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**RAMAN SPECTRAL EVIDENCE FOR MOLECULAR ORIENTATION
IN NATIVE CELLULOSIC FIBERS**

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INTRODUCTION

Our studies of the Raman spectra of single fibers have been directed at developing information which they contain, above and beyond information in the average spectra we usually record on pulps and powdered celluloses. Single fiber spectra provide additional information because they permit control of the polarization of the incident beam relative to the axis of the fiber; additionally, the polarization of the Raman scattered light can be analyzed to identify the type of molecular motion involved. The spectra reported in this paper reveal a type of molecular order not previously recognized in native fibers. The presence of such order, and its disruption in papermaking processes, could be important factors in understanding the response of fibers to process variables.

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Studies of the Raman spectra of individual native fibers have revealed new information concerning ordering of molecular chains within the cell walls. Cellulose, the primary polysaccharide component of the walls, is the β 1,4-linked polymer of anhydroglucose. It is unique among cell wall polysaccharides in that all heavy atom linkages to the pyranose rings are equatorial, and the methine groups are axial. Previous investigations, utilizing x-ray diffractometry and birefringence, detected the average angle of the molecular chains relative to the axes of the fibers (1,2). The Raman spectra suggest that there is also a preferential orientation of the anhydroglucose units in tangential planes, and a correlated preferential orientation of the methine CH bonds in the radial direction.

The evidence for preferential orientation is derived from the response of the intensities of characteristic bands in the spectra of single fibers to changes in the polarization of the incident exciting radiation relative to the axis of the fiber.

Three spectra are presented. The first two were recorded on a Spex 1401 double monochromator in the 180° back scattering mode. The unfolded schematic representation in Fig. 1 shows the relative polarizations of the incident exciting radiation, and the Raman scattered light in each recording mode; the depolarized spectra were identical for both orientations of the incident beam. The laser illuminated portion of the fiber was imaged in the plane of the entrance slit such that the fiber axis is parallel to the slit. The signal received is thus an average, characteristic of the portion of the fiber image admitted through the entrance slit. Figure 2 is the spectrum of a Ramie fiber; Ramie is known to have molecular chains

essentially parallel to the fiber axis (3). Manifestations of this molecular orientation are noted in the changes in relative intensities of a number of the polarized bands when incident beam polarization is altered. In particular, the 1098 cm^{-1} skeletal band (4) is very intense in the parallel mode and much reduced in the perpendicular mode. The reverse is true of the methine stretching bands at 2920 cm^{-1} (5), and this, of course, reflects the orientation of all the methine CH bonds essentially perpendicular to the direction of the cellulose chain.

Figure 3 shows analogous spectra of a cotton fiber recorded in the same modes. As was perhaps to be expected from a fiber with a variable fibril angle (6), the intensity of the 1098 skeletal band was of the same order of magnitude in both modes. The unexpected feature in this spectrum was that the methine stretching band does not follow a similar pattern, but is significantly more intense in the perpendicular mode. It appears that an orientation effect above and beyond that of the fibril angle is present. It was proposed that such an effect could be due to a preferential orientation of the methine groups in the radial direction and the anhydroglucose rings in the tangential direction (7), but further testing of this interpretation seemed wise in light of the complex morphology of native cotton fibers.

The interpretation proposed received confirmation from the spectra shown in Fig. 4. These were recorded in a back scattering mode developed for a Jobin Yvon Ramanor spectrometer. However in this instance the axis of the fiber was imaged perpendicular to the entrance slit. Thus it was possible to record the spectra of a section of fiber no longer than the width of the slit. By translating the fiber parallel to the direction of its axis, and thus moving its image in the plane of the slit perpendicular to the slit, it was possible to locate a point

at which the intensity of the 1098 cm^{-1} skeletal band was the same for both orientations of the polarization of the incident beam, suggesting an average fibril angle of 45° within this segment. Here again, however, the intensity of the methine band at 2920 cm^{-1} was significantly higher in the perpendicular mode than in the parallel mode. It appears unlikely that the consistency of the behavior of the methine band with that represented in Fig. 3 is coincidental. Rather it seems more plausible that both observations are indicative of preferential orientation of the anhydroglucose units when considered relative to cylindrical coordinates with an axis coincident with the fiber axis. In such a frame it would appear that the methine CH bonds are preferentially oriented in the radial direction and the anhydroglucose planes in the tangential direction.

Clear indication of coherence in the arrangement of the cellulose chains may be an indication of a lamellar organization of cellulose molecules rather than the fibrillar aggregates generally proposed. The basic concept of fibrillar aggregates could be retained if it were proposed that some coherence or cooperativity in their organization prevailed in the cell walls. In terms of the orientation of the axes of a unit cell, the implication of the present finding is that the c-axis, which is approximately parallel to the methine CH, is preferentially oriented in the radial direction, and the a-axis, which is approximately parallel to the plane of the pyranose rings, is preferentially oriented in the tangential direction. The b-axis, which is approximately coincident with the chain direction, is, of course, aligned parallel to the fibrils.

Although rigorously the present spectral evidence can be interpreted along the lines indicated above only for the case of 45° fibril angles, the ordering of the molecules which it suggests is expected to occur more generally. The ordering

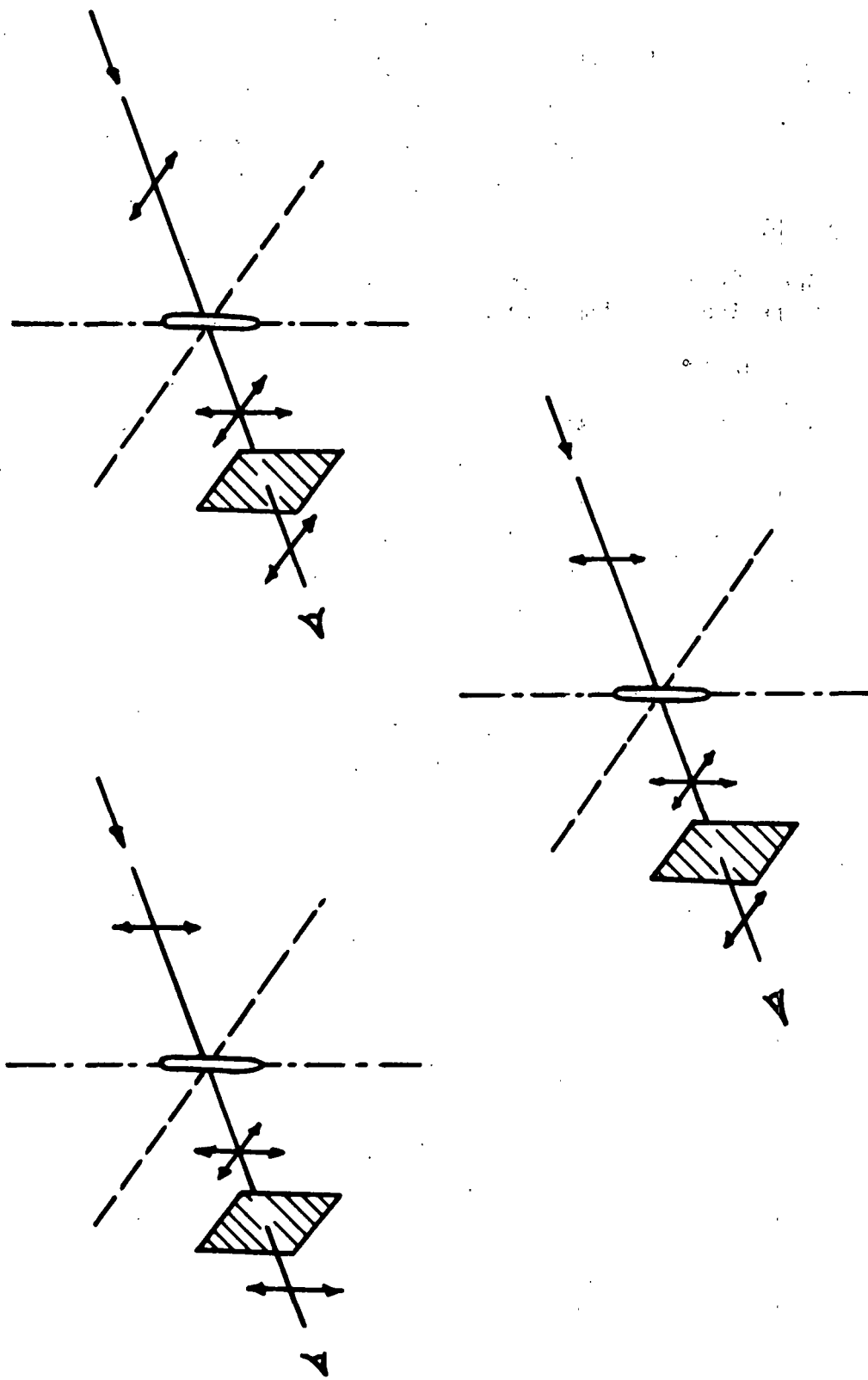
indicated by the spectra implies that a higher degree of anisotropy prevails in the organization of cellulose in cell walls than had previously been recognized.

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POLARIZED II TO FIBER AXIS

POLARIZED \perp TO FIBER AXIS



DEPOLARIZED

Figure 1. Unfolded Representation of the 180° Backscattering Experiments Showing Relative Polarizations of Incident and Raman Scattered Light

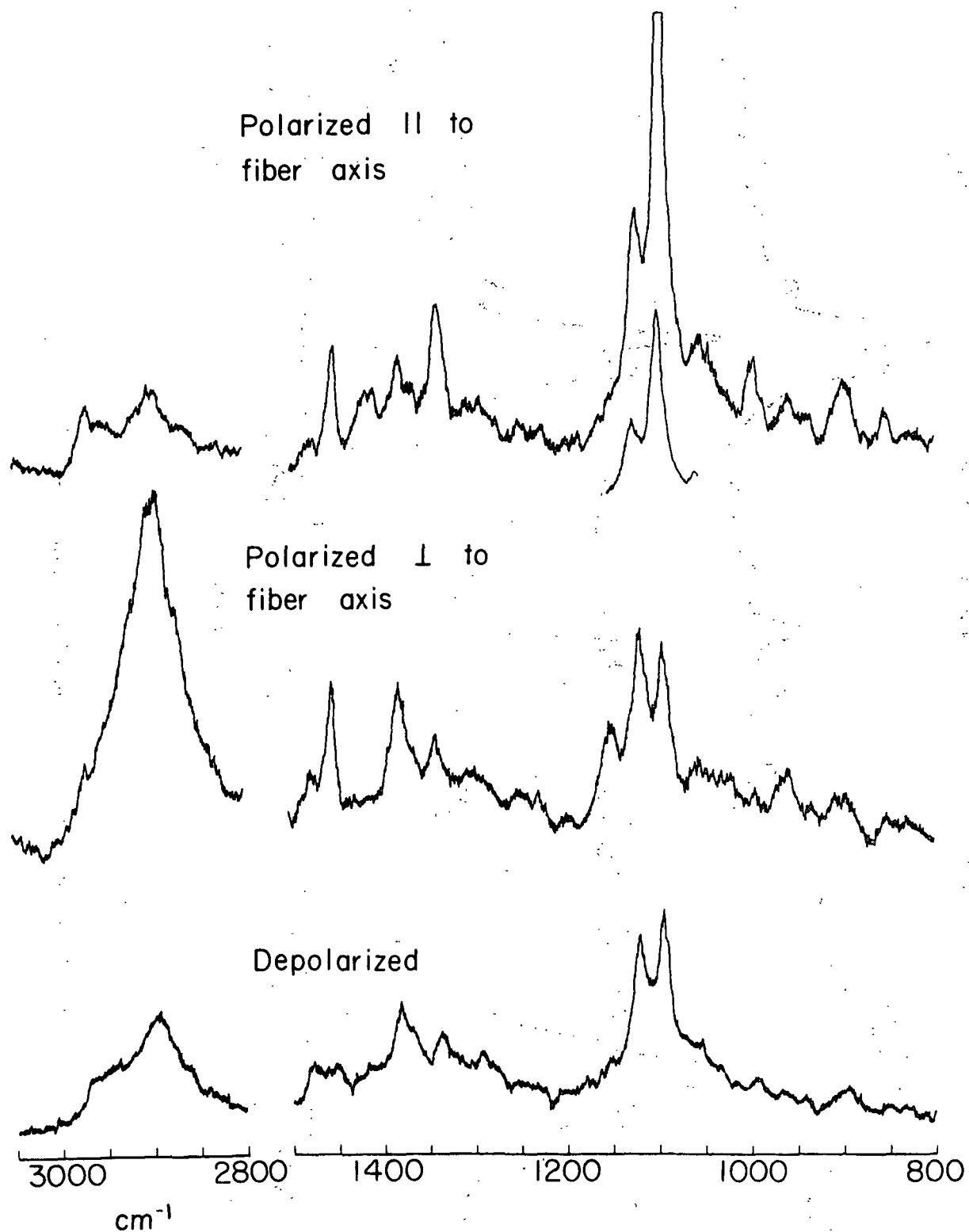


Figure 2. Raman Spectra of Ramie Fibers; Fiber Axis Parallel to the Slit

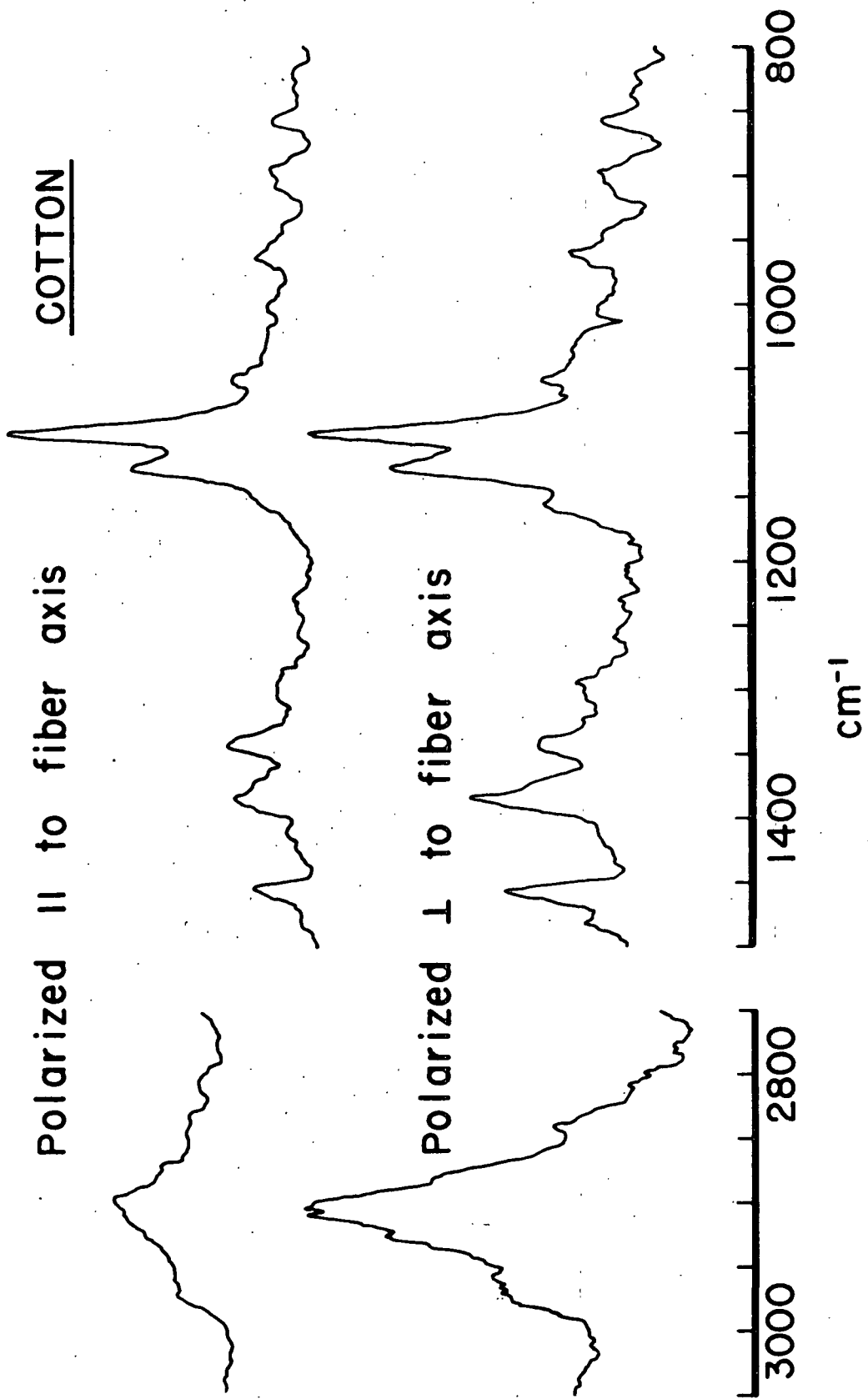


Figure 3. Raman Spectra of Cotton Fiber; Fiber Axis Parallel to the Slit

Cotton Fiber

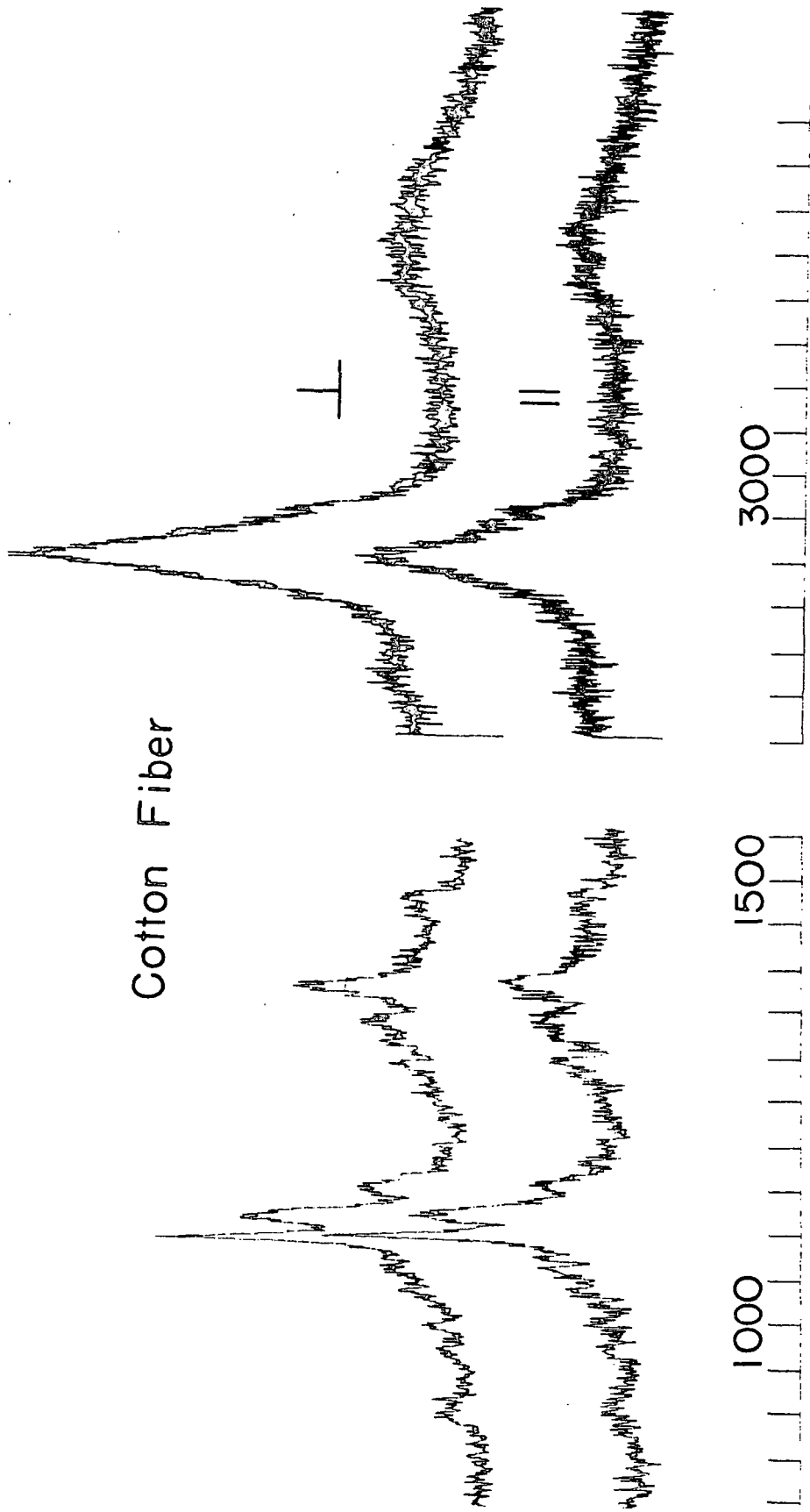


Figure 4. Raman Spectra of Cotton Fiber; Fiber Axis Perpendicular to the Slit