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Low-frequency IR spectroscopy in the study of the structures of cellulose and cellulose nitrates

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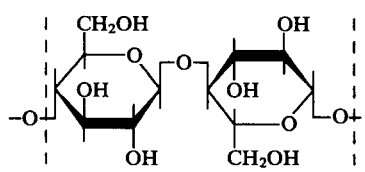
Abstract. The application of low-frequency IR spectroscopy in the structural analysis of polymers is examined. The vibrations of crystal lattices and polymer chains as well as deformation and torsional vibrations manifested in the low-frequency part of the IR spectrum are discussed. Studies in this field are reviewed critically and the experimental and theoretical data concerning the interpretation of the low-frequency spectra of monosaccharides, polysaccharides, and their nitro-derivatives are surveyed. Attention is concentrated on the establishment of 'spectrum–structure' correlations for cellulose in the course of its physical modification and chemical reactions (nitration). The bibliography includes 79 references.

I. Introduction

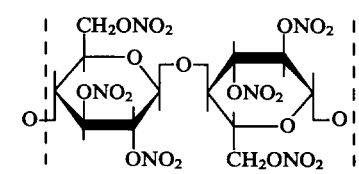
The high practical value of cellulose and its derivatives, especially its ethers and esters, has necessitated the study of the structural features of macromolecules in the course of their physical and chemical modifications. The structure of the polymer at the molecular and supermolecular levels of its organisation is associated with the packing of the macromolecules, intramolecular and intermolecular interactions, and the spatial orientation of the individual structural fragments.[1–15] The study of slight structural changes in the polymer requires the use of spectroscopic characteristics which are especially sensitive to such changes. The region of the 'atypical' low-frequency vibrations (30–700 cm^{-1}) is most sensitive to the changes in the structure of the polymers.[9–12] The interpretation of the spectrum in this region is impossible without theoretical calculations. Extensive experimental and theoretical data on model compounds of cellulose and cellulose nitrates (monosaccharides and disaccharides) have now accumulated. Their comparative analysis has made it possible to discover a series of spectroscopic features characterising the structural features of these low-molecular-mass polymer analogues.

A rigorous theoretical analysis of the vibrational spectra of such polymers is as yet impossible. On the other hand, in a number of recent studies it has been possible to find fairly rigorous correlations of the 'spectrum–structure–property' type in the analysis of the experimental spectra of cellulose in the course of its physical and chemical (nitration) modification and by comparing them with the spectra of model systems. The present review is devoted to the analysis of these investigations.

The cellulose macromolecule consists of a linear chain made up of β-D-glucose residues connected by 1,4-β-D-glycoside linkages.[1–3] The elementary unit of cellulose comprises two glucopyranose rings **1**. Different conformers can arise as a result of the change in the spatial orientation of the pyranose rings relative to one another and the hindered internal rotation of the OH and CH_2OH groups. In cellulose nitrates **2**, the hydroxy-groups have been substituted by nitrate groups and the polymer can contain units substituted to different extents (tri-, di-, and monosubstituted as well as unsubstituted units). Monosaccharides, disaccharides, and their nitro-derivatives are analogues of the structural fragments in the monomeric unit of cellulose and cellulose nitrates.



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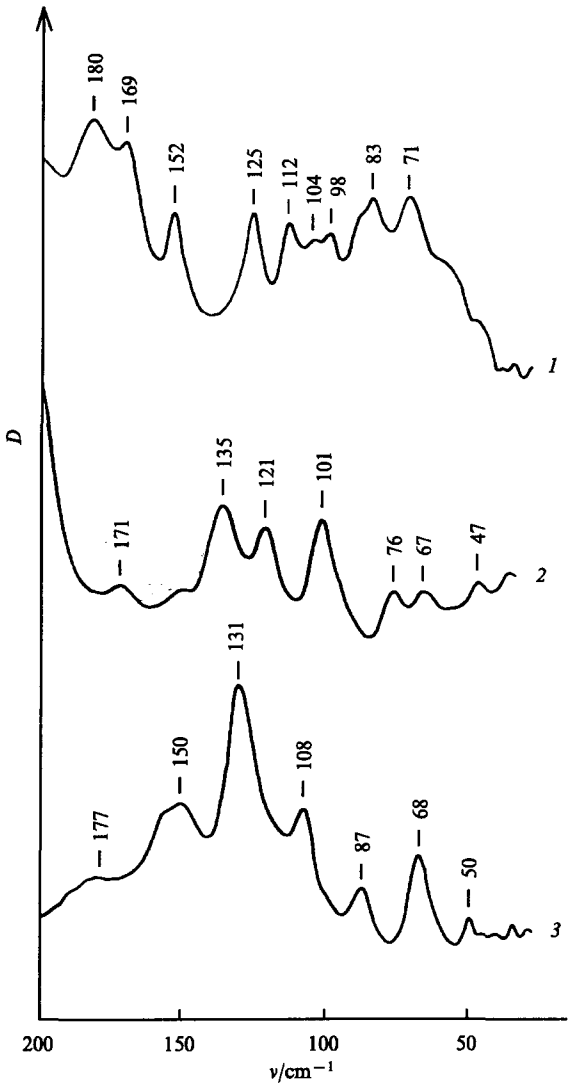


Figure 1. IR spectra of monosaccharides: (*1*) β-D-glucose; (*2*) β-D-mannose; (*3*) methyl β-D-glucoside.

II. Monosaccharides and disaccharides. Methyl β-D-glucoside nitrates

The experimental and theoretical methods of vibrational spectroscopy have been used fairly successfully for the analysis of monosaccharides, disaccharides, and their derivatives. It has been established that the vibrations at frequencies of 750–950 cm^{-1} depend on the type of the anomer: D-glucose, D-mannose, and D-galactose.[16–18] It has been shown[19, 20] that this dependence persists on formation of disaccharides and polysaccharides. Analysis of the low-frequency vibrations in the spectra of the monosaccharides was initiated in a number of studies,[21–23] which are mainly descriptive in character and do not contain correlations with the structural features of the molecules. Individual attempts have been made[24] to find the relationship between the structures of monosaccharides and disaccharides and their spectra. In particular, according to the authors, vibrations at frequencies in the range 500–700 cm^{-1} characterise the crystal structure of the compounds, while the vibrations at frequencies in the range 800–1 000 cm^{-1} characterise the type of configuration (α-, β-) of the glycoside bond in the disaccharides. The authors did not analyse the 40–500 cm^{-1} spectral range. A detailed study of the low-frequency vibrations resorting to data derived from theoretical calculations of the spectra of monosaccharides, disaccharides, and their nitro-derivatives[25–34] made it possible to solve a number of problems associated with the determination of the structure-

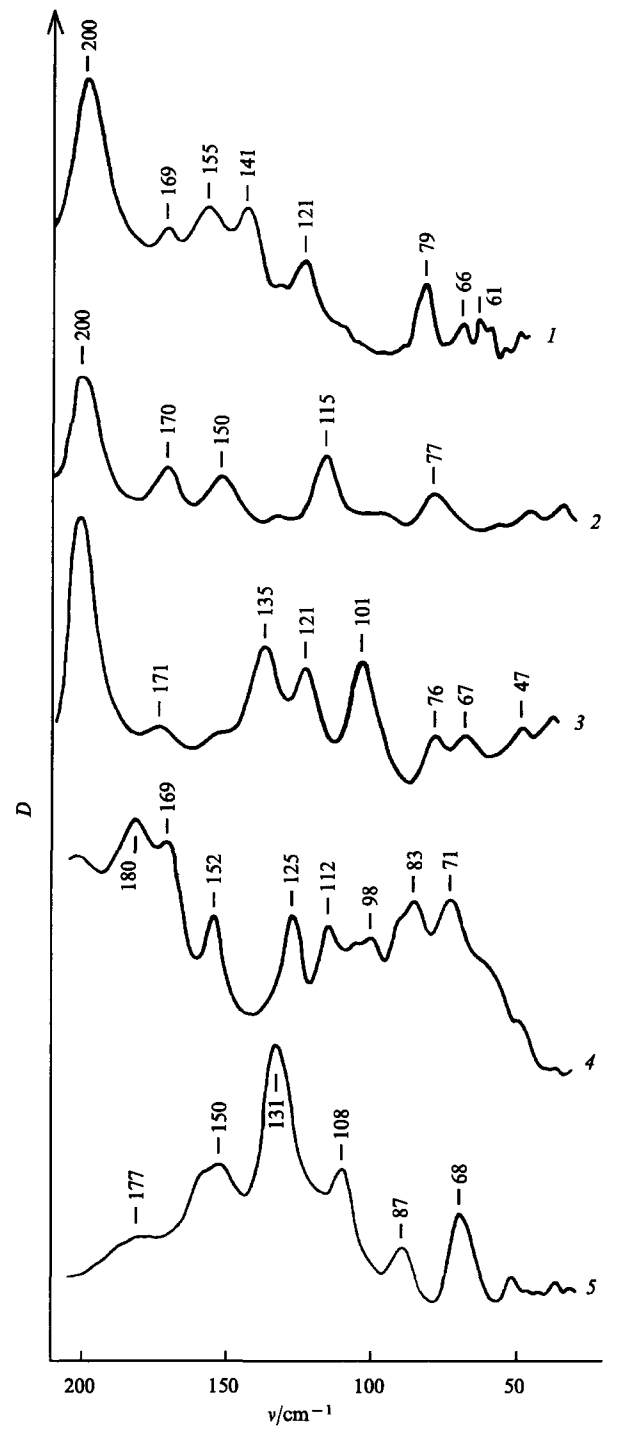


Figure 2. IR spectra of monosaccharides: (*1*) α-D-glucose; (*2*) α-D-galactose; (*3*) β-D-mannose; (*4*) β-D-glucose; (*5*) methyl β-D-glucoside.

sensitive absorption bands. Monosaccharides with different chemical structures of the fragments at the C(1) and C(5) atoms of the pyranose ring (OH, OCH_3, CH_2OH, H) (Table 1) and different configurations of the hydroxy-group at the C(1) atom [axial (*A*) and equatorial (*E*)], exhibiting rotational isomerism due to the rotation about the C–O bond, have been analysed.[26, 28, 29] In disaccharides, it is essential to note the difference between the types of glycoside bond connecting the glucose residues (the α- and β-configurations). The frequency ranges of the intermolecular vibrations of the crystal lattices (30–200 cm^{-1}) and of the intramolecular vibrations (150–700 cm^{-1}) were established in the above studies. The spectra of crystals of monosaccharides with a hydroxy-group at the C(1)

Table 1. Monosaccharides.

Compound	C(1)	C(5)	
α-D-Glucose	H	H	CH_2OH
β-D-Mannose	OH	H	CH_2OH
β-D-Glucose	OH	H	CH_2OH
Methyl β-D-glucoside	OCH_3	H	CH_2OH
α-D-Galactose	H	H	CH_2OH
α-L-Sorbose	OH	H	H
β-D-Xylose	OH	H	H
Arabinose	H(OH)	H	H
Ribose	H(OH)	H	H
Rhamnose	H(OH)	CH_3	H

atom (β-D-glucose, β-D-mannose are characterised by moderately intense absorption bands near 80, 120, and 170 cm^{-1} (Fig. 1). When the OH group is substituted by OCH_3, the 'crystallinity' bands undergo a slight hypsochromic shift owing to the change in the hydrogen bonds determining the crystal packing. This is also indicated by the results of Husain et al.,[34] who showed that, when the influence of the configurations of the CO(CH) bonds in the side fragments of the saccharide on the low-frequency vibrations is considered, it is essential to take into account the nearest structural elements. For the configurations *AEEEE* (α-D-glucose), *EAEEE* (β-D-mannose), and *AEEAE* (α-D-galactose) of the CO bonds at the atoms of the pyranose ring, the spectra show clearly an absorption band near 200 cm^{-1} (Fig. 2), while for the *EEEEE* configuration (β-D-glucose, methyl β-D-glucoside) this absorption is absent. In the region of the bands due to the 'crystallinity' of the disaccharide and the monosaccharides which it comprises, for example α-D-glucose and maltose or β-D-glucose and cellobiose, the spectra of all the substances were found to contain absorption bands at 200–220 cm^{-1} and 150–170 cm^{-1} (Fig. 3). This is explained by the similarity of the parameters of the crystal structures of the monosaccharide and disaccharides.

The uncharacteristic nature of the intramolecular vibrations in the range 200–700 cm^{-1}, deduced from theoretical calculations,[30–35] and their high sensitivity to slight structural changes in the crystal packing complicate the interpretation of the spectrum. Nevertheless, by analysing the spectra of crystalline and fused specimens and by resorting to calculated data for the steric structures of the saccharides, it has been possible to discover[26, 28, 29] the spectroscopic manifestations of different types of spatial orientation of individual fragments. It was shown that the position of the absorption band in the range 200–400 cm^{-1}, determined by the τ(CO) and τ(CC) torsional vibrations, depends on the orientation of the hydroxy-group at C(1) (Fig. 4). In the case of the axial disposition of the bond (α-D-glucose and α-D-sorbose), an intense absorption is observed near 300 cm^{-1}, while for the equatorial disposition (β-D-glucose, methyl β-D-glucoside, and β-D-xylose) it is observed near 312–325 cm^{-1}. The higher τ(CO) frequency for the equatorial orientation of the CO bond may be associated with its 'strained' state owing to the interaction with the lone pair of the oxygen of the pyranose ring. Calculations of the steric structures and the vibrational spectra of monosaccharides differing in the stereochemical disposition of the CO bonds at the C(1)–C(4) atoms confirmed the dependence of the torsional vibrations on the configuration of this group.[32] However, the calculations demonstrated a different trend in the variation of the frequencies on passing from axial to equatorial anomers. This can be explained by the fact that, in the calculations

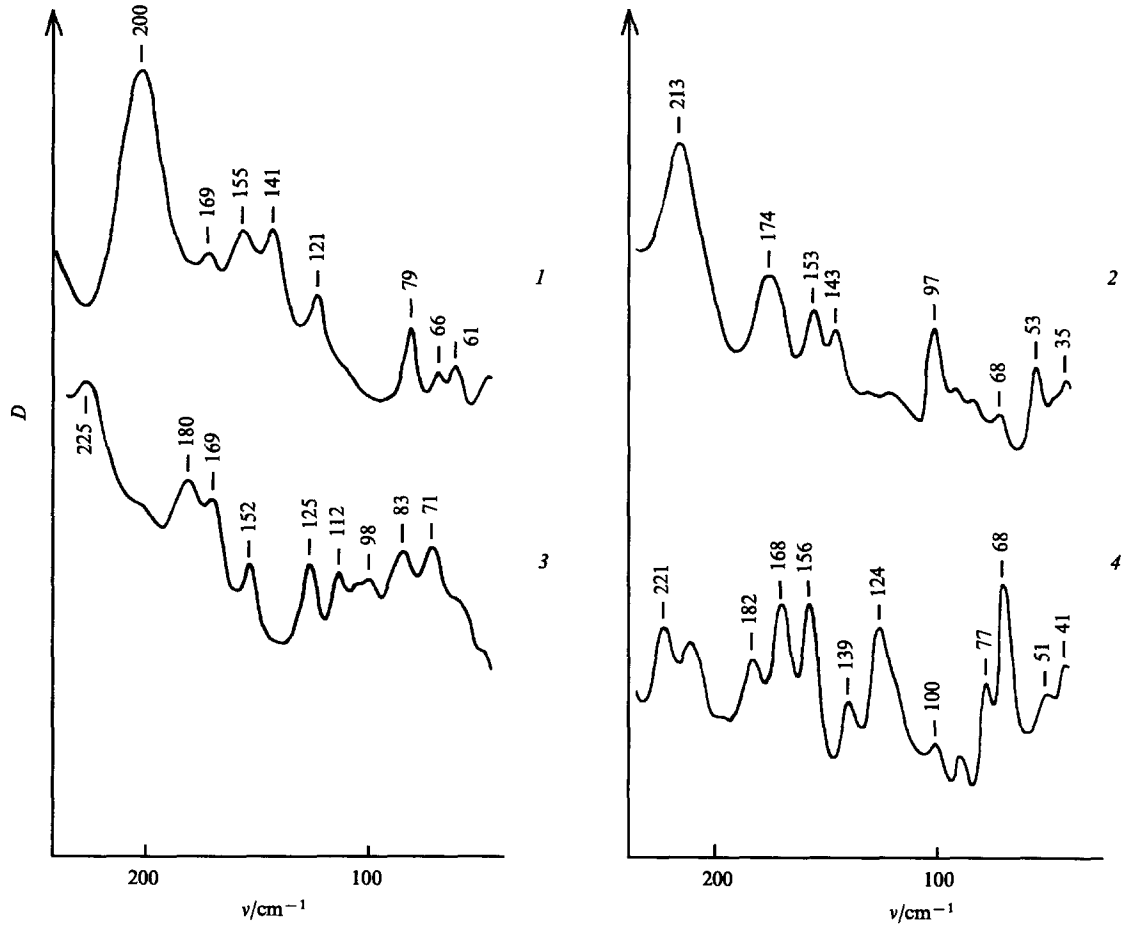


Figure 3. IR spectra of monosaccharides and disaccharides: (*1*) α D-glucose; (*2*) maltose; (*3*) β-D-glucose; (*4*) cellobiose.

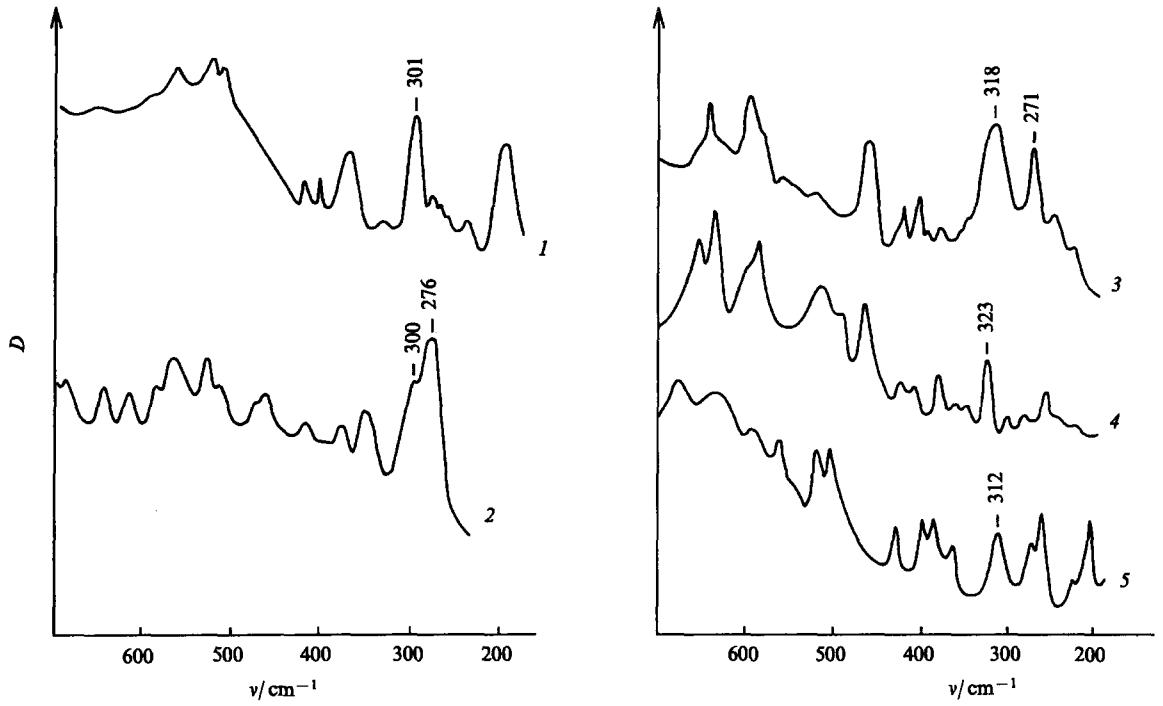


Figure 4. IR spectra of monosaccharides: (*1*) α-D-glucose; (*2*) α-L-sorbose; (*3*) β-D-glucose; (*4*) methyl β-D-glucoside; (*5*) β-D-xylose.

performed for isolated systems, no account was taken of the effects of the intermolecular interactions and of the crystal packing. Indeed, theoretical analysis of the spectrum of α-D-glucose taking into account the crystal field[33] demonstrated the dependence of the torsional vibration frequencies on the intermolecular interactions—the hydrogen bonds, determining the crystal packing of the molecules. Together with this, according to the calculations,[25, 29, 31, 32] the torsional vibrations and frequencies in the range 280–330 cm^{-1} are determined by the orientation of the CO bond of the hydroxy-methyl group at the C(6) atom. The conformational sensitivity of the torsional vibrations has been examined in fair detail in two investigations.[25, 29] The influence of the orientation of the hydroxymethyl group on the τ(CO) torsional vibrations in the range 160–400 cm^{-1} proved to be the most significant: variation of the frequencies by 30–60 cm^{-1} depending on the orientation of the CO and OH bonds of the CH_2OH fragment was observed. An increase in the complexity of the τ(CO) absorption band contour owing to the appearance of new constituent components was noted on fusion of the monosaccharides. One of the possible causes of this is the conformational transformations accompanying the fusion of the specimens. The influence of the spatial disposition of the structural fragments of monosaccharides and disaccharides on the vibration frequencies in the range 400–700 cm^{-1} has been treated systematically.[29, 35] According to calculations, this range contains the frequencies of the deformation vibrations of the CCO and COH groups at the C(1) and C(6) atoms, as well as those of the torsional vibrations of the C–OH bond. It has been shown that the transition from the *gauche*- to the *trans*-orientation of the C(6)–O(6) bond [relative to the C(5)–H(5) bond] is accompanied by an increase in the δ(CCO) and δ(COH) frequencies (620 and 470 cm^{-1}) by 30–40 cm^{-1}. The calculations made it possible to explain the experimentally observed differences between the spectra of the crystals and melts of β-D-glucose and methyl β-D-glucoside in the range 400–660 cm^{-1} by the difference between the conformations of the fragments at the C(1) and C(6) atoms. The dependence of the frequencies in the range 400–660 cm^{-1} on the configuration has also been noted.[29] A distinctive feature of the spectrum of the monosaccharide with the axial orientation (α-D-glucose) is the appearance of absorption bands at 514, 529, and 566 cm^{-1}. This frequency range is sensitive to the type of bonding of the glucose residues in the disaccharides. In the case of the α-configuration of the C–O–C group (maltose), the spectrum shows distinct absorption bands at 518 and 541 cm^{-1}. An intense absorption at 465 and 486 cm^{-1} is characteristic of the β-con-figuration (cellobiose).

The nitro-derivatives of monosaccharides and disaccharides are models of the monomeric unit of cellulose nitrate. The low-frequency spectra of selectively substituted methyl β-D-glucoside nitrates, namely 2,3-dinitro-, 2,3,6-trinitro-, and 2,3,4,6-tetranitro-methyl β-D-glucosides (Fig. 5), were first analysed by Mukhamadeeva and coworkers.[26, 29] According to the calculations, the frequencies and modes of the normal vibrations[36–39] corresponding to the absorption bands in the range 400–660 cm^{-1} are determined mainly by deformation vibrations involving the CCO, CON, and ONO group of atoms; in the frequency range 200–400 cm^{-1}, they are determined by the τ(CO) and τ(NO) torsional vibrations and δ(CCO) and δ(ONO) deformation vibrations. The characteristic features of the intermolecular interactions and the conformations of the hydroxy- and nitro-groups in the crystals and melts determine the contours and positions of the absorption bands. The sensitivity of the deformation vibrations at 400–660 cm^{-1} to the spatial orientation of the nitrate groups was predicted by calculations.[29, 37, 38] A characteristic feature of the spectra of methyl β-D-glucoside nitrates is absorption in the range 540–548 cm^{-1} (Fig. 5). According to calculations, these frequencies are characteristic of deformation vibrations involving nitrate groups: ON(2)O in the dinitrate, ON(6)O and CON(6) in the trinitrate, and ON(2)O and ON(4)O in the tetranitrate of methyl β-D-glucoside. It has been proposed that the absorption in this frequency range be used for the analysis of the nitrate groups. The frequencies in the range 30–200 cm^{-1} are sensitive to the presence of a crystal structure and the nature of the packing of the molecules in the crystal (Fig. 5).

Analysis of the spectra of model compounds made it possible to interpret the low-frequency spectra of cellulose and its nitrates.

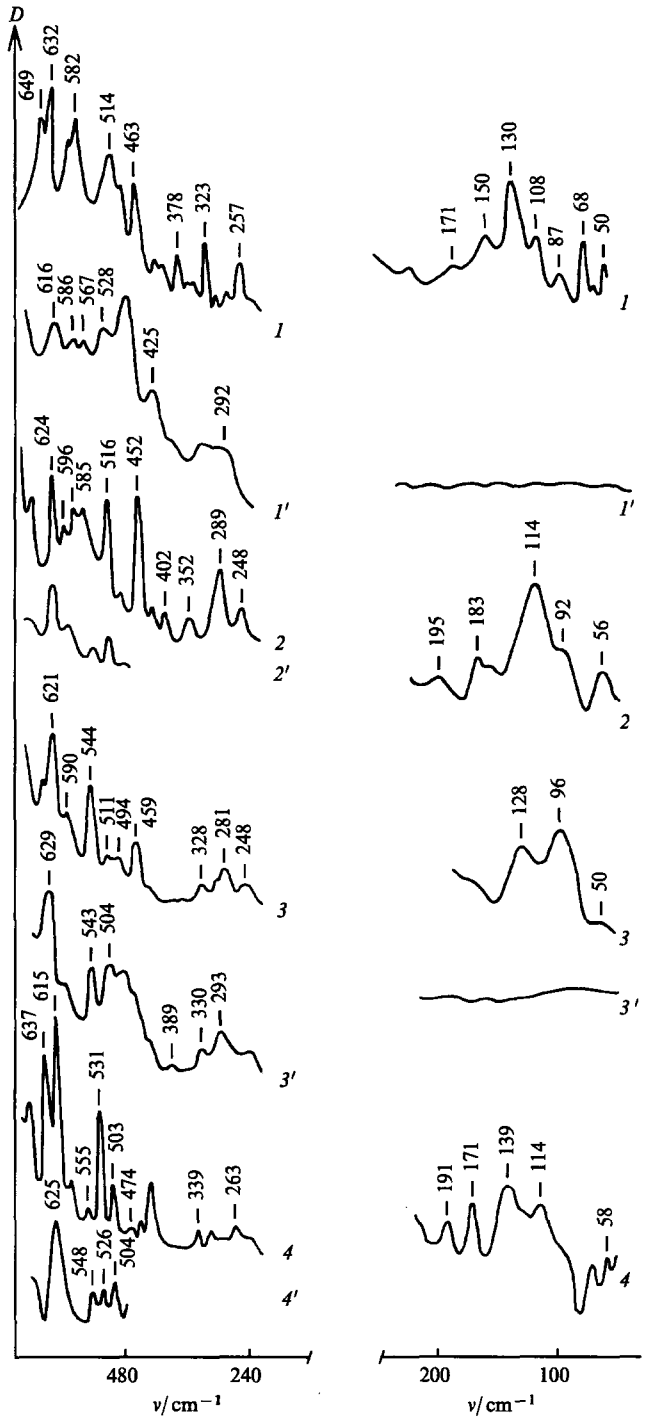


Figure 5. IR spectra of methyl β-D-glucoside nitrates: (*1*) methyl β-D-glucoside; (*2*) methyl 2,3-dinitro-β-D-glucoside; (*3*) methyl 2,3,6-trinitro-β-D-glucoside; (*4*) methyl 2,3,4,6-tetranitro-β-D-glucoside; (*1'*)–(*4'*) spectra of the corresponding melts.

III. Celluloses with different degrees of structural order

The properties of a polymer are determined by the structure of both its elementary unit and of the macromolecule as a whole.[9, 40] The intermolecular interaction forces between the polymer chains are significantly weaker than the intramolecular forces and, to a first approximation, their influence on the vibrational spectrum can be regarded as a perturbing factor. As mentioned above, in the interpretation of the spectrum of cellulose use is made of the comparative analysis of the spectra of the polymer and of the corresponding low-molecular-mass analogues. The identity of the structural elements of cellulose, β-D-glucose, and cellobiose is responsible for a series of similar absorption bands in the range of the δ(CCO), δ(CCH), and δ(COH) deformation frequencies and the τ(CO) and τ(CC) torsional frequencies at 200–700 cm^{-1} (Fig. 6). The complex diffuse contour of the absorption bands in the spectrum of cellulose compared with those of the low-molecular-mass analogues can be explained by a characteristic feature of the structure of its macromolecules: the multiplicity of intermolecular and intramolecular interactions and the conformational properties of the fragments of the polymer chain. In the range of the vibration frequencies of the crystal lattices (30–200 cm^{-1}), the differences between the spectra of cellulose and the model compounds are more significant (Fig. 7). The spectrum of cellulose shows moderately intense bands at 70, 100, and 170 cm^{-1}. A series of bands characteristic of mono-saccharides and disaccharides vanish. The reason for this is the complex structural organisation of the highly ordered cellulose formations.[28, 29]

The intermolecular order (two- and three-dimensional), determined by the conformation of the macromolecular chain and the system of intermolecular interactions, and the intramolecular order, characterised by the conformations of the pyranose rings and the hydroxy-groups and by the mutual spatial disposition of the elementary units, are distinguished in the structure of cellulose. The existing experimental methods[41–44] make it possible to estimate the degree of order in the polymer.

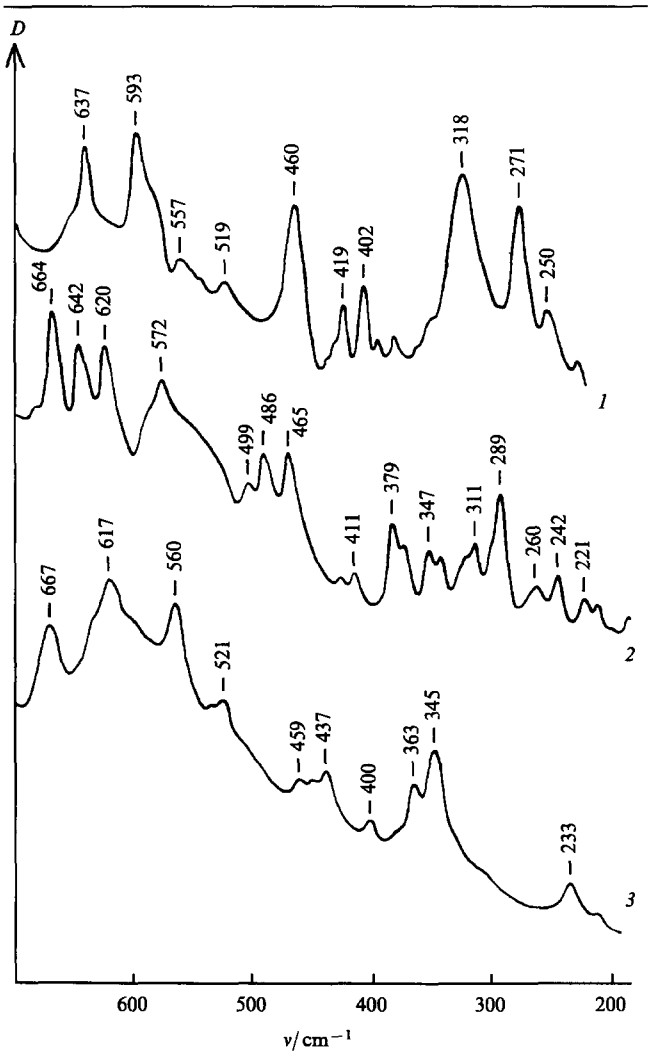


Figure 6. IR spectra (200–700 cm^{-1}): (*1*) β-D-glucose; (*2*) cellobiose; (*3*) cellulose.

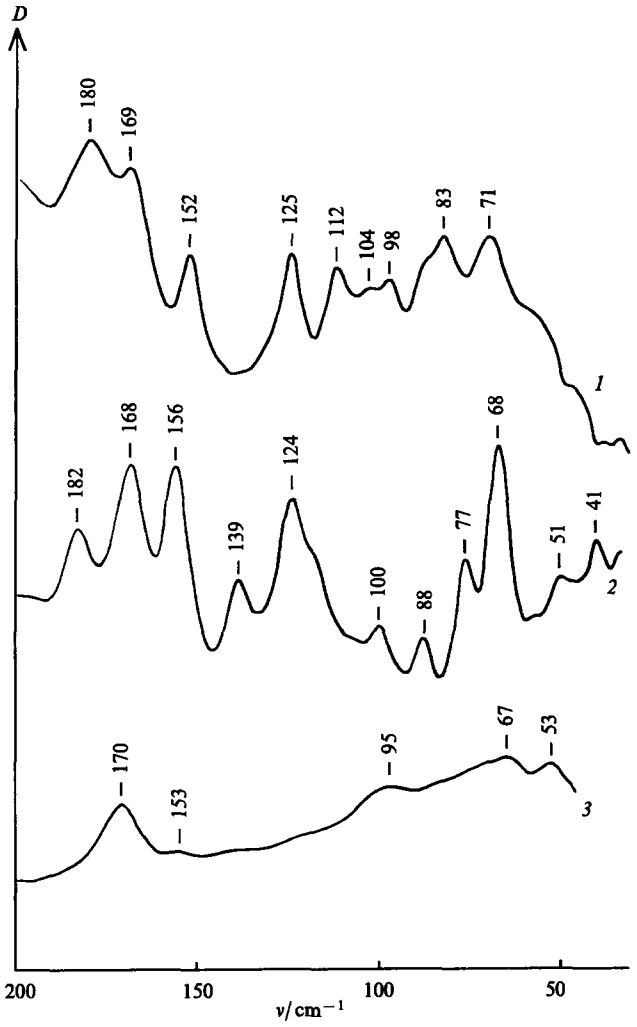


Figure 7. IR spectra (30–200 cm^{-1}): (1) β-D-glucose; (*2*) cellobiose; (*3*) cellulose.

X-Ray diffraction methods permit the estimation of the intermolecular three-dimensional order. The degree of intramolecular order associated with the rotation of the CH_2OH groups in the ordered sections of cellulose can be determined by analysing the IR absorption in the ranges 1 200–1 400 and 800–900 cm^{-1}.[3, 4] The study of the spectra in the range 30–200 cm^{-1} on these lines is particularly valuable, because low frequencies are characteristic of vibrations of the more complex structural elements—crystal lattices and polymer chains.[11, 12] A detailed quantitative analysis of the low-frequency absorption bands in the spectra of cotton and wood celluloses with different degrees of order has been carried out.[28, 29] Below 200 cm^{-1}, no distinct absorption bands were observed in the spectrum of disordered cellulose. Bands at 70, 100, and 170 cm^{-1}, which are a manifestation of the crystalline structure and can be used for the quantitative determination of the degree of order in cellulose, are characteristic of highly ordered cellulose.[29] According to the existing methods for the spectroscopic estimation of the degree of order in polymers,[9] the Beer–Lambert law for the optical density of the 'crystallinity' band (170 cm^{-1}) is defined by a relation of the type

$$D_{rel} = \varepsilon_{rel} K ,$$

where D_{rel} is the ratio of the optical density of the absorption band at 170 cm^{-1} to the optical density of the 'standard' absorption band at 520 cm^{-1} (the intensity of this absorption band is independent of the treatment of celluloses), ε_{rel} is the relative extinction coefficient at the above frequencies, and K is the degree of order (the volume concentration of the ordered fraction). The coefficient ε_{rel} can be determined by measuring D_{rel} in the spectrum of microcrystalline cellulose with a known degree of order—$K = 0.64$ (Magdalev et al.[43]); in this case $K = 0.54D_{rel}$. The spectroscopic estimates of the degree of order in natural celluloses based on low-frequency spectra and X-ray diffraction studies are presented in Table 2. Thus quantitative estimation not only of the intramolecular degree of order but also of the intermolecular degree of order (two- and three-dimensional) is possible with the aid of IR spectroscopy.

Table 2. Estimates of the degree of order in celluloses from spectroscopic and X-ray diffraction data.

Cellulose	IR spectroscopy[29]	X-Ray diffraction analysis[42, 43]
Microcrystalline	–	0.64
Cotton	0.45	0.50
Wood	0.36	0.41
Mercerised	0.14	0.42
Treated with liquid ammonia	0.22	–

IV. Celluloses of different origin and with different structural modifications

Cellulose can exist in different structural modifications.[1] The main ones are cellulose I (CI)—natural cellulose—and cellulose II (CIII), obtained from natural cellulose by reaction with concentrated solutions of alkali (NaOH). Treatment of CI and CII with liquid ammonia and subsequent removal of NH_3 vapour yields cellulose III (CIII).

Significant differences between CI and CII are observed in the study of these structural modifications by IR spectroscopy.[3–7, 45–47] Compared with the spectra of CI, the spectra of CII exhibit a broadening of the ν(OH) absorption band (3 000–3 600 cm^{-1}) and a change in the intensities of the absorption bands at 1 300–1 500 and 900 cm^{-1}. The spectral differences between CI and CII reflect the differences between the systems of hydrogen bonds and the orientations of the hydroxymethyl and hydroxy-groups noted in theoretical calculations.[48–51] The spectral changes in the structural transition from CI and CII (in the mercerisation process) have been established in a number of studies.[45–47] The process was monitored by measuring the optical densities of the 1 375 and 1 325 cm^{-1} absorption bands. A linear dependence of the absorption band intensities at 900 and 1 430 cm^{-1} on the sodium hydroxide concentration was established.[46] The spectroscopic characteristics of CI and CII have been explained by the conformations of the hydroxymethyl groups—the hydroxymethyl groups in the disordered regions make the main contribution to the absorption band at 900 cm^{-1} in the spectrum of natural cellulose, while in the spectrum of cellulose hydrate the main contribution comes from the hydroxymethyl groups in the ordered regions. Analysis of the characteristics of the ν(OH) absorption band (3 000–3 600 cm^{-1}) showed[45] that the cellulose mercerisation process is associated with the increase in the number of energetically weaker hydrogen bonds. A number of studies have been made on the low-frequency spectra of celluloses modified in different ways.[52–54] The most marked differences occur in the IR spectra in the frequency range 300–500 cm^{-1}. Differences in the range 200–600 cm^{-1} have also been observed in the Raman spectra of CI and CII. According to the results of Atalla and Dimick,[53] these spectroscopic features are due to the specific characteristics of the mutual orientation of the D-glucose residues in the polymer chain. A detailed study has been made[26, 29] of the spectra of different structural modifications of cellulose in the frequency range 30–700 cm^{-1} using data for model compounds. Characteristic features were observed in the spectra of celluloses I, II, and III in the frequency range corresponding to the vibrations of the ordered structural elements—crystal lattices and

polymer chains (30–200 cm^{-1}). The lattice vibrations in CI and CIII have frequencies of 100 and 170 cm^{-1}, while those in CII have frequencies of 125 and 170 cm^{-1}. A complex multicomponent absorption with maxima at 364 and 344 (CI), 380 and 351 (CII), and 349 cm^{-1} (CIII) was noted in the frequency range 200–400 cm^{-1}. These vibrations are sensitive to conformations[29] and are determined by the spatial orientation of the hydroxymethyl groups. Calculations showed that[29] the vibrations with frequencies of 340 cm^{-1} are characteristic of the *gauche*-orientation of the CO bond in the CH_2OH group regardless of the disposition of OH. These vibrations are more distinctive in CI, which indicates the predominance of the *gauche*-conformation in this structural modification. The data obtained agree also with the results of conformational calculations on the isolated cellulose I helix.[48–51] According to Mukhamadeeva,[29] the more distinct manifestation of the component at 380 cm^{-1} is due to the presence of the *gauche*-conformation of the CO bond for the *gauche*, *trans*-orientation of the hydroxy-group. The ratio of the intensities of the components of the 300–400 cm^{-1} absorption band is used for the comparative estimation of the conformational composition of the hydroxymethyl groups in various celluloses. Table 3 shows that the conformations of the hydroxymethyl groups are similar in celluloses of different origin and prepared in different ways but are different in CI and CII. Analysis of the spectra of model disaccharides[28, 29] demonstrated the possibility of estimating the comparative orientations of glucose residues along the glycoside linkage from the absorption bands in the frequency range 500–600 cm^{-1}. In the spectra of celluloses, the 520 and 560 cm^{-1} bands are most distinct in this range. The quantitative estimate based on the intensities of these absorption bands (Table 3) indicates significant differences between the celluloses as a function of their modification. The origin and the method of preparation of the cellulose have less influence on the degree of order in the macromolecules and on the conformational properties of individual fragments.

Low-frequency IR spectra have also been used to discover the mechanism of the structural (physical) modification of cellulose when it is treated with a solution of sodium hydroxide. The heterogeneity of the physical structure of cellulose is known to be responsible for the presence of two stages in the mercerisation process. In the initial stage, the interfibre space is filled (impregnation of pores) and this is followed by the diffusion of the reagent into the cellulose fibres. It was important to detect the second stage of the reaction. The principal structural changes in the cellulose at the molecular and supermolecular levels occurred at this instant. Three stages in the structural changes in cotton and wood celluloses have been differentiated[29] on the basis of spectroscopic data. In the first stage (Fig. 8), the structure of the celluloses is almost unaltered for a sodium hydroxide content up to 8%. In this case, the interfibre pores are filled with the alkaline solution. In the second stage of mercerisation, involving the penetration of the reagent into the fibre (8%–14%), there is a sharp change in the intensity ratios of the spectra of the absorption bands D_{560}/D_{520} (D_1), reflecting the characteristics of the orientation of the elementary units of the macromolecules, and D_{363}/D_{344} (D_2) and $D_{1\,430}/D_{900}$ (D_3), associated with the spatial orientation of the side fragments, particularly the CH_2OH groups. The hypsochromic shift of the ν(OH) absorption band maximum is induced by the increase in the number of energetically weaker hydrogen bonds[15, 55]—changes in the system of intramolecular hydrogen bonds of the type O(2)–H ... O′(6)H and O′(6)H ... O(2). These features are closely related to the conformational composition of the hydroxymethyl groups. Analysis of the 'crystallinity' band (170 cm^{-1}) showed that the second mercerisation stage (8%–12%) is accompanied by a sharp increase in the disorder in the cellulose chains (the degree of crystallinity K decreases from 0.44 to 0.16). At a solution concentration of 14%–18% (third mercerisation stage), the spectral changes associated with the structural transformations outlined above are gradually completed.

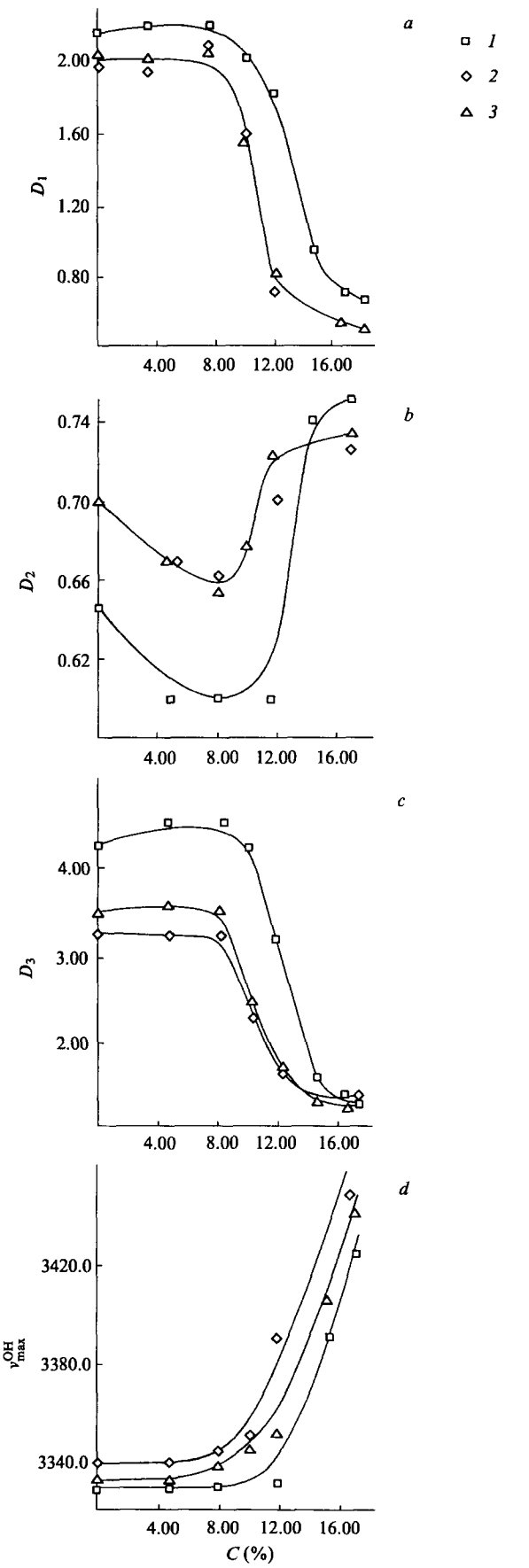


Figure 8. Dependence of the intensities D_1 (*a*), D_2 (*b*), and D_3 (*c*) and of the ν(OH) maxima (*d*) of the absorption bands on the concentration of sodium hydroxide (*C*, %): (*1*) cotton cellulose; (*2*) wood cellulose fibres; (*3*) wood cellulose paper.

Table 3. Intensity ratios of the low-frequency bands of different celluloses.[28, 29]

D_{rel}	Origin			Method of preparation			Structural modification		
	CC	WCF	WCP	SFI	SFA	NA	I	II	III
363/344	0.65	0.73	0.70	0.72	0.70	0.71	0.65	0.85	0.78
560/520	2.18	2.22	2.06	2.02	2.41	2.32	2.18	0.61	1.35

Note. CC = cotton cellulose, WCF = wood cellulose in the form of fibres, WCP = wood cellulose in the form of paper, SFI = cellulose obtained by the sulfite method, SFA = cellulose obtained by the sulfate method, NA = cellulose obtained by the nitric acid method.

A method has been proposed for monitoring the amount of CI which has been converted into CII in terms of the optical densities of the low-frequency absorption bands.[28, 29]

V. Formation of the structure of cellulose nitrate

The nitration of cellulose takes place, like the mercerisation process, in a heterogeneous medium, the rate of nitration being determined by the ratio of the rate of diffusion of the reagent into the fibre to the rate of the chemical reaction. The chemical reaction and the diffusion of the reagent are related in their turn to the accessibility of the reaction centres (hydroxy-groups) and the structure of the initial cellulose.[1] IR spectroscopy combined with other physicochemical methods, particularly with X-ray diffraction analysis and high-resolution ^{13}C NMR spectroscopy in the solid phase, is a fairly effective method for the investigation of the formation of the cellulose nitrate structure.[3, 7] The spectra of cellulose nitrate in the frequency range 600–4000 cm^{-1} contain absorption bands characteristic of the nitrate groups: an intense absorption in the frequency ranges 1500–1700 cm^{-1} and 1200–1300 cm^{-1}, due respectively to the antisymmetrical and symmetrical $\nu(NO_2)$ vibrations, and moderately intense absorption bands at 650, 750, and 840 cm^{-1} referring to $\nu(NO)$ and $\delta(ONO_2)$.[56, 57] In addition, the IR spectra of incompletely esterified specimens contain in the frequency range 3100–3600 cm^{-1} a diffuse absorption due to the residual OH groups. The position of the maximum of this band indicates the presence in cellulose nitrate (CN) of weak hydrogen bonds of the type OH ... ONO_2.[56] The molecular structure of cellulose nitrate has been analysed[58–60] as a function of the origin of the cellulose and the composition of the nitrating mixture. The degree of asymmetry of the $\nu(OH)$ absorption band contour has been used to estimate spectroscopically the uniformity of the substitution of the hydroxy-groups.[61] It was shown that, during the nitration of cellulose with nitric acid in a medium with methylene chloride, the hydroxy-groups are substituted fairly uniformly. This is associated with the ability of methylene chloride to loosen the packing of the polymer chains, which facilitates the penetration of the nitrating agent to the reaction centres.[58]

It has been proposed in a number of studies[57, 62–66] that the $\nu_{as}(ONO_2)$ absorption band (1500–1700 cm^{-1}) be used for analytical purposes in order to determine the nitrogen content and the locations of the nitric groups. However, the study of model compounds[62, 63] and cellulose nitrates in different stages of aggregation[4, 64] demonstrated that the determination of these structural parameters yields uncertain results. The complex contour of the $\nu_{as}(NO_2)$ absorption band is due to the superposition of the effect due to the crystal packing of the molecules, intermolecular interactions, the environment of the nitrate groups, and their conformational state. The spectroscopic manifestation of each of the above effects is determined by the state of aggregation of the cellulose nitrate test specimen and the degree of its esterification.

A theoretical study of the conformational properties of the monomeric and dimeric fragments of the cellulose trinitrate (CTN) macromolecules within the framework of the method of atom–atom potentials has been described.[65, 66] The stable conformations, determined by the rotation about the CO and CC bonds, were established. It was shown that, in the case of the nitrate groups at the C(2) and C(3) atoms, four rotational isomers can be formed preferentially. The CH_2ONO_2 group has a large number of stable conformations. The conformations of the dimeric fragment (elementary unit) of the cellulose trinitrate molecule have been calculated.[66] In the analysis of the potential surface as a function of the torsional angles at the glycosidic bond, which determine the conformation of the chain skeleton, two regions with low energies were discovered in the ranges from 0° to 20° and from 20° to 40°. It was established that the allowed region of possible cellulose nitrate conformations is smaller than a similar region in cellulose, which indicates a lower conformational liability of the monomeric units of cellulose trinitrate compared with cellulose. The steric forms of the macromolecules produced are determined mainly by the orientation of the side fragments.[3] As in the case of cellulose trinitrate, the conformational analysis of partly substituted cellobiose nitrates demonstrated the presence of two deep minima on the potential surface.[67] The authors noted only a slight difference in the steepness of the potential energy surfaces for partly and fully substituted cellobiose nitrates. Furthermore, in the partly substituted cellobiose nitrates the formation of intramolecular hydrogen bonds of the type O(3)H ... O(5) and O(3)H ... O(2)H or O(3)H ... O(2)NO_2 has been postulated. They are important for the stabilisation of cellobiose nitrate. The possibility of the formation of hydrogen bonds in partly substituted cellulose nitrates had been confirmed earlier in an analysis of experimental spectra.

A number of studies have been made on the low-frequency spectra of cellulose nitrates.[29, 68–71] The high sensitivity of the low-frequency vibrations to the characteristics of the crystal and molecular structures enabled the authors to solve a series of practical problems associated with the assessment of the kinetics of the nitration of cellulose. In the nitration of celluloses, the chemical reactions involve the formation of new structures.[3] The establishment of the relationship between the stages in the chemical synthesis, determined by the kinetic and diffusional processes, and the stages in the structural transformation, characterised by the disordering of the cellulose chains, the mutual orientation of the monomeric units, and the conformational state of the fragments of the macromolecules, is important. The spectra of cellulose nitrates with different degrees of substitution (γ) have been investigated.

Fig. 9 presents the low-frequency spectra of cellulose and cellulose nitrate. The frequencies and the assignments of the vibrations are given in Table 4. Analysis of the model compounds showed that the range of intramolecular vibrations of the macromolecules (200–700 cm^{-1}) and the frequency range of the intermolecular vibrations of the ordered polymer chains (30–200 cm^{-1}) can be differentiated arbitrarily in the spectra. During nitration, virtually the entire low-frequency spectrum changes. In the range of frequencies of the intramolecular vibrations, there are significant changes in the range 480–600 cm^{-1}. The multicomponent absorption observed in this frequency range is due to mixed vibrations with participation of the CCO, CON, and ONO groups of atoms.[29, 36–39] The positions of the bands and their intensities depend on the degree of substitution. Thus, for low values of γ, the spectra contain distinct bands with maxima at 560 and 520 cm^{-1}. The intensity of the 560 cm^{-1} band diminishes

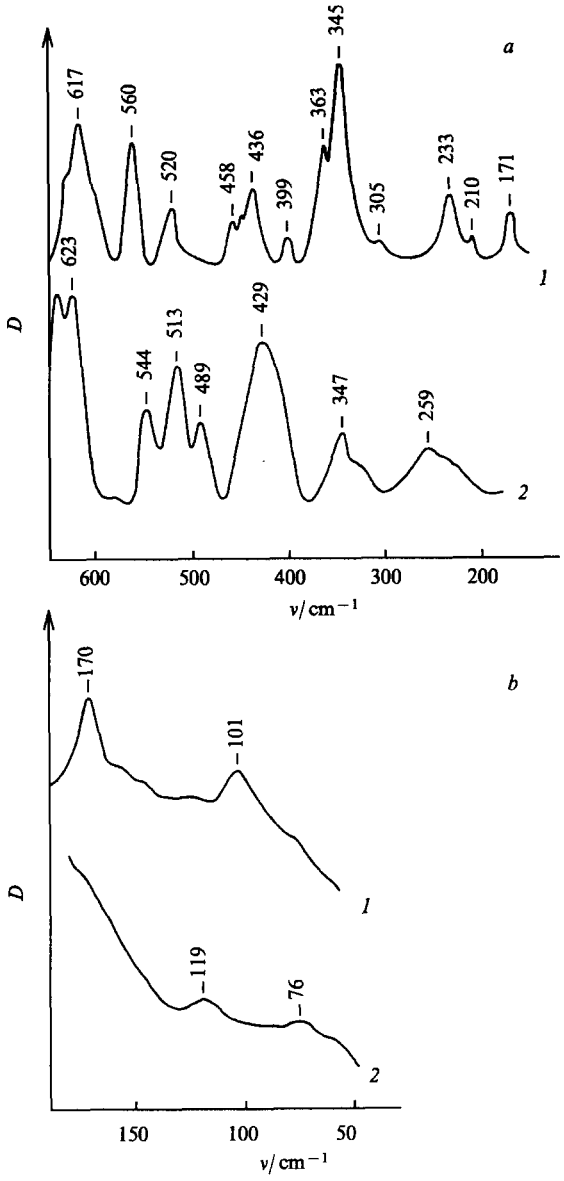


Figure 9. IR spectra of cellulose (curves *1*) and cellulose nitrate (curves *2*) (200–700 cm^{-1}).

with the increase in the degree of substitution. This has been explained by the characteristic features of the environment of the carbon atom involved in the glycosidic C–O–C linkage and by the orientation of the monomeric units. These structural changes are most significant in the first stage of the chemical synthesis (up to a degree of substitution of 1.6). The conclusions reached for vibrations at frequencies of 480–600 cm^{-1} are important. The increase in the absorption intensity at 544 cm^{-1} is explained by the substitution of the hydroxy-groups located at the C(6) atom. The triplet structure of this absorption band with maxima at 490, 513, and 544 cm^{-1}, manifested in the spectra for degrees of substitution in excess of 1.6 (the second stage of the chemical synthesis), has been attributed to the formation of the trinitrate units in the cellulose nitrate.

In the frequency range 300–500 cm^{-1}, where the δ(CCO), δ(CON), δ(ONO), τ(CO), and τ(NO) vibrations are manifested according to calculations,[29, 38] the increase in the intensity of the 436 cm^{-1} absorption band entails a decrease in the intensity of the absorption at 344 cm^{-1}. These spectral changes during the nitration processes have been attributed to the increase in the content of nitrate groups and the decrease in the number of residual hydroxy-groups. The spectra in this range are sensitive to conformations.[27–29, 38] For degrees of substitution of 1.6–1.8,

Table 4. Experimental and theoretically calculated frequencies of the normal vibrations of cellulose nitrate.[29, 38]

Frequency/cm^{-1}		Assignment
experiment	calculation	
644s	643[a]	δ[CON(2)] δ[ON(6)O] δ[CC(4)O]
623s	626[a]	δ[CON(2)] δ[CON(3)] δ[CC(2)O]
593sh	601[a]	δ[ON(3)O] δ[CC(1)O] δ[CC(3)O]
580w	–	–
576w	560[a]	δ[C(2)C(1)O(5)] δ[C(4)C(5)O(5)]
544m	540	δ[ON(6)O] δ[C(4)C(5)O(5)]
513m		
490m	484[a]	δ[ON(6)O] δ[ON(2)O] δ[CON(3)]
450sh	441	δ[ON(2)O] δ[CON(6)]
428s	425	δ[ON(3)O] δ[ON(2)O]
370sh	–	–
348m	360[a]	τ[N(6)O]
332sh	322[a]	δ[OC(1)O] δ[C(4)C(5)O(6)]
307sh	303[a]	τ[N(6)O]
280sh	–	–
253m	247[a]	τ[N(6)O]
242sh	–	–
120w	–	–
80w	–	–

Note. Absorption bands: s = strong (intense), m = moderately intense, and sh = shoulder.

[a] Vibration frequencies sensitive to conformations.

the conformational structure of the nitrate and the residual hydroxy-groups is virtually stabilised. In the frequency range 200–300 cm^{-1}, the frequencies of the τ(CO) and τ(NO) torsional vibrations shift from 233 to 251 cm^{-1} with increase in the degree of substitution of cellulose. The reason for this is the increase in the barrier to the internal rotation of the nitrate groups compared with the hydroxy-groups.

The absorption at 170 cm^{-1} has been used to analyse the changes in the crystal structure of cellulose. A significant disordering in the cellulose chains for a degree of substitution of 1.6 has been observed. At the same time, the appearance of new absorption bands at 80 and 120 cm^{-1} has been noted in the spectra of cellulose nitrates with increase in γ. They were assigned to the low-frequency vibrations of the cellulose nitrate macromolecules in the ordered regions. The disruption of the crystal structure of cellulose and the presence of elements of an ordered structure in cellulose nitrates for a degree of substitution of 1.6 have been confirmed also by the results of X-ray diffraction analysis.[67]

VI. Kinetics of the nitration of celluloses of different biological origin and with different structural modifications

The chemical reactions of cellulose and the formation of the structure of cellulose nitrates are in many respects determined by the biological origin and the structural modification of cellulose and by the conditions in its nitration. A number of studies[58, 59, 72] have been devoted to the X-ray diffraction analysis of the characteristic features of the formation of the crystal structures of different cellulose nitrates. By means of high-resolution ^{13}C and ^{15}N NMR spectroscopy,[73, 77] the establishment of the monomeric composition of cellulose nitrate was analysed. A number of studies[28, 29, 69–71] were devoted to investigations on the low-frequency IR spectra of the nitrates of cotton celluloses (CCN), wood celluloses in the form of fibres (WCNF) and paper (WCNP), as well as the nitrates of different types of cellulose (CCNII, CCNIII). The influence of the composition of the nitrating mixture on the formation of the structure of cellulose nitrate has

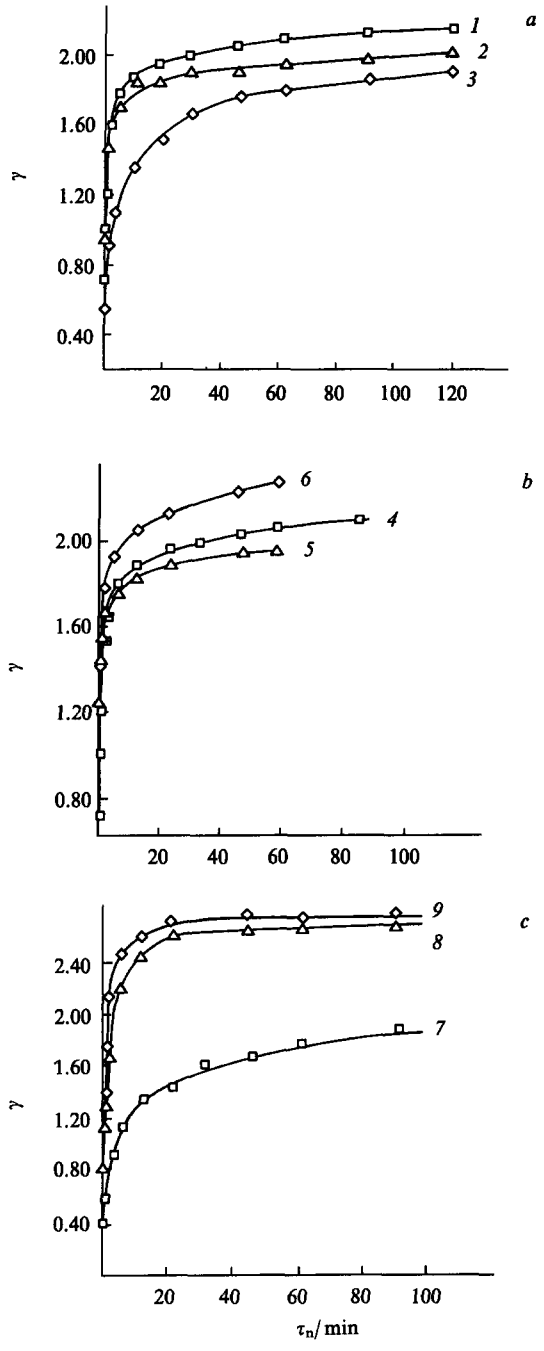


Figure 10. Kinetics of the nitration process: (*a*) cotton cellulose (curve *1*), wood cellulose fibres (curve *2*), and wood cellulose paper (curve *3*); (*b* cotton cellulose I (curve *4*), cotton cellulose II (curve *5*), cotton cellulose III (curve *6*); (*c*) cotton cellulose in reaction mixtures with different water contents (%): (*7*) 15; (*8*) 5; (*9*) 0.

also been investigated. The kinetic relations obtained are presented in Fig. 10. They are described fairly satisfactorily by an equation similar to that put forward in Refs. 78 and 79:

$$\gamma = \gamma_0[1-\exp(-k\tau^{\alpha})] ,$$

where $K = k^{1/\alpha}\alpha$ is the reaction rate constant. The parameters of this equation are listed in Table 5. The physical modification of cellulose and the composition of the nitrating mixture exert the strongest influence on the reaction rate constant K. The transition from the first (kinetic) to the second (diffusional) stage of the chemical synthesis takes place for degrees of substitution from 1.6 to 2.2.

Fig. 11 presents the spectra of cellulose nitrates with low degrees of substitution (γ = 0.5–1.8). Judging from the spectra, ordered cellulose chains are retained in nitrated cotton and wood celluloses for the above values of γ regardless of the composition of the nitrating mixture. In the cellulose nitrates subjected to a preliminary treatment (CCNII, CCNIII), the 'amorphisation' of the cellulose chains takes place virtually in the first seconds of the nitration process. The changes in the structure of the fragments of the macromolecules can be monitored on the basis of the frequencies of the intramolecular vibrations in the range 480–600 cm^{-1} [δ(CCO), δ(CON), δ(ONO)]. The ratio of the intensities of the 520 and 560 cm^{-1} absorption bands characterises the features of the environment of the C–O–C glycosidic linkage (Fig. 12). The relation can be represented approximately by a mathematical expression of the following type:

$$D_1 = D_{1,0}\exp(-B\gamma) ,$$

where D_1 and $D_{1,0}$ are the relative optical densities for a degree of substitution γ and for γ close to zero respectively and B are experimental constants. Their values for the spectra of the nitrates of different celluloses are presented in Table 6. The dependence of the relative optical density of the 544 cm^{-1} absorption band on the degree of substitution (Fig. 12), characterising the accumulation of nitrate groups at the C(6) atom, has been represented approximately by a mathematical expression of the type

$$D_2 = D_{2,0}[1-\exp(-A\gamma^{n})] .$$

The experimental constants A and n are listed in Table 7. The constants $D_{2,0}$, A, and B are maximum for CCNII and CCNIII. Bearing in mind the feature, noted above, involving the existence of order in the residual cellulose chains in cellulose nitrates with low degrees of substitution, the authors suggest that the characteristics of the spatial orientation of the monomeric units and the substitution of the primary hydroxy-groups on nitration of CCII and CCIII are associated mainly with the "amorphous" regions, while those in the nitration of cotton and wood celluloses are associated with sections of the polymer which are non-uniform as regards the degree of order. For $\gamma > (1.6-2.0)$ (the second stage of the chemical synthesis), the contour of the absorption band at 480–600 cm^{-1} in the spectra of cellulose nitrates (Fig. 13) assumes the form of a triplet with maxima at about 490, 514, and 544 cm^{-1} regardless of the biological origin of the celluloses

Table 5. The constants of the kinetic equation for the nitration of cellulose, $\gamma = \gamma_0[1-\exp(-k\tau^{\alpha})]$.

Constant	CCN	WCFN	WCPN (15%)	CCIIN	CCIIIN	WCPN (5%)	WCPN (0%)
γ_0	2.13	2.01	1.86	1.99	2.30	2.70	2.75
k	0.83	0.93	0.39	1.46	1.24	0.70	1.00
K	0.14	0.33	0.08	1.09	0.60	0.26	0.47
α	0.38	0.40	0.51	0.27	0.27	0.52	0.47
δ[a]	0.09	0.08	0.11	0.04	0.10	0.06	0.04

Note. CCN, WCFN, and WCPN are the nitrates of cotton cellulose and wood cellulose in the form of fibres and paper respectively; the water content in the $HNO_3 : H_2SO_4 : H_2O$ = 50 : 50 : 0, 58 : 37 : 5, and 58 : 27 : 15 nitrating mixtures are given in brackets.

* Here and henceforth δ denotes the error of the fit (%).

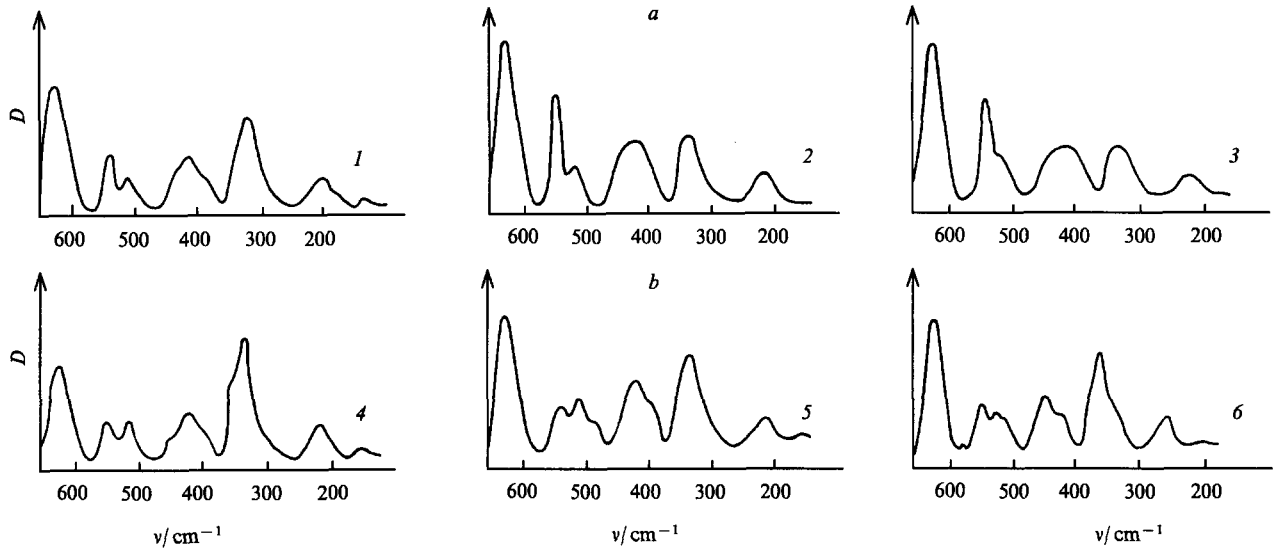


Figure 11. IR spectra of cellulose nitrates with degrees of substitution of 0.5–1.8 (the first of the chemical synthesis): (*a*) cellulose nitrate from cotton cellulose I (curve *1*), cotton cellulose II (curve *2*), and cotton cellulose III (curve *3*); (*b*) cellulose nitrates obtained in reaction mixtures with different water contents (%): (*4*) 0; (*5*) 5; (*6*) 15.

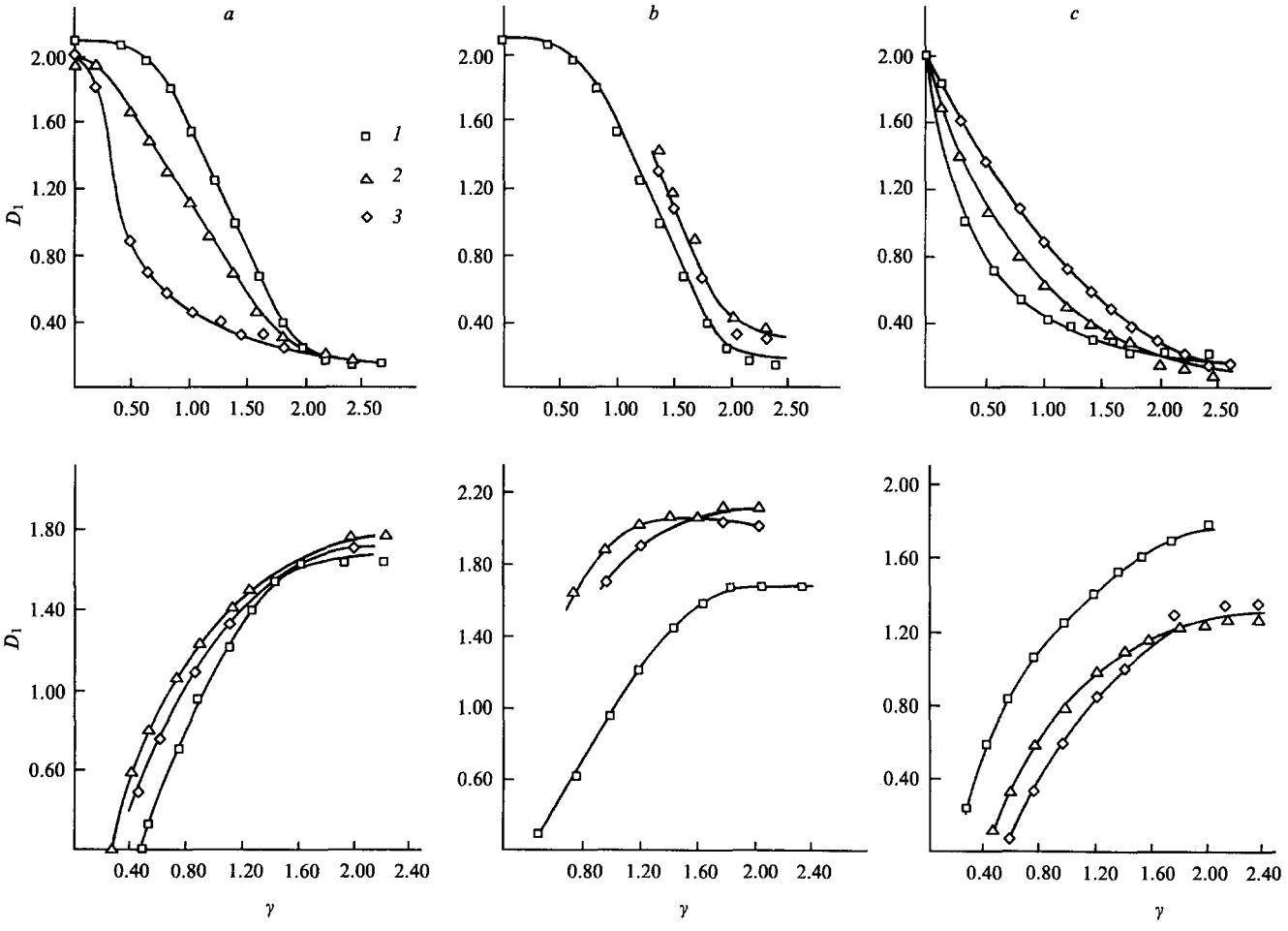


Figure 12. Dependence of the absorption band intensity ratios D_1 and D_2 on the degree of substitution γ: (*a*) nitrated cotton cellulose (curve *1*), nitrated wood cellulose fibres (curve *2*), and nitrated wood cellulose paper (curve *3*); (*b*) nitrated cotton cellulose I (curve *1*), nitrated cotton cellulose II (curve *2*), and nitrated cotton cellulose III (curve *3*); (*c*) cellulose nitrates obtained in reaction mixtures with different water contents (%): (*1*) 0; (*2*) 5; (*3*) 15.

Table 6. Parameters of the equation $D_1(560/520\ cm^{-1}) = D_{1,0}(560/520\ cm^{-1})\exp(-B\gamma)$.

Constant	CCN	WCPN	WCPN (25%)	CCIIN	CCIIIN	WCPN (5%)	WCPN (0%)
$D_{1,0}$	6.09	2.90	1.14	10.08	10.52	2.31	2.80
B	1.45	1.16	0.77	1.53	1.62	1.31	1.21
δ	0.15	0.13	0.14	0.14	0.12	0.04	0.15

Table 7. Parameters of the equation $D_2(544/520\ cm^{-1}) = D_{2,0}(544/520\ cm^{-1})[1-\exp(-A\gamma^n)]$.

Constant	CCN	WCFN	WCPN	CCIIN	CCIIIN	WCPN (5%)	WCPN (0%)
$D_{2,0}$	1.70	1.80	1.85	2.15	2.00	1.33	1.34
A	0.75	0.90	1.13	2.11	2.11	0.77	0.47
n	2.62	1.34	1.91	2.83	2.05	2.77	1.26
δ	0.05	0.12	0.04	0.10	0.13	0.08	0.05

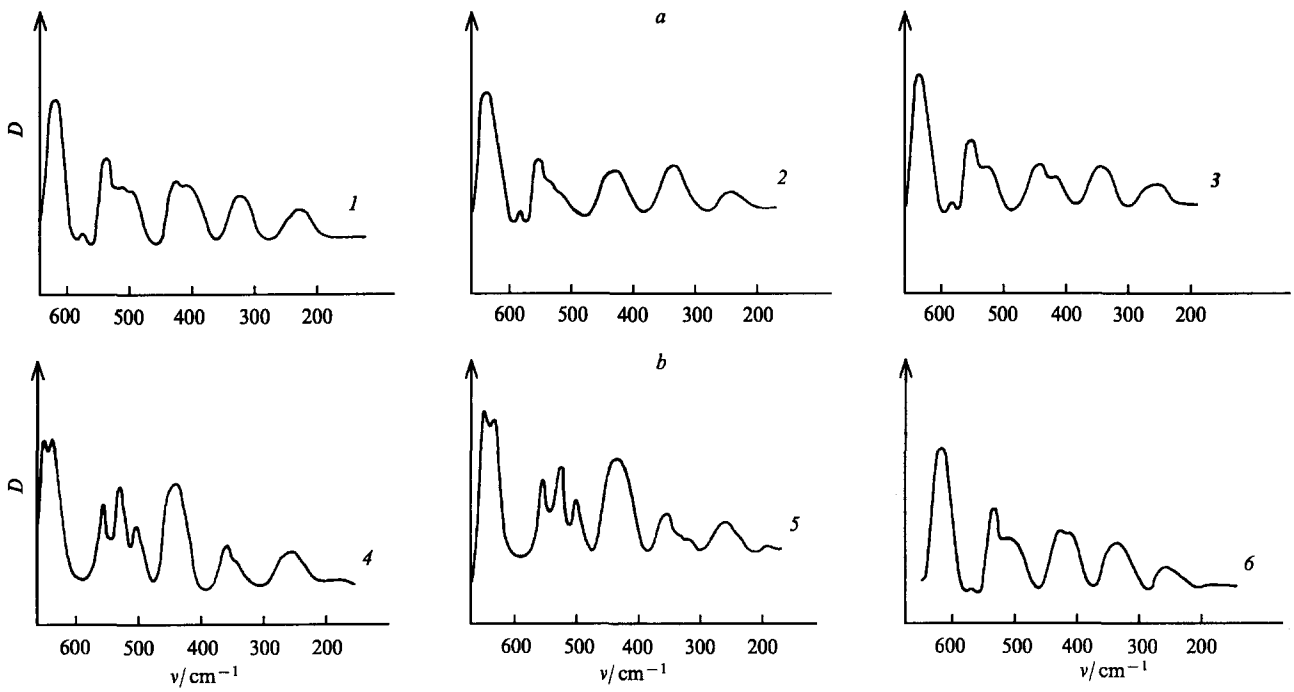


Figure 13. IR spectra of cellulose nitrates with degrees of substitution of 1.6–2.8 (second stage of the chemical synthesis): (*a*) cellulose nitrates from cotton cellulose I (curve *1*), cotton cellulose II (curve *2*), and cotton cellulose III (curve *3*); (*b*) cellulose nitrates obtained in reaction mixtures with different water contents (%): (*4*) 0; (*5*) 5; (*6*) 15.

and their structural modification. Comparison with experimental and calculated spectra of model compounds led to the conclusion that trinitrate units are formed when the nitrate groups are located at the C(2), C(3), and C(6) atoms. The triplet structure is distinctly manifested on nitration of cellulose under anhydrous conditions. The structural data for the cellulose nitrate molecules obtained from the spectra agree well with the results of the study of the monomeric composition of cellulose nitrates by ^{13}C NMR spectroscopy:[74–76] the cellulose nitrate specimens obtained in anhydrous nitrating mixtures and such mixtures diluted with water are characterised respectively by 75% and 46% contents of trinitrate units in the polymer chain.

*
* *

The data presented indicate the important role of low-frequency IR spectroscopy in the study of the structural features of monosaccharides and polysaccharides, including cellulose and its nitrates. Comparison of the experimental spectra with the results of calculations of the frequencies and modes of the normal vibrations and also of the steric structure of monosaccharides, disaccharides, and their nitro-derivatives permitted a detailed interpretation of the low-frequency vibrations. The frequency ranges of the vibrations of the crystal lattices (30–200 cm^{-1}) and intramolecular (deformation and torsional) vibrations (200–700 cm^{-1}) were established. It is shown that the frequencies of the 'lattice' vibrations are determined by the structure of monosaccharides and disaccharides: by the chemical structure of the side fragments (OH, OCH_3, CH_2OH, CH_2ONO_2), the spatial orientation of the OH groups (axial or equatorial), and the characteristic features of the bonding of the glucose residues (the α- and β-configurations). The observation of the conformational sensitivity of the δ(CCO), δ(CON), τ(CO), and τ(NO) vibrations in the range

200–700 cm^{-1} and the identification of the spectral manifestations of the location of the nitrate groups at the C(2), C(3), and C(6) atoms of the pyranose ring are important.

The use of the analysis of model compounds for the interpretation of the low-frequency spectra of cellulose and cellulose nitrates in order to solve a number of structural problems is of special interest and practical value: the determination of the three-dimensional degree of order in cellulose and cellulose nitrates and physically and chemically modified cellulose. Spectroscopic study of the mechanism of the physical modification of cellulose on treatment of the latter with aqueous solutions of alkali made it possible to identify three stages in the structural changes in the polymer determined by the degree of order in the macromolecules, the conformational state of the hydroxymethyl groups, and the system of hydrogen bonds. Analysis of the formation of the molecular crystal structures of cellulose nitrate demonstrated that the principal structural changes in cellulose nitrate, associated with the disorder in the cellulose chains and the spatial orientation of the fragments of the macromolecules, nitrate groups, and the residual hydroxy-groups, occurs in the first stage of the chemical synthesis for a degree of substitution in cellulose nitrate less than 1.6.

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