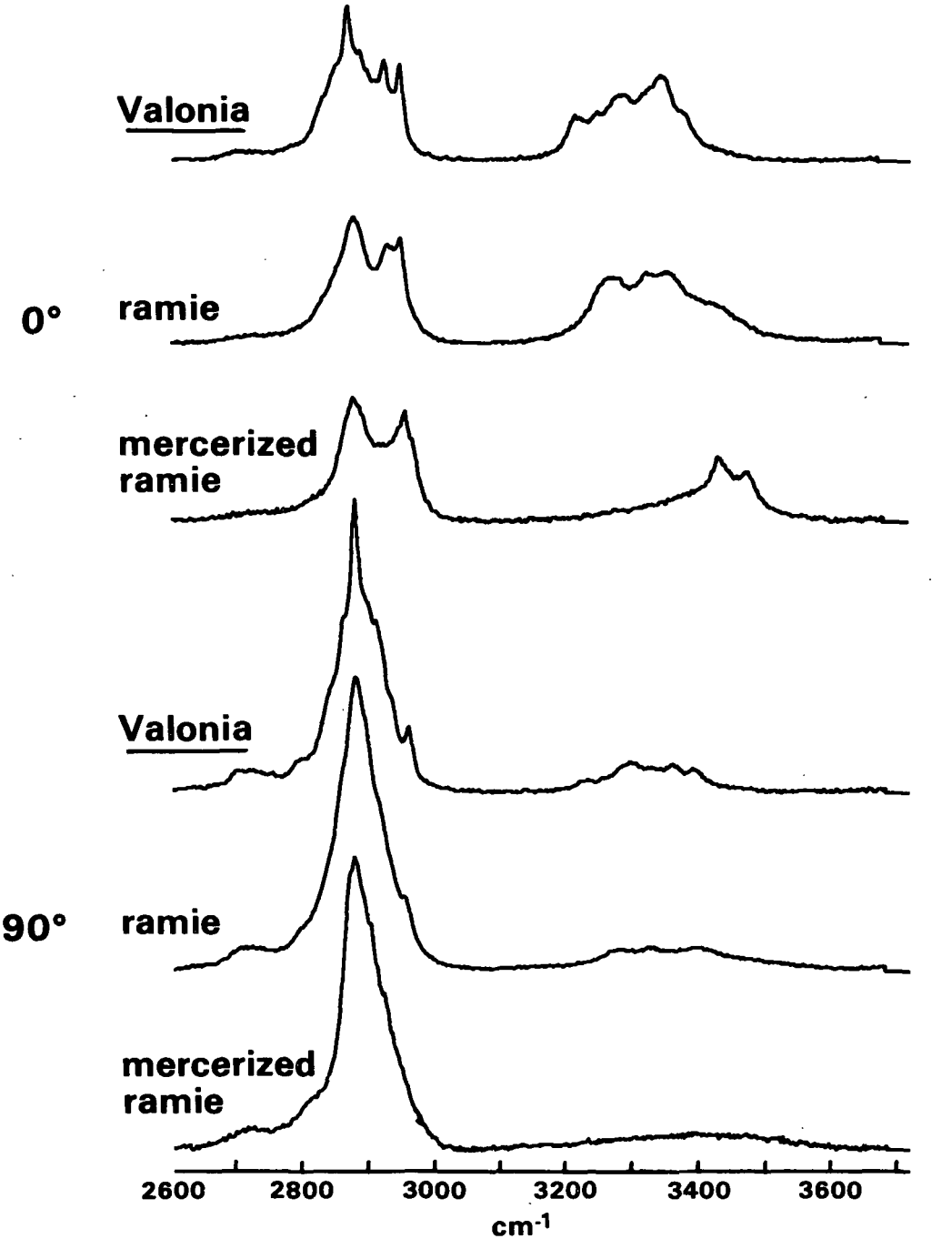

Figure 8. Comparison of the Raman spectra from Valonia, ramie, and mercerized ramie (high frequency region). Spectra were recorded with the electric vector at both 0° and 90°.

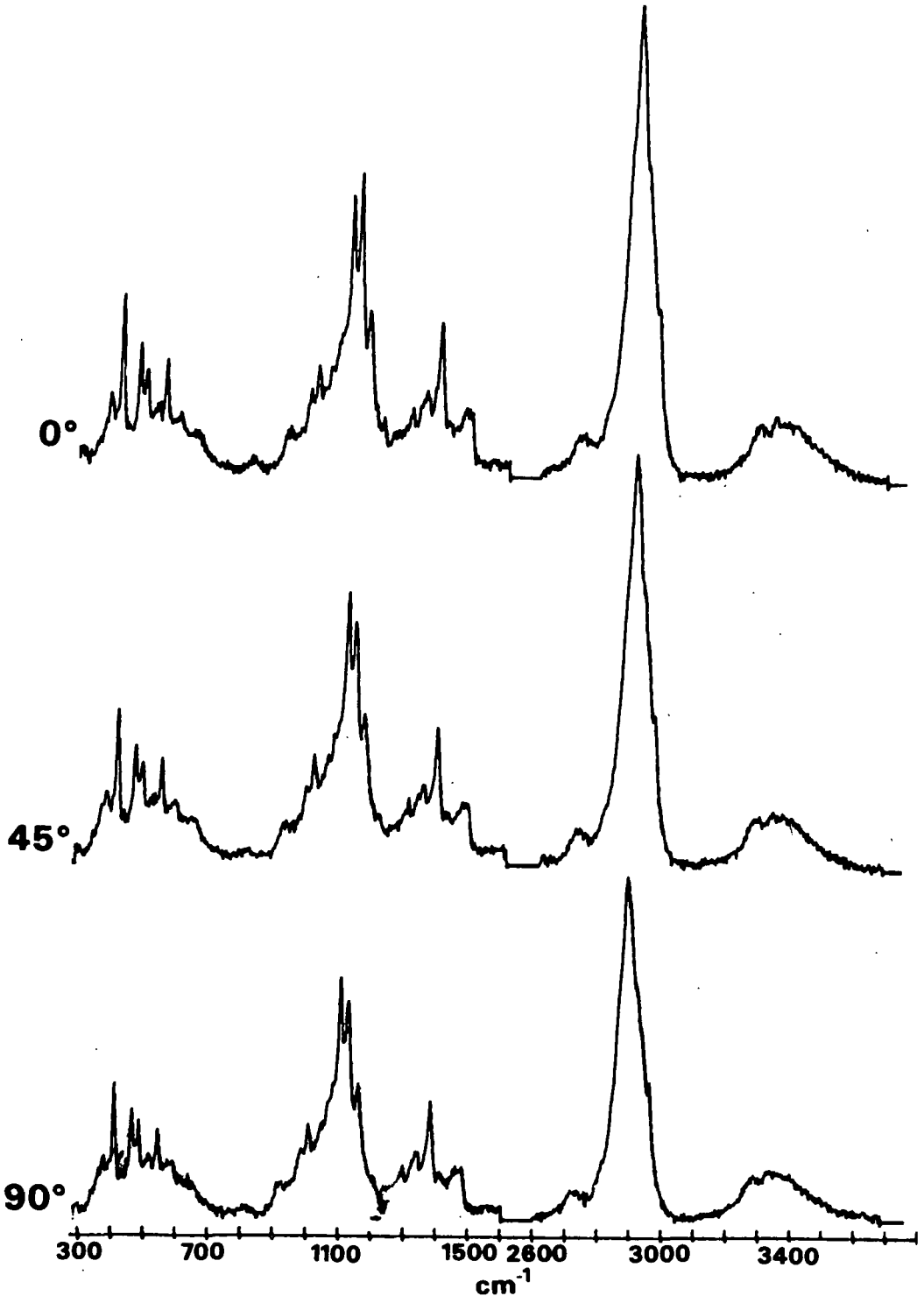

Figure 9. Polarized Raman spectra of a ramie cross section. The angle between the electric vector and the cell wall surface was varied from 0° to 90°.