

# Derivative Infrared Spectroscopy of Cotton Cellulose

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## Synopsis

A new technique of derivative infrared spectroscopy for the study of polymer structure with special reference to cotton cellulose is described. Absorption spectra of cotton cellulose are compared with second derivative spectra. In case of absorption spectra, while determining the wavelength and intensity of a given absorption, in many cases, difficulties arise due to the presence of an interfering band which, as a consequence of overlap, prevents the determination of the above properties. Derivative spectroscopy provides valuable information on structural properties of cellulose. It yields spectra gradient, which facilitates the separation of overlapping absorption bands to resolve and detect absorptions; neither were unresolvable as a consequence either of multiple bands overlap or of low intensity. Hence, the measured wavelength in the second derivative spectra are more precise than the absorption spectra. For fine structural studies of cellulose, derivative spectra may provide more useful information as the absorption bands are more clearly defined.

## INTRODUCTION

Infrared (IR) spectroscopy is employed as an important technique for detailed study of fine structural properties of polymers. In recent years computerised Fourier transform Infrared (FTIR) spectrometers and dispersive instruments have facilitated many applications of IR analysis which were extremely difficult with conventional technique.<sup>1-4</sup> For study on cellulosic materials potassium bromide (KBr) disc technique is employed for recording cellulose spectra by a number of workers.<sup>5-9</sup> When analyzing a sample, to determine the wavelength, half-width, and intensity of a given absorption, in many cases it becomes difficult to determine the above properties due to overlap of interfering bands. Such problems have often been overcome by the useful "differential spectra" in which the difference in absorption at a given wavelength is determined directly by placing a reference sample in the reference beam of a double beam instrument.<sup>10</sup> Such measurements, however, often lead to anomalous results particularly when a shift in the wavelength of absorption has occurred and also need a pure standard polymer.<sup>11</sup> Recently the technique of difference spectroscopy by absorbance subtraction has been used by several workers in a wide field of polymer analysis and polymer physics.<sup>12-18</sup> The technique of derivative spectroscopy reported in this paper, on the other hand, yields graphs of gradient plotted against time, which facilitates the separation of overlapping bands. From the absorption spectra of

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cotton cellulose it is observed that many bands are unresolvable as a consequence either of multiple band overlap or of lower intensity in absorption spectrum. To overcome this problem of band overlap, this technique of second derivative spectroscopy, to study the fine structure of cotton cellulose is reported in this paper for the first time. Derivative spectra of cotton cellulose has been compared with absorption spectra under different settings, viz., time constant, scan speed of the instrument. Further study on application of this technique for determination of crystallinity or accessibility of native and chemically modified cellulose is being reported separately.

### THEORETICAL BACKGROUND

The theory and different approaches to derivative spectrophotometry have been dealt with by a number of workers.<sup>19-21</sup> Brief mention of the theory will be made here. The shape of the infrared absorption curve is complex, and it is difficult to represent these by the single mathematical model. Two functions, (i) Gaussian and (ii) Lorentzian, approach this. These may be represented as given below:

$$(i) Y_1 = d_1 e^{-bx^2} \quad \text{and} \quad (ii) Y_2 = \frac{d_2}{1 + \alpha x^2}$$

where  $d$  is the amplitude,  $x$  is the wavelength,  $Y$  is the absorbance,  $b = 4IN^2/C^2$ , where  $C^2$  is the absorption width at half-height and  $\alpha = 4/C^2$ . On differentiating  $Y$  with respect to  $x$ , the graphs of  $d^2Y/dx^2$  plotted against  $x$  of both Gaussian and Lorentzian functions, together with the second derivative of an experimental singlet absorption show that any of these models can

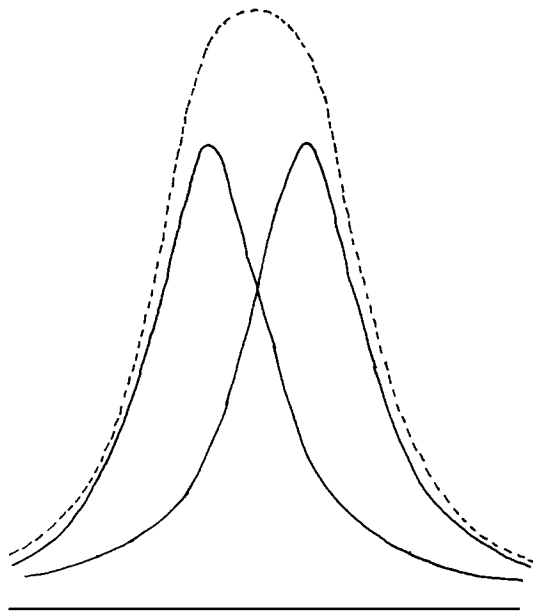


Fig. 1. Two superimposed absorption giving an apparent singlet.

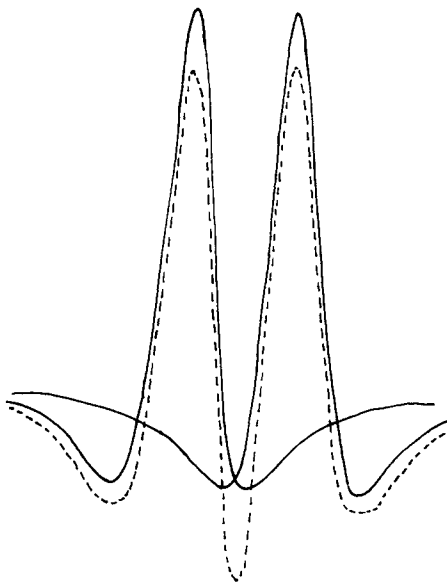


Fig. 2. Second derivative of Figure 1.

be used. The experimental curve has been expressed in terms of both functions<sup>22</sup> so that  $Y$  is given by

$$Y = (1 - F)Y_1 + FY_2$$

where  $F$  is the fraction of the Lorentzian component contributing to the total absorption. Changes in  $F$  value will hence have hardly any effect on the second derivative spectra. The second derivative of an absorption curve has both positive and negative peak with positive setellites. The sharpness of such a peak, or the width at half-height, is approximately one third that of its parent absorption, and this factor is responsible for the separation of overlapping bands by double differentiation. This is shown in Figure 1 in which an absorption formed by overlapping bands appears as singlet, and Figure 2 illustrates the second derivative of this.

The above theory is applicable, when measurements are recorded in term of optical density or absorbance, and it does not apply to  $I$  values where absorptions are plotted as functions of percentage transmission against wavelengths, since each absorbing component may be envisaged to absorb a proportion of the light incident upon it. When using differentiator, experimental parameters need to be carefully chosen to obtain optimum performance. The more accurate differentiation is obtained at a low scan speed and low time constant. In some cases, where low and high intensity absorptions are to be examined, it is necessary to repeat examinations at different concentrations or cell lengths in order to obtain maximum information from derivative spectrum.

## EXPERIMENTAL

Purified lint sample of 170-CO<sub>2</sub> cotton was finely cut with scissors into a small glass weighing bottle and a few milligrams of this material were ground in a high speed ball mill (Beckman-RIIC Vibromill VM 100) to pass a 20-mesh screen. The samples were dried by placing them at 60°C for 24 h. Two milligrams of dry cellulose was added to 200.0 mg of spectral grade potassium bromide (KBr). The mixture of KBr and cellulose was ground in a mortar until thoroughly mixed. This mixture (150 mg) was pressed into a disc in the evacuable die, and a transparent disc was formed.

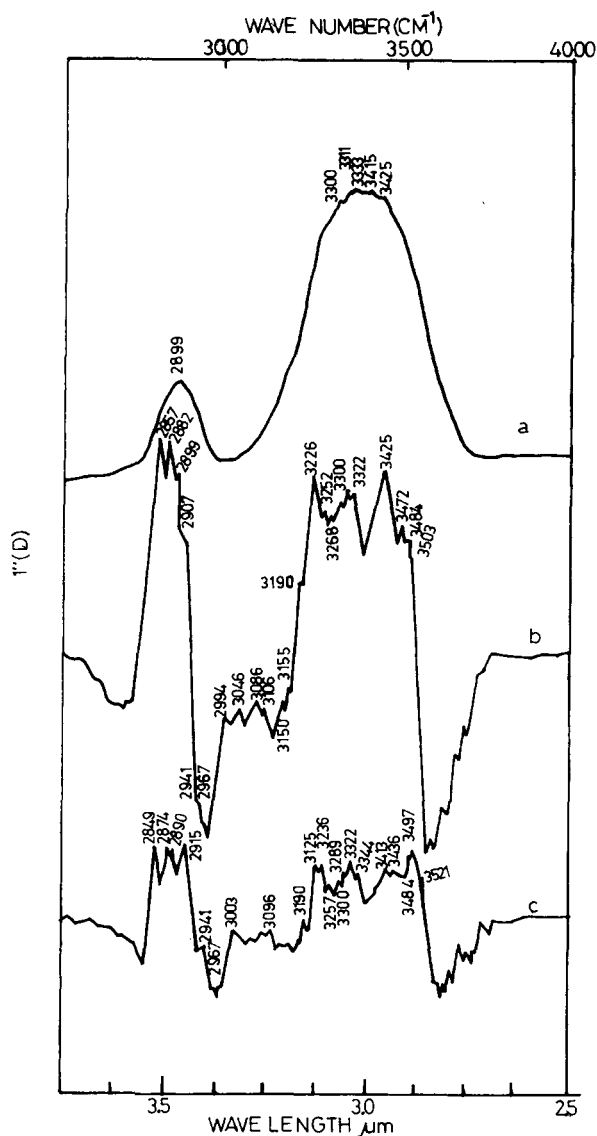


Fig. 3. Absorption and derivative spectra of cotton cellulose in the 3 μ region: (a) absorption spectrum; (b) derivative spectrum at scan speed 1 and high time constant; (c) derivative spectrum at scan speed 1 and low time constant.

Absorption spectra were recorded on a Grubb Parsons Spectromaster Mark II Infrared spectrophotometer, and derivative spectra were recorded with the help of a differentiator capable of giving second derivatives connected with the above instrument. Second derivative spectra were recorded at different scan speeds and time constants keeping other conditions constant.

## RESULTS AND DISCUSSION

### The 3 $\mu$ Region (4000–2500 $\text{cm}^{-1}$ Region)

In the infrared spectrum of cellulose 3  $\mu$  region is the most interesting part from structural point of view as the absorption bands due to O—H and C—H stretching vibrations are observed here. The absorption and derivative spectra of cotton at scan speed 1 (SS1) in this region are shown in Figure 3. Absorption spectra [Fig. 3(a)] shows two broad bands one each in the 3333 and 2857  $\text{cm}^{-1}$  regions due to O—H and C—H stretching vibrations. The broad band in the 3333  $\text{cm}^{-1}$  region exhibits five poorly resolved small absorption bands at 3425, 3415, 3333, 3311, and 3300  $\text{cm}^{-1}$  and the C—H stretching vibrations show a broad band at 2899  $\text{cm}^{-1}$  [Fig. 3(a)]. The

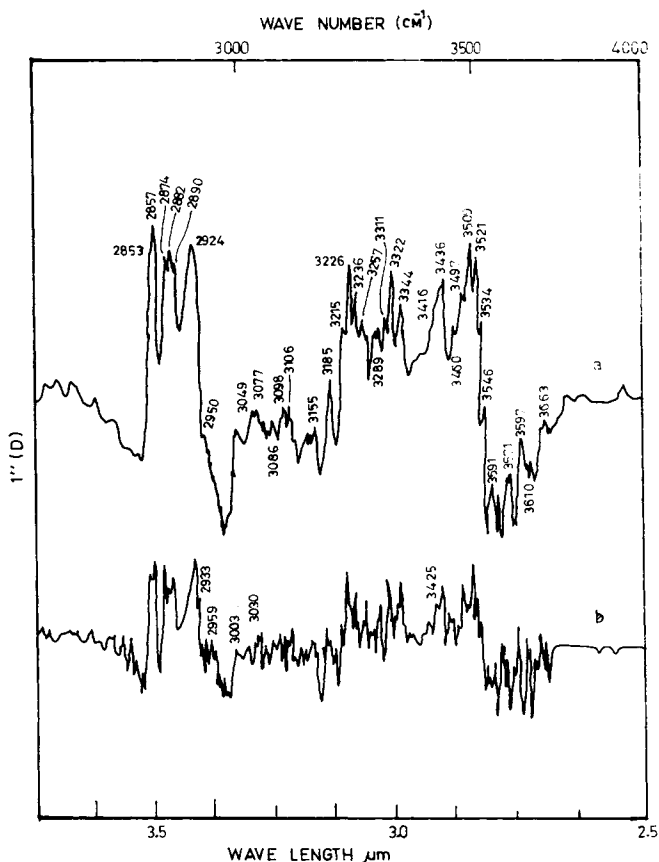


Fig. 4. Derivative spectra of cotton cellulose in the 3  $\mu$  region: (a) at 0.5 scan speed and high time constant; (b) at 0.5 scan speed and low time constant.

derivative spectra of cotton cellulose at high time constant [Fig. 3(b)] show a number of peaks in the  $3333\text{ cm}^{-1}$  region. The peak at the frequency of  $3472\text{ cm}^{-1}$  is narrow, at  $3425$  is broad, at  $3322$  is intermediate, and at  $3226\text{ cm}^{-1}$  is of sharper intensity. Besides there are other peaks which are very short and narrow and these are at frequencies of  $3503$ ,  $3484$ ,  $3300$ ,  $3268$ ,  $3252$ ,  $3190$ ,  $3155$ ,  $3150$ ,  $3106$ ,  $3086$ ,  $3046$ , and  $2994\text{ cm}^{-1}$ . The C—H stretching region shows six peaks. These are at the wave frequencies of  $2967$ ,  $2941$ ,  $2907$ ,  $2899$ ,  $2882$ , and  $2857\text{ cm}^{-1}$ . The latter two bands are of higher intensity than the other bands, and the band at  $2857$  is of higher intensity and narrower than the band at  $2882\text{ cm}^{-1}$ . The second derivative spectra at SS1 and low time constant [Fig. 3(c)] shows 15 bands in the  $3333\text{ cm}^{-1}$  region, and these bands occur at the frequencies of  $3521$ ,  $3497$ ,  $3484$ ,  $3436$ ,  $3413$ ,  $3344$ ,  $3322$ ,  $3300$ ,  $3289$ ,  $3257$ ,  $3236$ ,  $3125$ ,  $3190$ ,  $3096$ , and  $3003\text{ cm}^{-1}$ . The C—H stretching bands are better resolved, and these occur at the wave frequencies of  $2967$ ,  $2941$ ,  $2915$ ,  $2890$ ,  $2874$ , and  $2849\text{ cm}^{-1}$ . This spectrum shows that the band at  $2899\text{ cm}^{-1}$  is composed of number of bands and the three bands, namely, at the frequencies of  $2915$ ,  $2874$ , and  $2849\text{ cm}^{-1}$ , are almost of the same intensity and broader than the other bands.

Second derivative spectra of cotton cellulose at scan speed of 0.5 with high and low time constants is shown in Figure 4. In all, 28 bands are found in the O—H stretching region and seven in the C—H stretching region [Fig. 4(a)] at high time constant. At low time constant, three more bands are seen in the O—H stretching region and two more in C—H stretching region [Fig. 4(b)]. These bands are located at wave frequencies of  $3425$ ,  $3030$ ,  $3003$ ,  $2959$ , and  $2933\text{ cm}^{-1}$ . These bands at low time constant show higher intensity than those at high time constant.

### The $2000\text{--}700\text{ cm}^{-1}$ Region

The region  $2000\text{--}700\text{ cm}^{-1}$  of the cellulose infrared spectrum is known to be practically the most useful part both from qualitative and quantitative point of view. Figure 5 shows absorption and second derivative spectra of cotton cellulose in  $2000\text{--}700\text{ cm}^{-1}$  region at SS1 under high time constant (HTC) and low time constant (LTC). Absorption spectra [Fig. 5(a)] show marked differences compared to the derivative spectra [Figs. 5(b) and 5(c)]. It may be seen that many of the absorptions in Figure 5(a) are not clearly defined and appear as shoulder, while in derivative spectra these bands are clearly defined and have higher intensity. The absorptions near  $1626$ ,  $1429$ ,  $1370$ , and  $1316\text{ cm}^{-1}$  have relative intensities, which do not change with the change in rate of wavelength sweep and differentiator time constant, viz., the relative heights are nearly the same in all spectra. Similarly the relative heights of absorptions near  $1227$ ,  $1205$ ,  $1163$ , and  $995\text{ cm}^{-1}$  do not change significantly with the change in instrumental conditions. Therefore, these absorptions are of equivalent half-width. The absorption near  $1709\text{ cm}^{-1}$  increases relative to that of  $1626\text{ cm}^{-1}$  with low time constant, showing that the former is narrower than the latter. The absorptions near  $1370$ ,  $1205$ ,  $1163$ ,  $1026$ , and  $995\text{ cm}^{-1}$  are clearly singlet whereas the absorption bands near  $1626$ ,  $1538$ ,  $1429$ ,  $1316$ ,  $1235$ ,  $1111$ ,  $1058$ ,  $954$ ,  $929$ , and  $894\text{ cm}^{-1}$  are multicomponent bands. Many of these bands can be detected in the absorption spectra, but these are poorly resolved

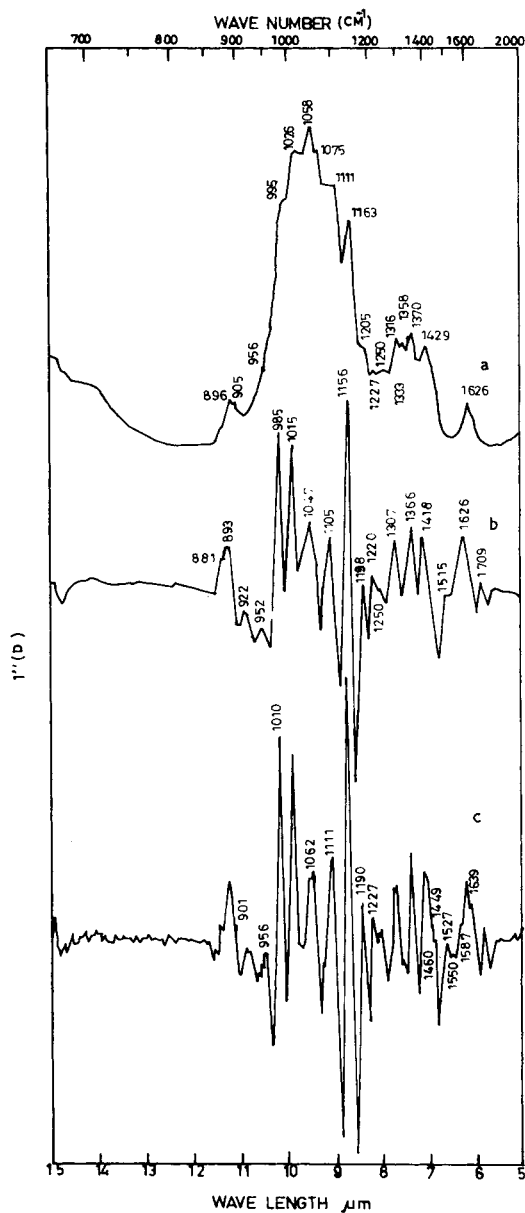


Fig. 5. Absorption and derivative spectra of cotton cellulose in the  $2000\text{--}700\text{ cm}^{-1}$  region: (a) absorption spectrum; (b) derivation spectrum at scan speed 1 and high time constant; (c) derivative spectrum at scan speed 1 and high constant.

due to band overlap. It has been shown that the absorption wavelength is influenced by neighboring bands which overlap. When two such bands overlap to produce unresolved or resolved spectrum, the wavelength at peak maximum appears closer together than the absorption from which they originate. Hence the wavelength of these bands in absorption spectra is very approximate. In derivative spectroscopy, however, the bands appear at the actual absorption

wavelength even when overlap occurs. Hence the measured wavelength in second derivative spectra of cellulose are more precise than the absorption spectra. This is very clearly shown for the absorption at  $1163\text{ cm}^{-1}$ , which appears at  $1156\text{ cm}^{-1}$  in the second derivative spectrum. In the absorption mode this appears as a resolved side band and has shifted slightly to shorter wavelength due to band overlap. In the derivative mode, however, this is clearly well resolved and occurs at  $1156\text{ cm}^{-1}$  (Fig. 5).

Derivative spectra recorded with low scan speed (Fig. 6) show the presence of several sharp bands in the region  $1818\text{--}1408\text{ cm}^{-1}$ . Some of these bands

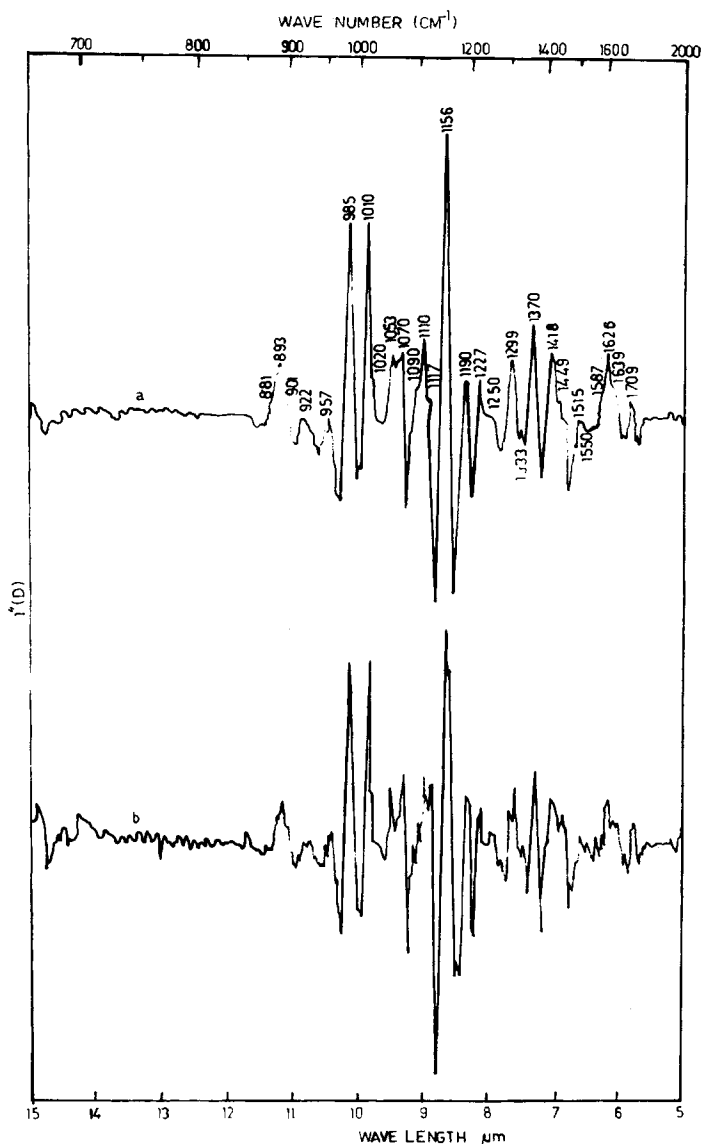


Fig. 6. Derivative spectra of cotton cellulose in the  $2000\text{--}700\text{ cm}^{-1}$  region: (a) derivative spectrum at scan speed of 0.5 and high time constant; (b) derivative spectrum at scan speed 0.5 and low time constant.



namely 1709, 1626, 1537, and 1418  $\text{cm}^{-1}$  exhibited fine structure due to water absorption, which superimposed the cellulose absorptions. These bands were found reproducible. However, the absorption band at 1418  $\text{cm}^{-1}$  exhibits a shoulder near 1449  $\text{cm}^{-1}$ , whereas the above-mentioned peaks are singlets. Additional sharp absorptions are seen from 985  $\text{cm}^{-1}$  onwards, which superimposed the absorptions 957, 922, and 893  $\text{cm}^{-1}$ . It is also possible that these three absorptions are singlet with superimposed fine structure. The absorption near 1227 exhibits shoulder near 1250  $\text{cm}^{-1}$ . The peaks near 1110 and 1070 arise from 5- and 3-component spectra, respectively. Derivative spectra shown in Figure 6(b) (at low scan speed and low time constant) is similar to that observed in Figure 6(a), but several absorptions are better resolved such as absorption at 1639, 1537, 1515, 1449, 1299, 1250, 1117, 1070, 1053, and 922  $\text{cm}^{-1}$ .

### SUMMARY

In this article absorption spectra of cotton cellulose is compared with the second derivative spectra at different scan speeds and time constants. It is well known that the infrared spectra of polymers simplify with the increasing molecular weight to the point where the recorded absorptions are considered, mainly from the repeating unit. When the polymer is subjected to certain chemical treatments, the changes produced in chemical and physical properties of polymers are not detectable to a satisfactory level in its absorption spectrum. Therefore, the absorption technique is of little use for the study of such materials. From the study it is shown that derivative spectra provide more precise and detailed information compared to the absorption infrared spectra. In absorption spectra, while determining the wavelength and intensity of a given absorption, in many cases difficulties arise due to presence of an interfering absorption, which as a result of overlap prevents the determination of above characteristics. It is evident from the second derivative spectroscopy that it is capable of extending the use of infrared since it is possible to resolve and detect on a semiquantitative basis, absorptions which were not resolvable as a consequence either of multiple band overlap or of low intensity. It is clear that derivative spectroscopy provides band separation when superimposed absorptions have bandwidths which are large compared with the resolution of the spectrophotometer.

The derivative spectroscopy provides valuable detailed information on structural properties of polymers. It can be used in the characterization of absorptions produced by overlapping bands, their wavelengths, intensity, and half-width. In the case of cotton cellulose absorption spectra show broad bands in the 3333 and 2857  $\text{cm}^{-1}$  regions of O—H and C—H stretchings. The broad band in 3333  $\text{cm}^{-1}$  region exhibits poorly resolved five small absorption bands and C—H stretching bands show a broad band at 2899  $\text{cm}^{-1}$ . In the second derivative spectra at scan speeds of 1 and 0.5 with high and low time constants, these bands are better resolved, and a larger number of peaks are found. It is interesting to note that, in all, about 28 absorption bands are found in the O—H stretching region and seven in the C—H stretching region. Similarly in the 2000–700  $\text{cm}^{-1}$  region a number of new peaks are observed in second derivative spectra, and they are better resolved compared to absorption spectra. From the second derivative spectra more detailed structural

information can be obtained about fine structural properties of cotton cellulose and other polymers. This technique will be very useful in evaluation of chemically modified cellulose products and similar products and will lead to a better and clearer understanding of the structure of cellulosic and similar products.

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