# Effect of Crystalline Structure on the Infrared Spectra of γ-Irradiated Cotton Cellulose

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## Synopsis

The effect of crystalline modifications on the infrared spectra of γ-irradiated cotton cellulose is presented. The crystalline modifications were brought about by treating cotton material with an aqueous solution of NaOH of various concentrations. The infrared spectra of the irradiated samples indicate an absorption band corresponding to the absorption of C=O groups. It was found that the intensity and frequency of this band depend on the crystalline structure. Thus, it appears at $1735 \text{ cm}^{-1}$ in the spectrum of cellulose I and at $1610 \text{ cm}^{-1}$ in the spectrum of cellulose II.
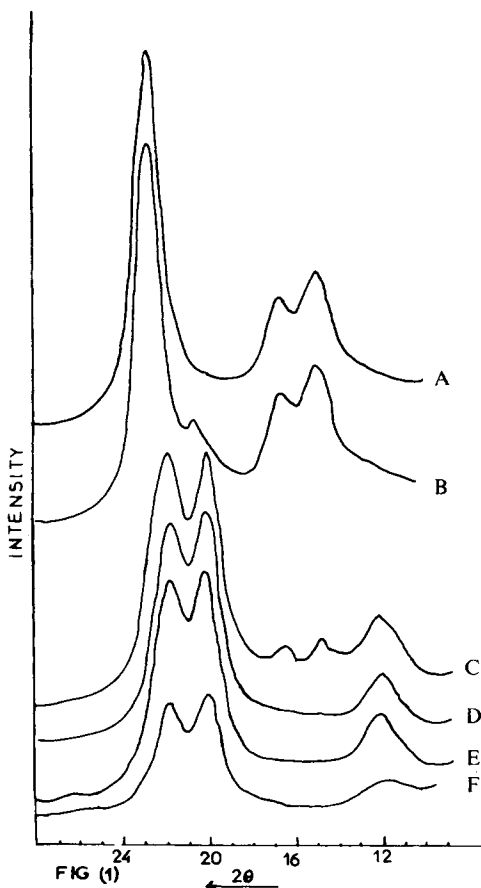
Fig. 1. X-ray diffraction patterns of: A, raw cotton; B, cotton treated with 10% NaOH solution; C, cotton treated with 14% NaOH; D, cotton treated with 22% NaOH; E, cotton treated with 22% NaOH; F, cotton treated with 26% NaOH.
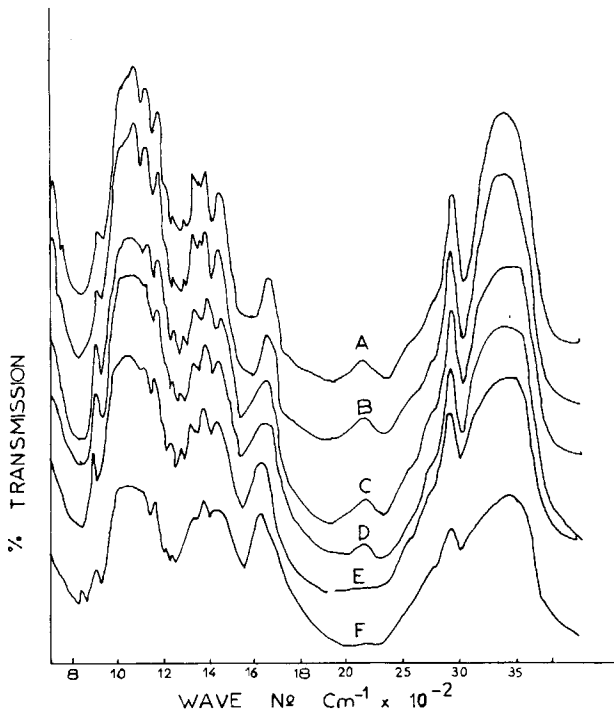
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Fig. 2. IR Spectra of cotton treated with NaOH solution: A, untreated cotton; B, 10% NaOH; C, 14% NaOH; D, 18% NaOH; E, 22% and 26% NaOH.

## INTRODUCTION

It is well known that the modern trend in cotton research is to impart new or improved properties to the fiber material through certain modifications so that cotton may be able to compete with synthetic fibers.[1-6]  In fact, in the past few years various authors have investigated the principal reactions that cotton cellulose will undergo on exposure to $\gamma$-radiation.[7-14]  However, the quantitative relationship between the crystalline modifications and such reactions has not yet been fully investigated.  Accordingly, the present study was undertaken to investigate the effects of the changes in the crystalline structure on the infrared spectra of $\gamma$-irradiated cotton cellulose.

## EXPERIMENTAL

Fibers of Giza 66 were first washed with hot ethanol, then boiled for 25 hr in a solution of 1% NaOH, washed with distilled water and dilute acetic acid, neutralized with dilute NH$_4$OH, and finally washed several times with distilled water.

The dried fibers were cut into small pieces and then ground in a hardened steel vial containing two hardened steel balls.  The vial was fitted to a Spex-Mixer mill which was rotated several times for short periods.  The obtained powder was then sieved to particle size fractions of 0.167 mm in diameter.

The powder was immersed in NaOH solution of various concentrations at room temperature (27°C) for 12 min.  The material:liquor ratio was 1:50.  The powder

was then washed with distilled water and then treated with 1% acetic acid solution for 5 min. The samples were then irradiated from a $^{60}$Co source, a Noratom Control A-S gamma 3500 unit, 67 Hz.

KBr discs were prepared from the treated samples. The infrared spectra were recorded on a Beckman spectrophotometer. The x-ray diffraction patterns were obtained on a Siemens D 500 diffractometer.

## RESULTS AND DISCUSSION

Samples of cotton powder of the same particle size (0.167 mm in diameter) were immersed in aqueous solutions of NaOH under various concentrations, namely, 10, 14, 18, 22, and 26% (w/w) for 12 min and at room temperature (27°C). The x-ray diffractograms of the experimental materials were first evaluated for defining the lattice type.

As will be seen from Figure 1, the diffractogram of raw cotton shows peaks located at $2\theta = 14.8$, 16.4, and 22.5, which are the characteristics of cellulose I.[15,16] Each of the diffractograms of the samples treated with 18, 22, and 26% NaOH solution exhibits peaks at $2\theta = 12$, 20, and 21.6, which are the characteristics of
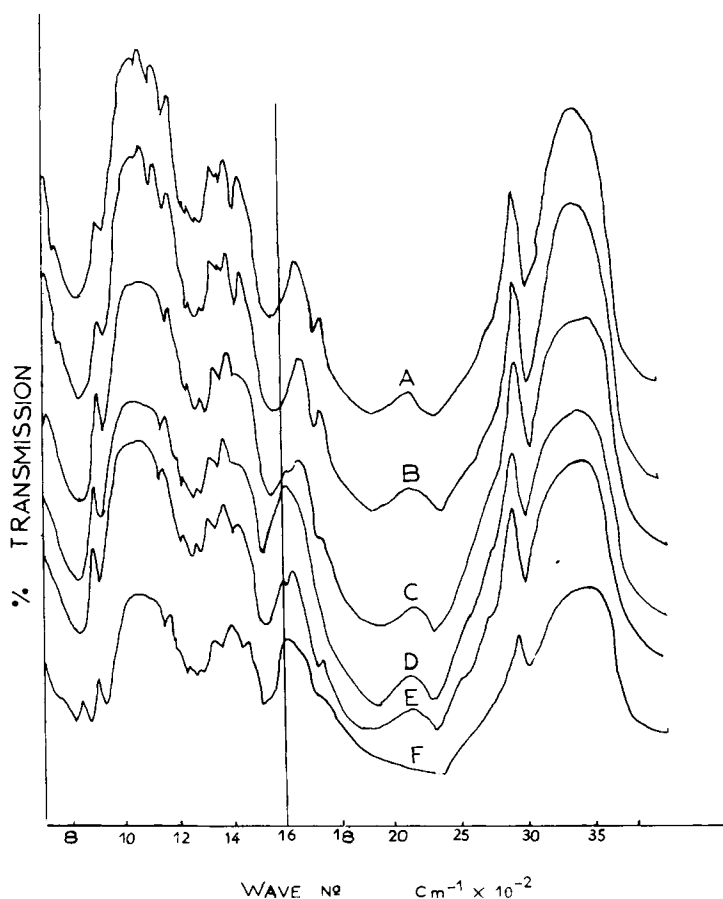


Fig. 3. IR spectra of $\gamma$-irradiated NaOH-treated cotton cellulose: A, untreated; B, treated with 10% NaOH; C, with 14% NaOH; D, with 18% NaOH; E, with 22% NaOH; F, with 26% NaOH.
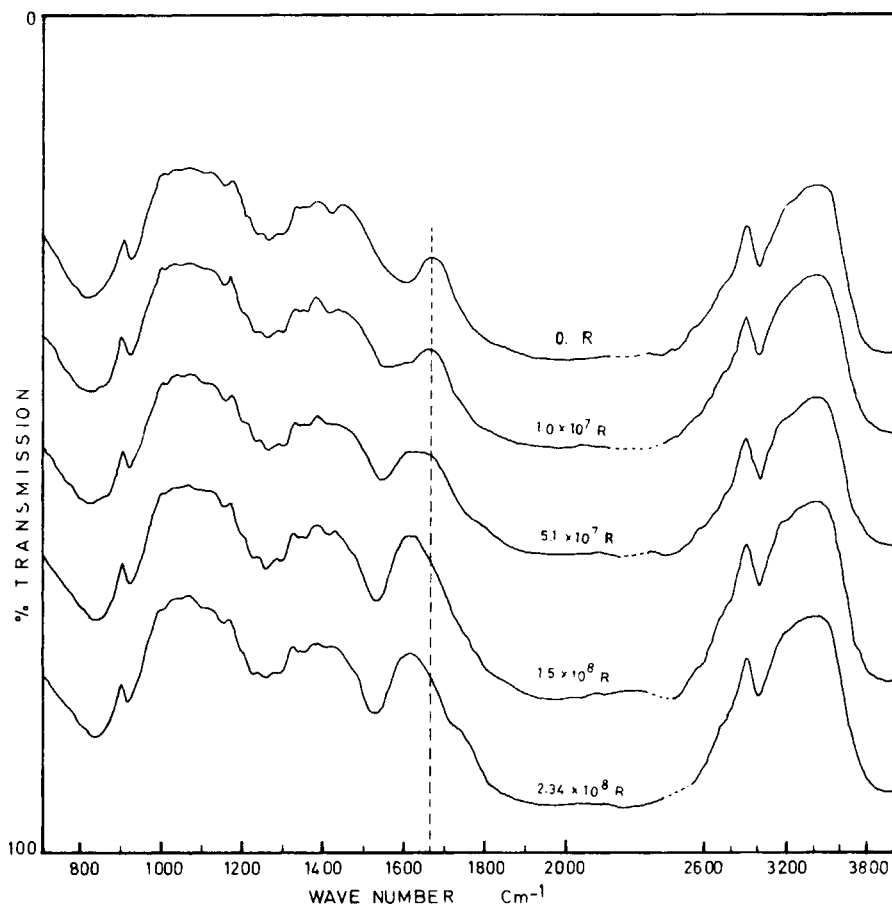
Fig. 4.  IR spectra of $\gamma$-irradiated cotton treated with 22% NaOH solution for 8 min.

cellulose II.[15,16]  It can be seen that raw cotton and the samples treated with 18 and 22% are highly crystalline, whereas the sample treated with 26% is of lower crystallinity.   The sample treated with 10% is highly crystalline cellulose I with a small amount of cellulose II.   The peaks in the diffractogram of the sample treated with 14% indicate that this sample is a mixture of celluloses I and II.

The samples under investigations were then exposed to $\gamma$-radiation at a dosage level of $4 \times 10^7$ rad.   The x-ray diffraction patterns of the irradiated samples revealed that there is no striking difference between the diffraction patterns of $\gamma$-irradiated and nonirradiated cotton samples.

The infrared spectra of raw and NaOH-treated samples are shown in Figure 2.   It shows that treatment of cotton powder with NaOH solution gives a broadening of the OH stretching band at about 3400 cm$^{-1}$ toward a lower wave number and shifts its maximum to a higher wave number.   However, the intensities of the bands at 1025, 1060, 1125, 1245, 1285, and 1475 cm$^{-1}$ decrease while the intensities of the bands at 900, 1345, and 1380 cm$^{-1}$ increase with increasing concentration of NaOH solution.

The infrared spectra of the $\gamma$-irradiated samples are shown in Figure 3.   This figure indicates that the most striking differences in the spectral curves of the
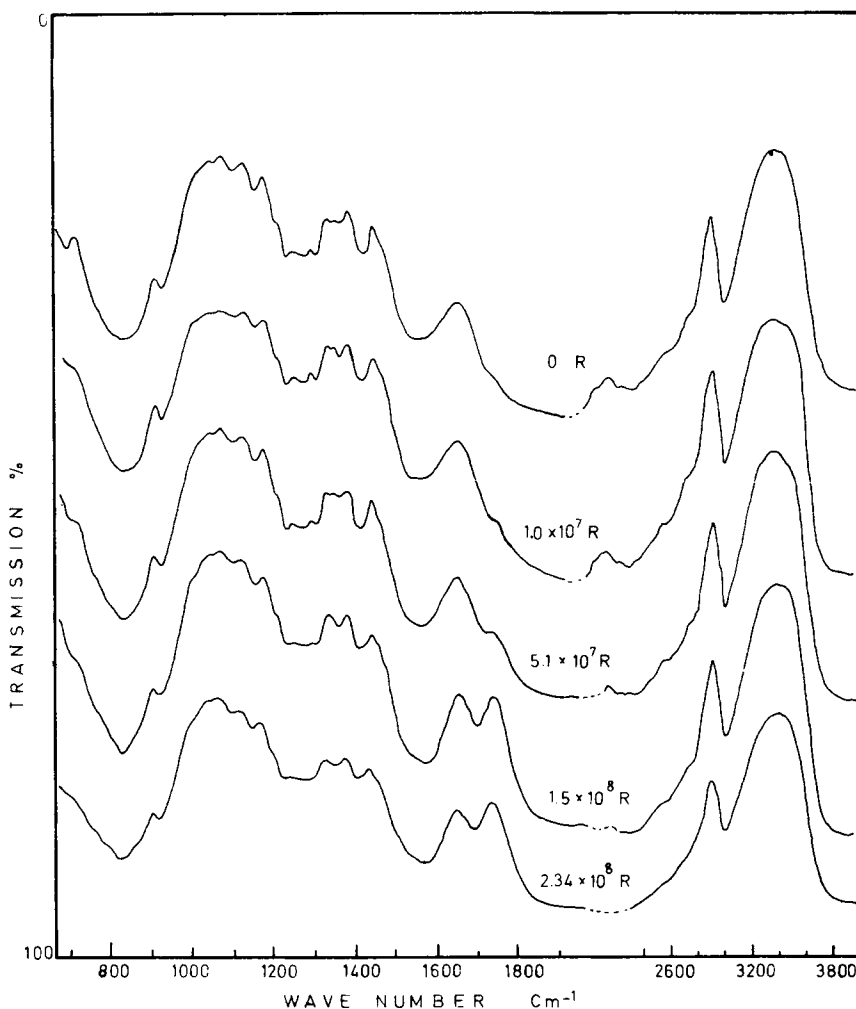
Fig. 5. IR spectra of γ-irradiated raw cotton.

irradiated samples from the unexposed cotton curves is the appearance of C=O band corresponding to both carbonyl and carboxylic groups. Figure 3 reveals that the position and intensity of this band vary with the crystalline structure of the treated samples. In the spectrum of raw sample, the C=O band appears at 1735 cm$^{-1}$, while in the spectrum of the sample treated with 18% NaOH solution, which is highly crystalline cellulose II, it appears at about 1610 cm$^{-1}$. The spectra of the samples of mixed lattice type exhibit the two bands at 1735 and 1610 cm$^{-1}$. The appearance of the band at 1610 cm$^{-1}$ in cellulose II compared to the band at 1735 cm$^{-1}$ in cellulose I is evidence of differences in the internal forces in the unit cell on change of the lattice type I to type II. This could be interpreted as a rearrangement in hydrogen bonding in the unit cell of cellulose II compared with cellulose I.

It should be mentioned here that the experiments carried out in this work have shown that radiation dosages lower than 10$^7$ rad give no detectable C=O band. It was also found that it is not easy to detect the band at 1610 cm$^{-1}$ even though

the dosage is higher than $10^7$ rad. The reason is that the band at 1610 cm$^{-1}$ is always overlapped by the $H_2O$ band at 1645 cm$^{-1}$. Figure 4 illustrates the variation of the 1610 cm$^{-1}$ band in the spectra of highly crystalline sample of cellulose II with radiation doses. The variation of the intensity of the 1735 cm$^{-1}$ with radiation dosage in highly crystalline cotton cellulose I is given in Figure 5.

From the above-mentioned data one can come to the conclusion that the infrared spectrum of $\gamma$-irradiated cellulose I could be distinguished from that of $\gamma$-irradiated cellulose II. In the spectrum of cellulose I, the C=O band appears at about 1735 cm$^{-1}$, while in the spectrum of cellulose II it appears at about 1610 cm$^{-1}$.

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