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RAMAN SPECTRAL STUDIES OF POLYMORPHY IN CELLULOSE.
PART 1: CELLULOSES I AND II

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INTRODUCTION

Variations in the supermolecular structure, which are known to influence fiber properties in regenerated celluloses and synthetics, appear to occur in native cellulose fibers as well. In the program of investigation of supermolecular structure currently underway, Raman spectroscopy has been developed as the primary technique for exploring macromolecular conformations. During the course of this development we have achieved some basic new insights into the nature of the different polymorphs of cellulose.

Essentially we believe we have established that the most basic difference between cellulose I (native) and cellulose II (mercerized or regenerated) is that the molecules occur in different conformations. These two conformations can be represented as small left- and right-handed departures from the commonly assumed twofold helix structure. For any particular sample, the distribution of molecules between the two conformations is dependent on sample history.

The present paper focuses on celluloses I and II. Future papers in this series will deal with celluloses III and IV, and with the influence of temperature history on molecular conformation.

Raman Spectral Studies of Polymorphy in Cellulose

Part 1: Celluloses I and II

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ABSTRACT

The Raman spectra of celluloses I and II have been investigated and found to be quite sensitive to the variation in polymorphic form. Spectra of highly crystalline samples of forms I and II are quite distinct, particularly in the low frequency region. The features occurring between 800 and 1500 cm^{-1}, which are due to methylene, methine and hydroxyl deformations as well as to the skeletal and ring stretching vibrations, differ primarily in relative intensities. In the region below 800 cm^{-1}, where the dominant bands are due to skeletal and ring bending and to torsional motions, common features are very few. The differences between the spectra have been interpreted as evidence for two different conformations of the molecular chains. This interpretation has been supported by a theoretical analysis of the influence of conformational variation on vibrational frequencies, and is consistent with published potential energy mappings. The interpretation is also consistent with changes in the spectra of related systems wherein conformational changes are independently established.

INTRODUCTION

Quite early in x-ray diffractometric studies of cellulose it was recognized that its crystallinity is polymorphic. It was established that native cellulose, on the one hand, and both regenerated and mercerized celluloses, on the other, represent two distinct crystallographic polymorphs (1). Little has transpired since the early studies to change these basic conclusions. There is, however, much less agreement regarding the structures of the two forms. For example, Petitpas, et al. (2), on the basis of extensive analyses of electron-density distributions from x-ray diffractometric measurements, have suggested that the chain conformations are different in celluloses I and II, whereas Norman (3) has interpreted the results of his equally comprehensive x-ray diffractometric studies in terms of similar conformations for the two polymorphs.

Perhaps more basic than the comparison of celluloses I and II, the structure of the native form itself remains in question. Most recently, for example, Blackwell and Gardner (4) have carried out an analysis of the structure of Valonia cellulose aimed at resolving questions of relative polarity of neighboring chains as well as the hydrogen bonding patterns; they assumed conformations which possess two-fold screw-axes as well as the $P2_1$ space group. Hebert and Muller (5) on the other hand, in an electron diffraction study of a number of celluloses, including Valonia, found no systematic absences of $0k0$ reflections, and concluded that the unit cells do not fall in space group $P2_1$. These are but the most recent instances of differing interpretations, and are perhaps illustrative of the types of conflict which earlier led both Jones (6), and Tonnessen and Ellefsen (7,8), in their respective reviews, to suggest that some basic questions concerning the structure of cellulose remain unresolved.

In efforts to resolve the uncertainties Rees and Skerrett (9) and, more recently, Sarko and Muggli (10) have carried out potential energy calculations. Rees and Skerrett examined cellobiose while Sarko and Muggli studied cellulose. In both investigations the energies of the nonbonded interactions were summed up and their variation with the dihedral angles at the glycosidic linkage mapped. In both instances multiple minima were found and they were generally somewhat removed from the locus of two-fold helical conformations. Because the minima were rather shallow both studies suggested that interchain packing energies could more than compensate for the energies favoring departures from two-fold helical structures. Thus the basic questions regarding the structure of individual chains remained unresolved.

The other investigative technique most often used for exploring the structure of cellulose is infrared spectroscopy. The work of Liang and Marchesault (11-13), which utilized measurements of dichroism in infrared absorption of oriented specimens, led to proposal of a particular hydrogen-bonding scheme. Here the differences between the spectra of celluloses I and II were explained in terms of differences in the packing of molecular chains and associated variations in the hydrogen-bonding patterns. In another application, infrared absorption measurements were used as the basis for a crystallinity index by Nelson and O'Connor (14,15). In most of these applications one of the problems has been the difficulty of minimizing scattering losses, particularly in the low frequency region. In dealing with native fibrous samples, where preservation of the morphology is desired, it becomes necessary to resort to immersion in fluids of matching refractive index (16).

Raman spectroscopy, which is the most common alternative for investi-
gating molecular vibrations, has enjoyed a very significant growth in applic-
ation since development of the use of lasers as exciting sources. Among
the new applications have been studies of many synthetic polymers (17-19)
as well as of a number of biological systems (20). The Raman spectrum of
Valonia cellulose has been reported by Blackwell, et al. (21), and interpreted
in relation to studies of the infrared spectra.

In the author's laboratory the Raman spectra of fibrous celluloses,
such as cotton, ramie, and high alpha pulps, have been investigated; these
spectra, which are quite similar for the native forms, differ in significant
ways from the spectrum of Valonia. The approach to interpretation of the
spectra has been based on studies of a number of classes of model compounds,
and on extensive characterization of the response of the spectra to polymorphic
variation. Preliminary accounts of some of the results have been
published (22,23). In the present report the differences between the spectra
of celluloses I and II, and, in particular, their implications concerning
molecular conformations, are considered in a more comprehensive manner. Some
results on the spectra of celluloses III and IV are also described.

EXPERIMENTAL

A variety of celluloses have been used in this study in native,
mercerized, and regenerated forms. The spectrum in Fig. 1 is for a sample of
Hercules chemical cotton (linters), used as received in sheet form. The samples
used for Fig. 2 were selected for their high crystallinity. The cellulose I
sample was regenerated by the procedure described in reference (22). Its Raman
spectrum is very similar to those of highly crystalline native celluloses; it
is used here because the spectral features are somewhat better resolved. The

cellulose II is a low-d.p. sample, regenerated from phosphoric acid at room

temperature, chosen because of both its high crystallinity and its very low

level of residual cellulose I. The spectra in Fig. 4 are for Whatman CF-1

powder, in the native form and mercerized to different degrees of conversion.

The spectrum identified as II represents the maximum degree of conversion

attainable using the most concentrated NaOH solution. The mercerization procedure

is described in detail elsewhere (24). Both regenerated and mercerized samples

were freeze dried, after the final washes in the respective preparations, and

then pressed into pellets which were used for both Raman and x-ray scattering

measurements. The pellets used for the data in Fig. 5 had TiO_2 added as an

internal standard; it is responsible for the sharp peak at $2\theta = 27.46°$.

The Raman spectra were recorded on a Spex Raman system using the 5145 A

line of a coherent Radiation 52 A laser for excitation. The spectrum in Fig. 1

was recorded using scattering at 90° to the incident beam. The spectra in Fig.

2 and 4 were recorded using the back-scattering (180°) mode. In most instances

the laser excited fluorescence (25) decayed to acceptable levels in approxi-

mately 30 minutes. The x-ray diffraction measurements were made with a Norelco

diffractometer utilizing nickel filtered copper K alpha radiation.

RESULTS AND DISCUSSION

The Raman spectrum of a sample of chemical cotton, shown in Fig. 1,

is fairly typical of the spectra of fibrous native celluloses of relatively high

crystallinity. Almost identical spectra have been recorded for a microcrystal-

line cellulose from a high alpha pulp, for filter papers, and for a variety

of cotton samples, both as native fibers and as acid hydrolyzed powders.

The spectra of bleached kraft and sulphite pulps, which typically are less

crystalline, are similar also though the bands are generally somewhat broadened.
In contrast, the bands are sharper and more clearly resolved in the spectra
of ramie fibers, which are relatively more crystalline. Experience with
many samples for which both Raman spectra and x-ray diffractograms have been
recorded indicates that the sharper bands and more clearly resolved spectra
are usually correlated with a high level of crystallinity. The spectra of
Valonia cellulose recorded in the present study, as well as that reported
by Blackwell, et al. (21), differ in a number of respects from those repre-
sented in Fig. 1.

[Fig. 1 here]

The spectra represented in Fig. 1 illustrate some of the advantages
of Raman spectroscopy in studies of cellulose. The relatively high intensity
and good resolution of the skeletal modes, and the absence of interference
from broad bands due to water, which are problematic in the infrared, reflect
the different bases for activity of molecular vibrations in Raman and infra-
red spectra. That is, whereas activity in the infrared region requires finite
transition moments involving the permanent dipoles of bonds undergoing dis-
placement, activity in the Raman spectrum requires finite transition moments
involving the polarizability of the bonds. It is useful in this connection
to view bonds in terms of Pauling's classification along a scale between
the two extremes of polar and covalent (26). Bonds which are highly polar
and possess relatively high dipole moments tend, when they undergo vibra-
tional variations, to result in bands which are intense in the infrared and
relatively weak in Raman spectra. Conversely, bonds which are primarily
covalent in character and have a relatively high polarizability, generally
result in bands which are intense in Raman spectra but relatively weak in
the infrared. Thus, while the O-H bonds, whether of cellulose itself or

of adsorbed water, are responsible for the dominant spectral features in the infrared, the skeletal and C-H vibrations dominate the Raman spectra. A further simplification in the Raman spectra results from the circumstance that the selection rule forbidding activity of overtone and combination bands is generally more rigidly adhered to than in the infrared (27).

Another important advantage is that scattering due to optical heterogeneity does not pose a serious problem except in the region below 200 cm^{-1}, so that the spectra of fiber mats and, indeed, of individual fibers can, and have been recorded. The extension to the region below 200 cm^{-1} is anticipated in the near future.

Although it is not the object of the present study to examine the assignments of the bands in the spectra it is important to note the classes of internal motions associated with the different spectral features, particularly in the regions below 1500 cm^{-1} which are the most sensitive to polymorphic change. The bases for this discussion are our extensive investigations of the vibrational spectra of model compounds wherein normal coordinate analyses and force constant refinements have been carried out for a number of classes of closely related systems. These include the 1,5-anhydro pentitols (27), the pentitols and erythritol (29), the pentoses (30), and glucose (31). Although there are occasional variations in detail, certain general patterns emerge, and these should, in most instances, be equally valid for cellulose.

In addition to the C-H and O-H stretching motions, which are much above the frequency region of interest, the internal deformation of the methyl group is the only vibration which closely approximates a group mode in the usual sense; the HCH bend generally occurs above 1450 cm^{-1}. The bands between

1200 and 1450 cm^{-1} are due to modes involving considerable coupling of methine bending, methylene rocking and wagging, and COH in-plane bending; these are angle bending coordinates involving one bond to a hydrogen atom. Significant contributions from ring stretching begin below 1200 cm^{-1}, and these modes, together with C-O stretching motions, dominate between 950 and 1150 cm^{-1}. Below 950 cm^{-1} angle bending coordinates involving heavy atoms only (i.e., CCC, COC, OCC) begin to contribute, though ring and C-O stretches and the external modes of the methylene groups may be the major components. The region between 400 and 700 cm^{-1} is dominated by the heavy atom bending, both C-O and ring modes, although some ring stretching coordinates still make minor contributions. In some instances O-H out-of-plane motions may contribute in this region also. Between 300 and 400 cm^{-1} the ring torsions make some contribution, and below 300 cm^{-1} they generally dominate.

In addition to the above generalizations concerning modes which occur in one or another of the classes of model compounds investigated, the spectrum of cellulose can have components due to modes centered at the glycosidic linkage. Preliminary computations on cellobiose indicate that these modes are strongly coupled with modes involving similar coordinates in the adjacent anhydroglucose rings.

Conversion of cellulose from the native (I) form to the mercerized or regenerated (II) form has a dramatic effect on the Raman spectrum, particularly in the low frequency region. The change is illustrated in Fig. 2, where the Raman spectra of very high crystallinity samples of both forms are compared; the x-ray diffractograms of the same samples are compared in Fig. 3. Some changes occur in the region above 800 cm^{-1}, but these are most often changes

in relative intensities of bands that are unchanged in frequency. In the region below 700 cm^{-1}, in contrast, the main features appear quite different in the two spectra.

[Fig. 2 and 3 here]

Though the spectra shown in Fig. 2 were selected to illustrate the extremes, similar changes are consistently observed in the spectra of native celluloses upon mercerization or regeneration at room temperature. Typical results are shown in Fig. 4 where the spectra of samples of cellulose powders mercerized to different degrees are compared; the corresponding x-ray diffractograms are shown in Fig. 5. In Fig. 4 it is clear that the intermediate spectra can be viewed as superpositions of the spectra of I and II. It is also evident that for the completely mercerized sample, some of the spectral features of cellulose I persist, suggesting that a residue of the native form has resisted mercerization. This is an effect often noted in past studies of mercerization, particularly with cotton celluloses.

[Fig. 4 and 5 here]

In the analyses of the spectra of model compounds changes of the magnitude indicated in Fig. 2 and 4 were usually associated with the occurrence of different conformations of a particular species. It seems very probable, therefore, that the differences between the spectra of celluloses I and II reflect a change in molecular conformation accompanying the transition from one form to the other. Since the basic ring structure is not expected to change (9) it would appear that variations of the dihedral angles at the glycosidic linkage provide the only opportunity for conformational variation. Because of the controversy surrounding similar conclusions based on crystallographic studies, a number of experimental and theoretical avenues for validating this interpretation have been pursued.

The first consideration was whether a multiplicity of stable conformations is consistent with the results of the conformational potential energy calculations cited earlier. In both studies (9,10) the potential energy surfaces were found to possess multiple minima. When the additional constraint of a repeat length of approximately 5.15 A per anhydroglucose unit is added, two minima, representing both left and right handed departures from the two-fold helix, appear to be likely locii of stable conformations.

Next inquiry was made into the degree to which changes in the dihedral angles about the bonds in the glycosidic linkage could influence the modes of vibration responsible for the spectral features in the different regions of the spectra. An adaptation of the matrix perturbation treatment used by Wilson, Decius and Cross (32) to discuss the effects of isotopic substitution was used to examine the consequences of variations in the dihedral angles. Changes in the dihedral angles were found to influence skeletal stretching and bending modes primarily through changes in some of the corresponding off-diagonal terms in the inverse kinetic energy matrix G. Examination of the general expressions for these terms (33) reveals that only one of the four classes of terms which influence stretching is sensitive to the dihedral angle, and it is a class representing stretch-bend interactions. The interactions influencing the bending modes, in contrast, are more sensitive to the dihedral angles. Among these, three of the four classes of bend-bend interactions change with the dihedral angle; these are in addition to the stretch-bend mode cited above, which would also influence the bending modes. Finally, the majority of terms involving torsional coordinates are sensitive to variations in the dihedral angles. These considerations lead to the expectation that the skeletal bending and torsional modes will be

altered to a greater degree than the skeletal stretching modes by any rotation about the bonds in the glycosidic linkage. The changes noted in Fig. 2 and 4 are consistent with this expectation.

Experimental validation of the interpretation put forth above centered on examination of the spectral manifestations of conformational change in related oligomeric and polymeric systems where independent evidence concerning conformational change is available. Although there are a number of biological polymers wherein conformational changes are known to result in changes in the vibrational spectra (20), the systems considered in greatest detail in the present instance were amylose and two of its cyclic oligomers, with primary emphasis on the latter.

The α- and β-Schardinger dextrins are cyclic α-1,4-oligomers of anhydroglucose also often identified as cyclohexa- and cyclohepta-amylose. Their structures differ in the dihedral angles about the bonds in the glycosidic linkage which are necessary to accomodate the different number of monomer units. The Raman spectra of the α- and β-dextrins are compared in Fig. 6. Similar spectra have been reported by Cael, et al. (34); they are included here to facilitate comparisons with the spectra of the celluloses. It is evident from Fig. 6 that the differences between the two oligomers have associated with them differences in the spectra which are relatively minor above 800 cm^{-1} while somewhat more pronounced in the region dominated by the skeletal bending and torsional modes. These differences are similar in kind and distribution, though of lesser magnitude than the differences between celluloses I and II shown in Fig. 2. It is also noted in this regard that, in their studies of the spectra of amylose, Cael, et al. (34) found that forms V_a and V_h, which are very similar in conformation but of different

hydration, had almost identical spectra. In contrast, form B, which is known
to have a distinctly different helix period, has a spectrum which differs
from the spectra of the V_a and V_h forms to a degree approximating the differ-
ences between the α- and β-dextrins. Thus it seems clear that observations
of the changes in the spectra, which result from conformational changes in
the amyloses, are entirely consistent with the interpretation put forth above
for the differences between the spectra of celluloses I and II.

[Fig. 6 here]

Yet another experimental avenue to validating the interpretation
of spectral changes was based on examination of solution spectra. In studies
of the model compounds it was found that aqueous solutions wherein the solute
stays predominately in the same conformation as in the solid state, have
spectra that are similar to those of the solid, though most of the bands
are somewhat broadened. When a number of conformations are probable in solution,
in contrast, new bands appear and, in many regions, fairly well resolved
bands give way to rather broad continua. In this light, the interpretation
of the spectra adopted above would require that dissolution of cellulose
bring about changes in its spectrum which are consistent with a range of
conformations. The spectrum of a relatively low DP cellulose in near saturated
aqueous calcium chloride showed the anticipated changes. In the region below
700 cm^{-1} the features merged into a broad envelope, while above 800 cm^{-1}
some of the features common to spectra of celluloses I and II persisted,
though somewhat broadened. The spectrum of the cellulose solution, to be
discussed in detail elsewhere, thus provides confirmation of the sensitivity
of the Raman spectrum to conformational change.

In summary then, both theoretical considerations and experimental observations support the view that the differences between the spectra of celluloses I and II are due to the existence of the molecules in two distinct conformations in the two polymorphic forms. Before examining some important implications of this conclusion it is well to address briefly the question whether differences of the magnitude observed can be explained, as they have been in the case of the infrared spectra, in terms of differences in molecular packing and in hydrogen-bonding patterns. A number of considerations make this unlikely. As noted earlier, the dominant bands in the Raman spectrum are due to skeletal modes. In the absence of conformational changes such modes tend to be quite insensitive to changes in hydrogen-bonding patterns (35). Studies on the dissolution of model compounds generally confirm this tendency. Beyond those, however, the Raman spectra of the amyloses indicate that changes in hydration, as in the transition from form V_a to form V_h, or as in the dissolution of the α-dextrin, result in relatively minor changes in the structure of the spectra in spite of what must be significant changes in hydrogen bonding.

Nor is it likely that rotation of the CH_2OH group can result in the changes noted in Fig. 2. Calculations on glucose indicate that such rotation would cause more limited spectral changes, and these predominantly above 600 cm^{-1} (36).

It was noted earlier that the potential energy calculations, when taken together with the constraint of a repeat period of 5.15 A, suggest two locii likely to represent stable conformations. The spectra of celluloses I and II when viewed in light of the considerations presented above, now appear convincing evidence that the cellulose molecule possesses two stable

conformations. Both the potential energy calculations and the spectra, however, allow only two stable conformations. An important implication, which at the same time provides the most severe test of the interpretation, is that these same two conformations must prevail in all polymorphic forms of cellulose in which the chains are ordered to any degree. Thus examination of the Raman spectra of celluloses III and IV can lead to further validation of the interpretation put forth above.

The Raman spectra of both celluloses III and IV have been investigated; the results will be reported in detail in part II of this series. The major finding, and the one most relevant to the present study, is that the spectra of both forms are in essence superpositions of the spectra of celluloses I and II. In every instance the major distinguishable features are characteristic of I or II, and the variations of relative intensities are such that the spectra appear to be linear superpositions of the spectra of forms I and II. Indeed some spectra of both III and IV are almost indistinguishable from the spectra of suitably chosen samples of partially converted cellulose II.

It seems clear that the studies on celluloses III and IV confirm the interpretation in terms of two and only two stable linear conformations. They also provide further evidence concerning the relatively minor influence of hydrogen-bonding on the Raman spectra, as it is probable that forms III and IV represent different packing modes for the linear chains.

CONCLUSIONS

The primary conclusion of the present investigation is that the molecular chains in celluloses I and II possess conformations which are different and distinct. This conclusion was developed, in the first instance,

from comparison of the response of the Raman spectrum to conversion from one form to another with the spectra of model compounds. It was further validated by consideration, in a theoretical analysis, of the effects of conformational change on the vibrational modes, by comparison with the spectra of different forms of amylose and its oligomers, and by examination of the response of the spectra to dissolution. When this conclusion is viewed in light of published mappings of the potential energy as a function of dihedral angles at the glycosidic linkage, together with the constraint of a repeat distance of approximately 5.15 A per anhydroglucose unit, it emerges that only two stable conformations are possible. These can be represented as small left- and right-handed departures from the two-fold helix structure; that they are relatively small departures may account for approximate adherence of some x-ray and electron diffraction patterns to selection rules of group $P2_1$.

The important implication of the conclusion that only two conformations are stable is that these same conformations must prevail in the other polymorphic forms of cellulose. The Raman spectra of celluloses III and IV are consistent with this expectation.

ACKNOWLEDGMENTS

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CHEMICAL COTTON
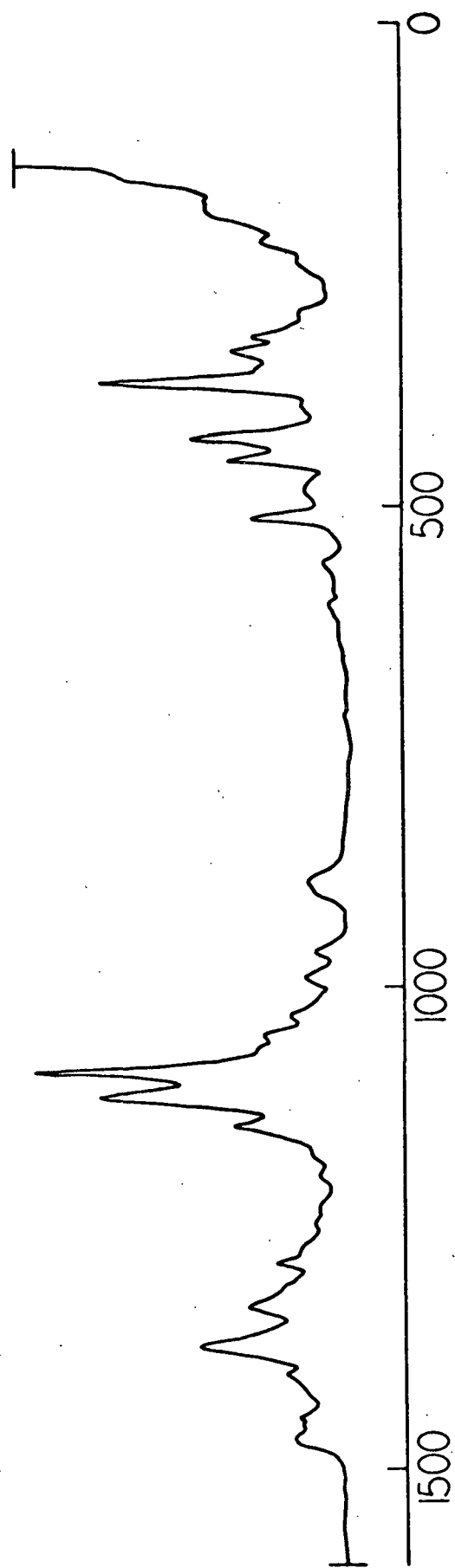
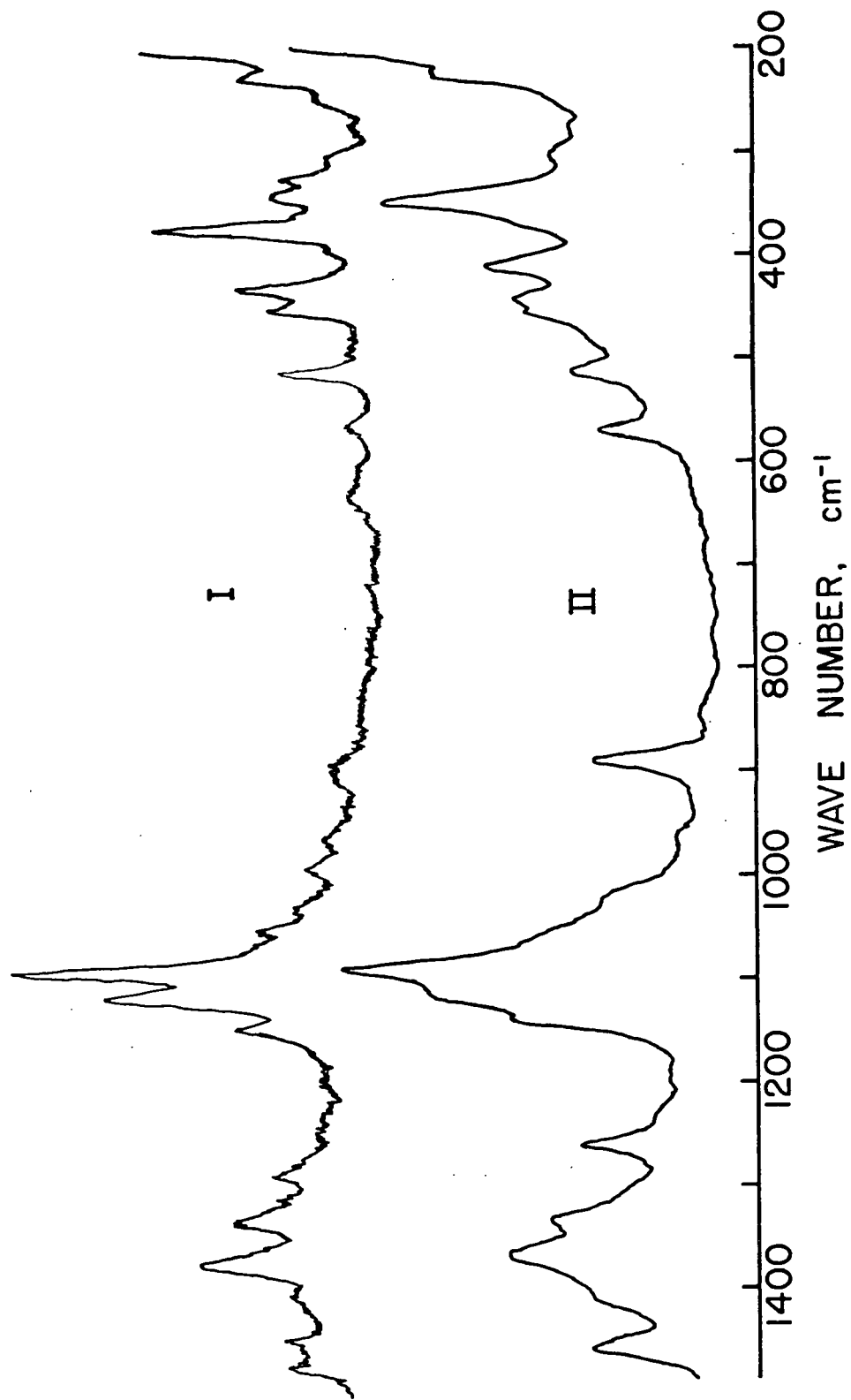WAVE NUMBER, cm⁻¹

Figure 1. Raman spectrum of chemical cotton

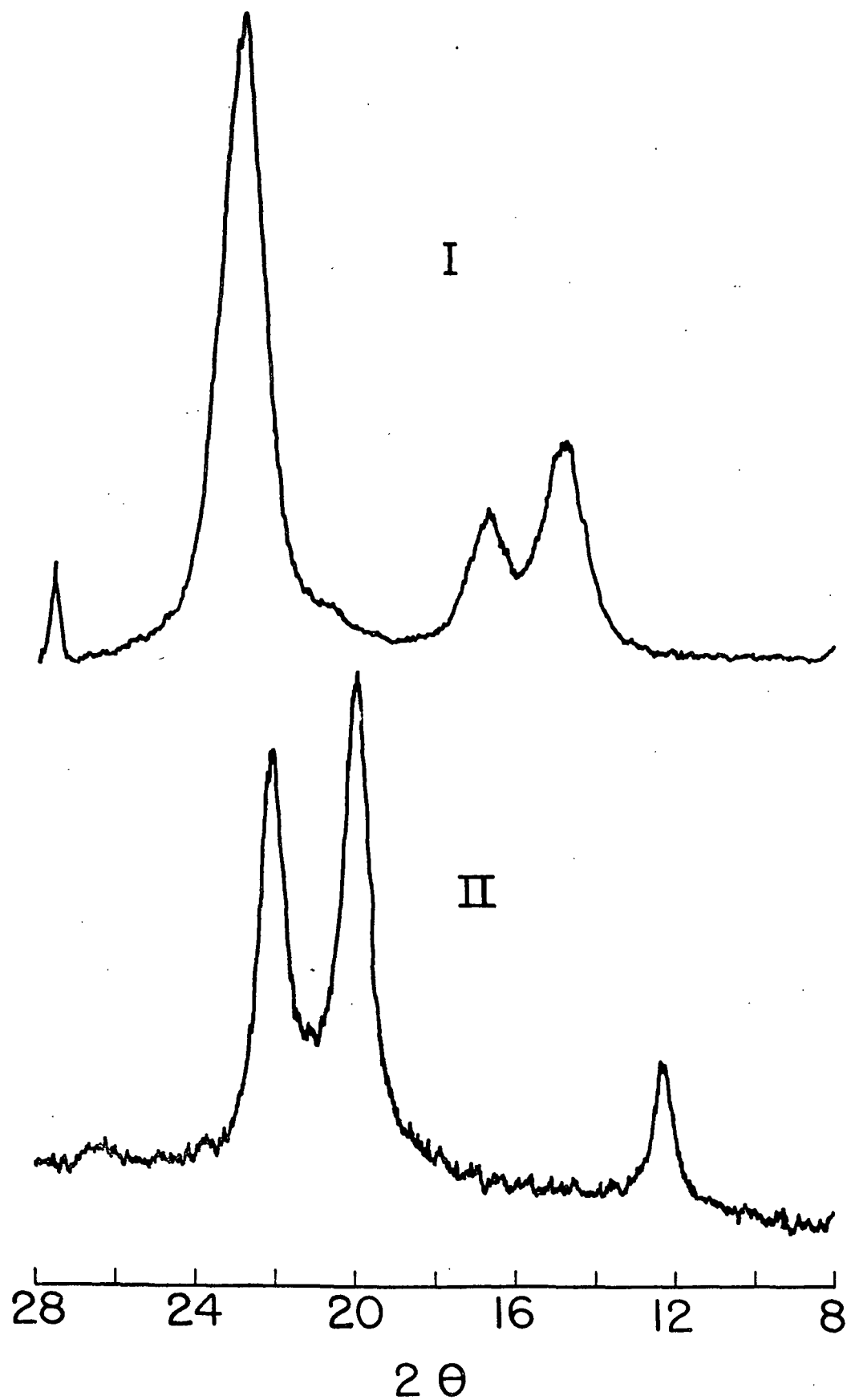Figure 2. Raman spectra of high crystallinity celluloses I and II

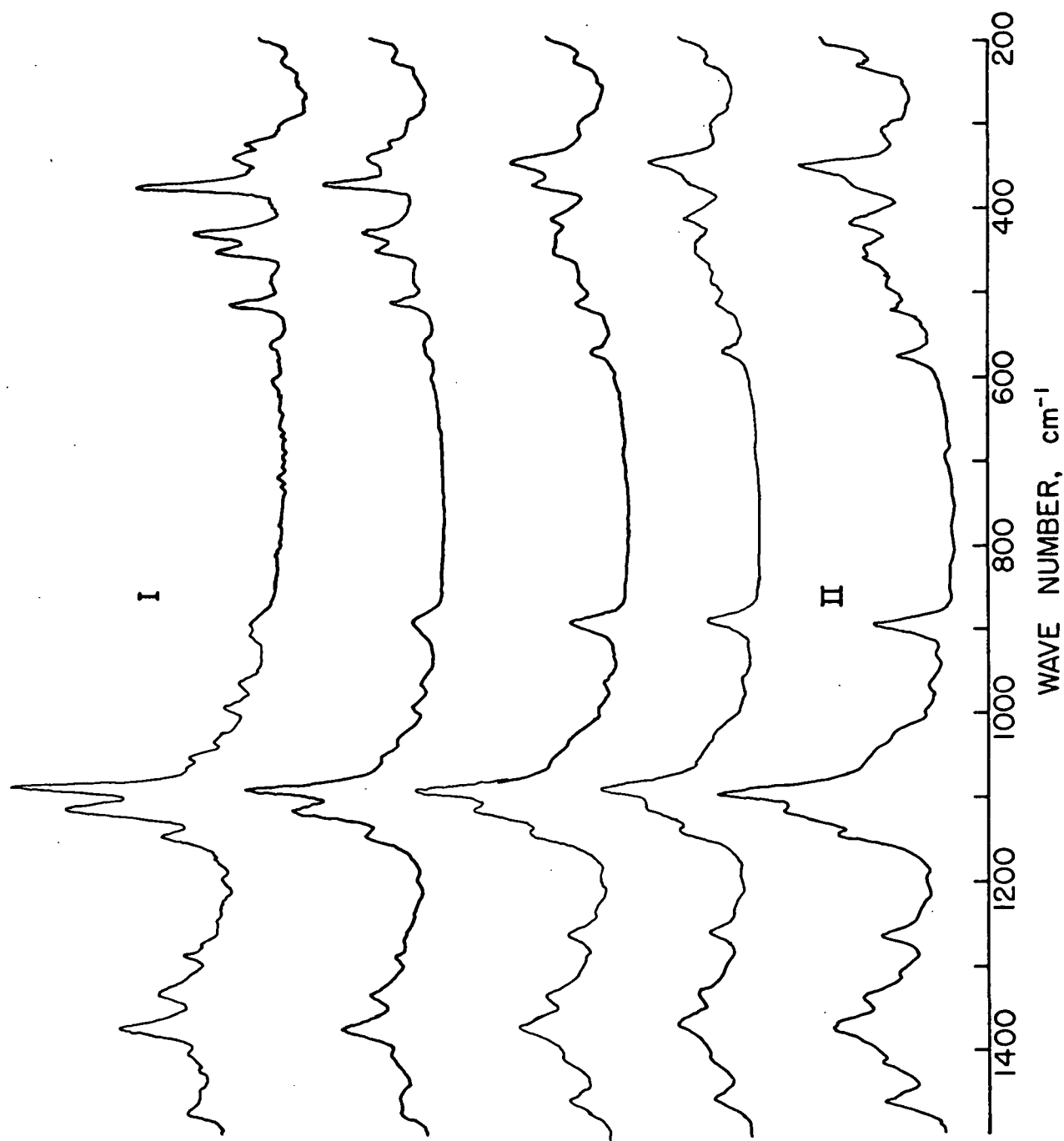Figure 3. X-ray diffractograms of samples in Fig. 2

WAVE NUMBER, cm⁻¹

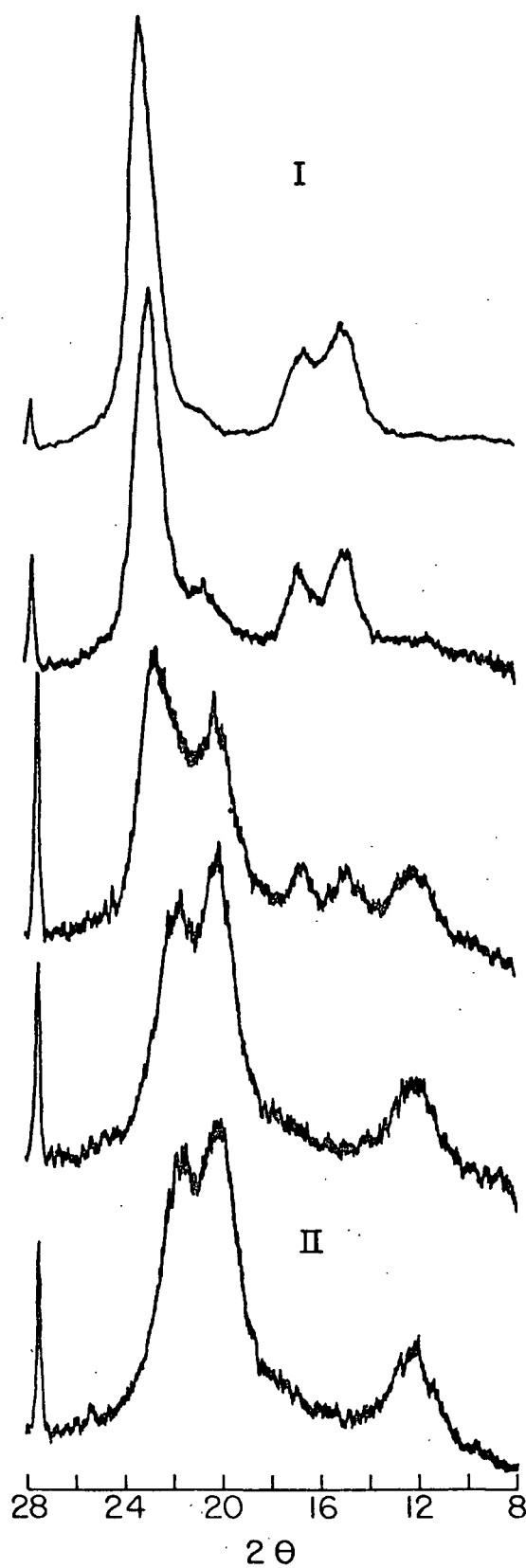Figure 4. Raman spectra of cellulose powder converted, by mercerization, to varying degrees

Figure 5. X-ray diffractograms of samples in Fig. 4

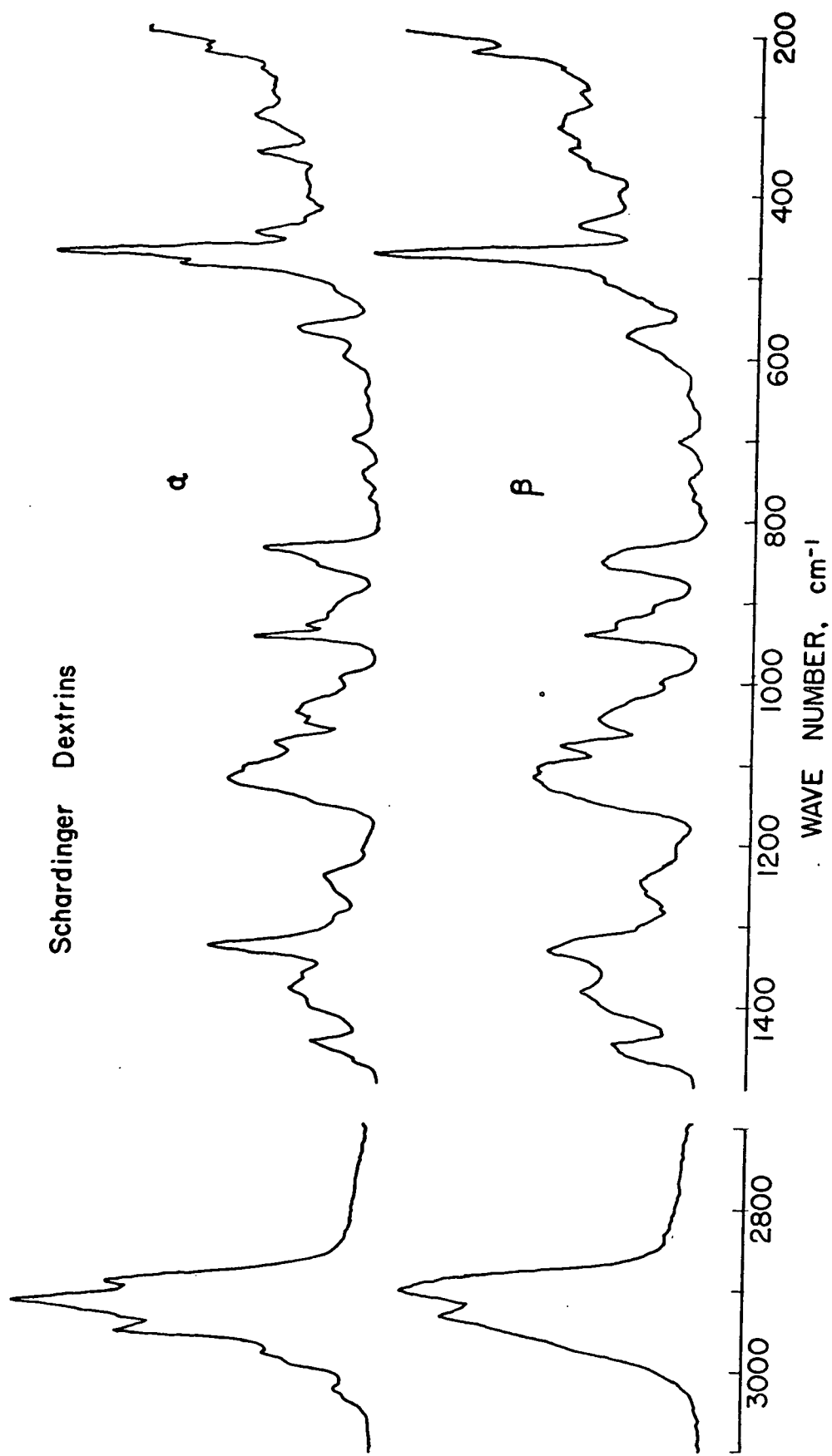Schardinger Dextrins

α

β

WAVE NUMBER, cm⁻¹

Figure 6. Raman spectra of Schardinger dextrins α and β