INTERPRETATION OF THE IR SPECTRUM AND
STRUCTURE OF CELLULOSE NITRATE

V. I. Kovalenko, R. M. Mukhamadeeva,
L. N. Maklakova, and N. G. Gustova

Based on our experimental data on the polarized IR spectra of the oriented fiber of cellulose nitrate (CN), the IR spectra of ^{15}N CN, and its structural data published earlier, we have revised the interpretation of the IR spectrum of CN and give a more specific interpretation. We established a relationship between the form of vibration bands of the nitrate groups and their position and conformation state in the glucopyranose cycle of CN. The relative intensities of the valence vibration bands of the CH_2 groups are explained by the Fermi resonance with a complex tone of valence vibrations of the nitrate groups. In view of the strong dichroism of some low-frequency bands in the IR spectrum of CN, we offer assignments of these bands to vibrations of the chain skeleton and suggest the rationale for the high orientation of CN macromolecules both in the ordered and disordered regions. Such an orientation is assumed to be "inherited" by CN from the starting cellulose.

The IR spectrum of cellulose nitrate (CN) was interpreted more than twenty years ago [1, 2]. Since then, reliable structural data have been obtained for CN, as well as the IR spectra of CN and its analogs [3-8]. We have recorded the polarized IR spectra of the oriented CN fiber and the IR spectra of ^{15}N CN. Analysis of the IR data of ^{15}N CN obtained for the first time, of the data on the dichroism of CN, and of literature data seems to be quite timely. It allows us to give a revised and more detailed assignment of some IR bands of CN and to correlate the spectrum to the molecular structure of this important practical polymer.

Polarization of bands in the IR spectrum of the oriented CN fiber (Fig. 1) coincided with that given by Watanabe et al. [1], excluding the 1427 cm^{-1} band. Moreover, we have first obtained the data on band polarization in the region of 700-400 cm^{-1}. In contrast to the weakly polarized spectrum of the oriented film [1], in the polarized IR spectrum of the oriented CN fiber the dichroic relation $R = A_x/A_z$ may be measured to a sufficient precision (A_x and A_z are optical densities of bands measured with the electric vector of IR radiation being, respectively, perpendicular and parallel to the fiber orientation axis); also, the average angle of the moment of transition θ may be calculated from
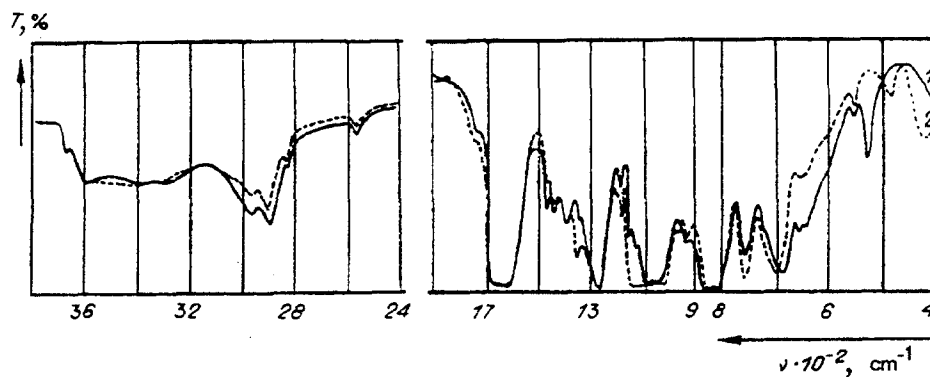

Fig. 1. IR spectrum of oriented CN fiber (DS = 2.54): the polarization plane is 1) orthogonal and 2) parallel to the fiber axis.

TABLE 1. Band Assignments in the IR Spectrum of Nitrocellulose

Frequency, cm^{-1} (^{14}N)	Dichroism, $R = A_x/A_z$	θ, deg	Frequency, cm^{-1} (^{15}N)	Assignment
3573 m.*	0.82	52	3575 m.	νOH(OH...NO)
3430 w.	0.90	53	3430 w.	νOH(OH...OH)
3330 v.w.	~1	55	3251 v.w.	$2\times\nu_aNO_2$
2966 m.	1.13	56	2969 m.	ν_aCH_2FR
2916 s.	1.15	57	2917 w.	ν_sCH_2, $(\nu_aNO_2 + \nu_sNO_2)$FR
			2882 m.	$(\nu_aNO_2 + \nu_sNO_2)$FR
2856 v.w.	1.11	56	2857 v.w.	?
2554 v.w.	1.35	59	2531 v.w.	$2\times\nu_sNO_2$
1733 w.sh.	0.62	48		$\nu C = O$
1680 v.w.	not determined		1641 v.w.	
1663 v.w.	»		1629 v.w.	ν_aNO_2
1646 v.w.	»		1611 v.w	
1460 w.	2.21	65	1456 w.	δCH_2
1427 w.	0.75	51	1426 m.	δCOH
1378 m.	~1	55	1378 m.	δCH
1328 m.	0.37	41	1327 m.	γ_wCH_2
1274 v.w.			1262 v.w	ν_sNO_2
1208 w.	0.64	49	1208 w.	
1161 s.	0.47	44	1160 s.	$\nu_aC - O$, pyranose cycle
1117 v.w	not determined		1117 v.w	
1061 v.w.	»		1062 v.w.	
1020 v.w	»		1022 v.w.	$\nu C - O$
1001 v.w.	»		1001 w.v.	
947 w.	~1	55	948 w.	δCH, out-of-plane
917 w.sh.	1.31	58	918 w.sh.	
860 s.sh.	>1	>55	847 s.sh.	
827 v.s.	not determined		815 v.s.	$\nu N - O$
747 s.	0.48	44	728 s.	γ_wNO_2
692 s.	0.85	53	691 s.	δNO_2
685 s.sh.	1.34	59	685 s.sh.	pyranose cycle
638 m.	2.83	67	636 m.	» »
625 m.sh.	1.63	61	622 m.sh.	γ_rNO_2
543 w.	0.94	54	542 w.	pyranose cycle
516 w.	9.75	77	514 w.	» »
490 w.	0.26	36	491 w.	» »
430 w.	0.28	37	428 w.	» »
419 w.	0.33	39	418 w.	» »
346 w.	not determined		348.w.	» »
328 w.	»		326 w.	» »
250 w.	»		250 v.w.	lattice
170 v.w.	»		160 v.w.	»

Note. s is strong; m, medium; w, weak; v, very; sh, shoulder.

the relation $R = \tan^2 \theta/2$ [9]. It is interesting to note that the strongest dichroism is found in the low-frequency region of the spectrum at 516, 490, 430, and 419 cm^{-1} (Fig. 1 and Table 1).

ASSIGNMENT OF THE BANDS OF THE NITRATE AND HYDROXYL GROUPS

The position of the bands of the nitrate groups in the IR spectrum of CN has been reliably identified and confirmed by the calculated and experimental IR spectra of model glucoside nitrates [4, 6] and alkyl nitrates [5]. The
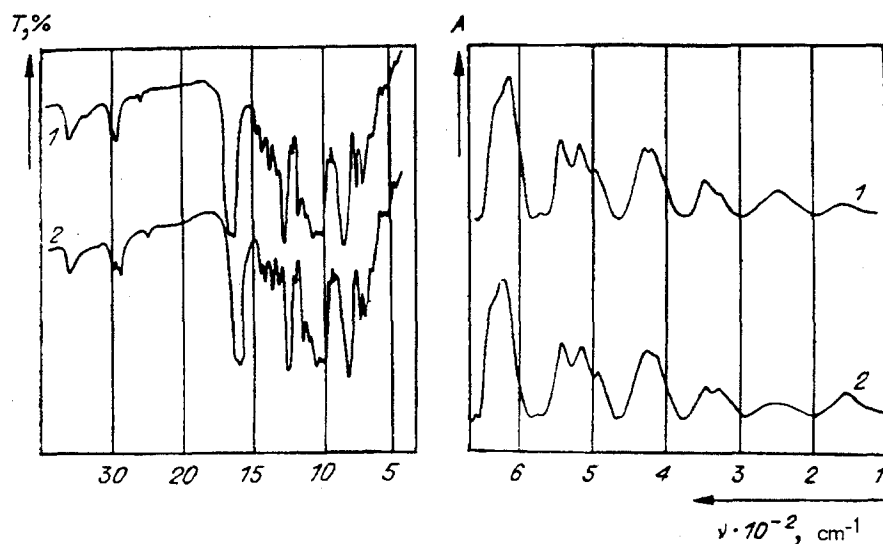
Fig. 2. IR spectra of CN (DS = 2.35) obtained in identical conditions: 1) normal and 2) ^{15}N-substituted CN. In the low-frequency part of the spectrum, the optical density scale is used.

weak bands 3330 and 2554 cm^{-1} were unambiguously assigned to overtones of the antisymmetric and symmetric valence vibrations of the nitrate groups shifted in the spectrum of ^{15}N CN to 3251 and 2531 cm^{-1}, respectively (Fig. 2 and Table 2). The band around 2916 cm^{-1} in the spectrum of CN, which shifted to 2882 cm^{-1} in the spectrum of ^{15}N CN, should be assigned to the complex frequency $v_aNO_2 + v_sNO_2$ strengthened by the Fermi resonance (FR) with the band v_aCH_2.

In the absorption region of the antisymmetric valence vibrations v_aNO_2 of the diluted solution of CN, there is a doublet 1662 and 1646 cm^{-1} (Fig. 3). The corresponding frequencies for the isotope-substituted CN are 1629 and 1611 cm^{-1}. Analysis of the intensity ratio of the doublet components for CN with different degrees of substitution (DS) permitted the following assignment [8]: the band 1662 cm^{-1} was assigned to v_aNO_2 of the nitrate groups bonded to the CH groups of the glucopyranose cycles of CN (C-2 and C-3 position); and the band 1646 cm^{-1}, to v_aNO_2 of the nitrate groups bonded to the CH_2 groups of the glucopyranose cycles (C-6 position). This is in good agreement with the assignment of the band v_aNO_2 of the nitrates of primary and secondary alcohols [10].

The width of the above doublet is about 30 cm^{-1}. In the IR spectra of the CN samples not plasticized nor dissolved (fibers, powders), there is a wide band in this region that has several maxima $\Delta v_{1/2} \sim 85$ cm^{-1} (see Fig. 3, Table 1). It is seen that the position of the two maxima is fixed enough, whereas the spectrum of CN fiber shows a high-frequency component around 1680 cm^{-1} (see Table 1). After plasticization or molding a CN film from solution, the v_aNO_2 band becomes more narrow, $\Delta v_{1/2} \sim 50$ cm^{-1} (see Fig. 3). The reason for such a broadening may be differences in the phase or conformation states of CN. For the changed phase (for example, amorphous or crystallized amorphous films) of CN, no significant changes in the bandwidth of the antisymmetric valence vibration of the nitrate groups have been found. Variations in this bandwidth are, evidently, due to the differences between the conformation states of the CN chains (and the nitrate groups) in solution, film, and fiber, as reported in [3]. In a very dilute solution, which is a thermodynamically stable system with knots of CN chains not interacting with each other [11], the set of conformers is confined to the most stable ones; the width of each doublet component after decomposition is about 18 cm^{-1}, which is typical of isolated bands in the IR spectra of liquids. After nitration of cellulose, which is a nonhomogeneous process, one could expect that the resulting CN would contain some constant percent of sterically hindered conformations responsible for the increased frequency of vibration v_aNO_2 and, accordingly, for the broadening of the whole band. After addition of a plasticizer or dissolution, the strained CN chains relax with conversion of

TABLE 2. Shifts of Absorption Bands in the IR Spectra of Isotope-Substituted CN

Frequency, cm^{-1}		$K = \nu/\nu_{iso}$
^{14}N	^{15}N	
3330	3251	1.024
2916	2882	1.012
2554	2531	1.009
1680	1641	1.024
1663	1629	1.021
1646	1611	1.022
1274	1262	1.010
827	815	1.015
747	728	1.026
	Calc.	1.018

unstable conformers into the energetically more favorable ones. The ν_aNO$_2$ band considerably narrows (see Fig. 3). Thus, the ν_aNO$_2$ bandwidth is due to differences in the types of substitution (C-2, C-3, or C-6) and the conformation state of the CN chains. The latter suggests that this parameter may be used to evaluate CN materials according to the degree of their internal strain.

As for the band ν_sNO$_2$ at 1274 cm^{-1}, it is virtually insensitive to the type of substitution or to conformation differences; its width and position vary much less upon the above transformations of CN. Its isotope substitution coefficient (see Table 2) is also smaller than for ν_aNO$_2$.

The bands 827, 747, and 692 cm^{-1} were assigned to vibrations of the nitrate group: the valence νNO, the wagging γ_wNO$_2$, and the scissoring δNO$_2$ vibrations, respectively. This is in good agreement with the calculated and experimental data of model nitrates [4, 6]. We have assigned the band 625 cm^{-1} to the rocking vibration γ_rNO$_2$ by analogy with the assignment for model alkyl nitrates [5]. Judging by the orthogonally polarized high-frequency wing of the band 827 cm^{-1}, the band is complex. This is confirmed by the analysis of the spectra of CN samples with increasing DS. At small DS this region contains a symmetric band 850 cm^{-1} that is absent in the spectrum of cellulose; the band grows with DS and moves into the low-frequency range, acquiring the observed contour. It is interesting how the 692 cm^{-1} band transforms during nitration. At first, a band at 720 cm^{-1} appears and grows in that region, then at DS of about 1 it diminishes in intensity, and a pair of bands 696 and 674 cm^{-1} appears near it. Further they merge into a wide band with a maximum of 692 cm^{-1}. The complex contour of these bands is probably due to the same reasons
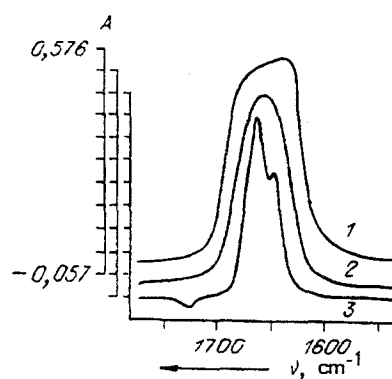

Fig. 3. IR spectra of CN (DS = 2.7) as: *1*) compacted film from powder after nitration; *2*) the film moulded from the THF solution; *3*) the THF solution, *c* = 0.01 M, THF absorption compensated.
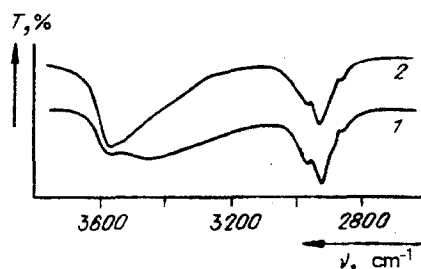
Fig. 4. IR spectra of CN (DS = 2.0) obtained by nitration in mixtures: *1*) nitric acid–sulfuric acid–water and *2*) nitric acid–dichloromethane.

as for the band $\nu_a NO_2$: differences in positions of the nitrate groups in the pyranose cycle and in their conformation states.

The frequency shifts of different magnitude in passing to ^{15}N CN (see Table 2) are probably due both to the symmetry of vibrations and the contributions of other vibrations to the given frequency. For that reason there is virtually no frequency shift for some bands assigned to nitrate group vibrations, for example, for the 692 and 625 cm^{-1} bands. Such a situation has been observed in the IR spectra of nitromethane and its isotopic analogs [5].

The residual hydroxyl groups in CN have a wide band of valence vibrations in the region of 3650-3300 cm^{-1}. Its contour may vary significantly depending on the nitration conditions even for CN with the same DS (Fig. 4). In one case we observe a clear-cut maximum at 3570 cm^{-1}, in another case there are two maxima − at 3570 and 3430 cm^{-1}. These bands were assigned to νOH of the hydroxyl groups involved in hydrogen bonding –OH...O$_2$NO– and –OH...OH [3]. From the ratio of optical densities of these bands one can estimate the uniformity of the respective CN [8]. The band 1427 cm^{-1} in the IR spectrum of cellulose, decreasing in intensity with growth of DS of CN, was assigned to the deformation vibration δOH.

ASSIGNMENT OF BANDS OF THE GLUCOPYRANOSE CYCLE

The region of CH and CH$_2$ group vibrations in the IR spectrum of CN has always been an object of discussion [1, 3]. It was not clear why the intensity of $\nu_s CH_2$ at 2916 cm^{-1} is higher than that of $\nu_a CH_2$ at 2966 cm^{-1}, while the intensity ratio of these bands is usually inverse [12-14]. The shift of the band 2916 cm^{-1} to 2882 cm^{-1} upon replacement of ^{14}N by ^{15}N in CN allows us to explain this "anomaly." As mentioned above, in this case we have the Fermi resonance (FR) of the bands of the main vibration $\nu_a CH_2$ and the complex frequency $\nu_a NO_2$ + $\nu_s NO_2$. The reinforced low-frequency component of the FR doublet is superimposed on the band $\nu_s CH_2$ to give the picture observed in the spectrum of CN (see Fig. 2). In passing to ^{15}N CN the lowered frequencies of the main valence vibrations of nitrate groups and, accordingly, of the composite tone $\nu_a NO_2$ + $\nu_s NO_2$ changes the frequencies of the Fermi resonance doublet and they become 2969 and 2882 cm^{-1}. Probably because of its small intensity [13], the absorption νCH is masked by the bands νCH_2. The assignment of the band around 2856 cm^{-1}, which usually disappears in the spectrum of CN with high DS [1], is still not clear; it may be due to the residual absorption of cellulose fragments appearing as a result of nonuniformity of nitration.

We have assigned the orthogonally polarized band 1460 cm^{-1} to the scissoring vibration δCH_2, which is in agreement with the data of Zhbankov [3] conflicting with [1]. The intensity of the band grows with DS; starting from DS of ~1.7 and above, when all the primary hydroxyl groups have been substituted by the nitrate groups, its intensity stops changing. The assignment of the band 1328 cm^{-1} to the wagging vibration $\gamma_w CH_2$ is confirmed by its parallel polarization and accordingly by the orthogonal polarization of the bands $\nu_a CH_2$ and δCH_2. The band 1378 cm^{-1} may be assigned to the deformation vibration δCH. This usually weak band becomes more intense due to the environment

TABLE 3. Conformation Degrees of Freedom of the Monomer Unit of CN

Bond	Number of bonds before the chain skeleton										
	$\underset{O}{\overset{C}{\downarrow}}$	$\underset{C}{\overset{C}{\downarrow}}$	$\underset{H}{\overset{C}{\downarrow}}$	$\underset{H}{\overset{C\text{-}6}{\downarrow}}$	$\underset{O}{\overset{C\text{-}6}{\downarrow}}$	$\underset{N}{\overset{O}{\downarrow}}$	$\underset{H}{\overset{O}{\downarrow}}$	$\underset{N}{\overset{O\text{-}6}{\downarrow}}$	$\underset{H}{\overset{C\text{-}6}{\downarrow}}$	$\underset{O}{\overset{N}{\downarrow}}$	$\underset{O}{\overset{N\text{-}6}{\downarrow}}$
	0	0	0	1	1	1	1	2	2	2	3

of the polar nitrate groups [14]. The weakly polarized bands around 947 and 917 cm^{-1} were assigned [1] to the out-of-plane vibration δCH. The series of bands in the range of 1210-1000 cm^{-1} is assigned to the valence vibrations νCO; owing to their strong dichroism, the bands 1208 and 1161 cm^{-1} may be attributed to stretching vibrations of the glycoside bond.

Very weak bands 250 and 160 cm^{-1} were assigned to natural vibrations of the crystal lattice of CN [15].

BAND DICHROISM IN THE IR SPECTRUM OF ORIENTED CN FIBER

From measurements of the dichroism of the IR spectrum one can, in principle, extract information about the structure of a spatially ordered molecular system, such as a single crystal. However, the relation between the dichroism and the geometrical structure of a molecule may be complex. It depends on the structure of the molecule, and on the number and spatial arrangement of molecules in a unit cell [14]. In polymers the situation is still more grave because of deviations from the three-dimensional order [9]. For cellulose and its derivatives such as CN, it is especially difficult to determine the correlation between the dichroism and the geometrical structure.

Prior to analyzing the dichroism of the IR spectrum of CN, consider the structural factors of CN capable of affecting this characteristic. ▴

Spiral Configuration of the CN Chain. It is known [16] that the chains of crystal cellulose trinitrate (CTN) are rolled up into helices 5_2 (five pyranose units per two coils) with an identity period 25.4 Å.

Complex Nature of a Monomer Unit of CN. In the glucopyranose cycle of CN there are several identical groups that are differently oriented in space, for example, three nitrate groups (in CTN), and five CH groups. The transition moments of the cycle vibration are averaged throughout the unit cell [9], which contains ten monomer units.

Conformational Freedom of Substituents, determined by the distance between them and the skeleton of the CN macromolecule (Table 3). CN is known to have moderate crystallinity (less than 50% [17]). Consequently, in disordered (amorphous) regions of CN, there are different sets of conformations and conformers of the nitrate, hydroxyl, and methylene groups, as was mentioned above. Hence, even for the ideally packed CTN, determination of its steric structure by dichroism will require analysis of all of the above-mentioned effects, while the experimentally observed values of dichroism should give $R \sim 1$ and, hence, $\theta \sim 54.4°$ [9]. Then R and θ observed in the IR spectrum of CN (see Table 1) should be regarded as an estimate demanding further information for structure interpretation. (It should be noted for the sake of fairness that the orientation type of even an idealized CN helix is a more complex case than all of the models analyzed by Zbinden and Elliott [9].)

The observed dichroism of the IR spectrum of CN agrees well with the above arguments: the band polarization varies mainly within $0.6 < R < 2.5$ ($47° < \theta < 65°$); a strong dichroism is shown by the vibration bands of the CH_2 and $C=O$ groups, and of the skeletal $C-O$ and $C-C$ groups. The band $\gamma_w NO_2$ also has a high enough dichroic ratio; it was supposed [4] to be mixed with vibrations of the CN skeleton, but the high value of its isotope shift (see Table 2) indicates that this vibration is highly characteristic.

The strongest dichroism is shown by the low-frequency vibration bands; it reflects the high degree of orientation of the corresponding groups. These vibrations should belong to the skeleton of the CN macromolecule, most likely to the pyranose cycles, being just the vibrations that fit all of the above-stated structural features of CN. Such dichroic ratios (R 9.75 or 0.26) give us reasons to believe that the configuration of chains in the amorphous regions of CN should be almost identical to that in the ordered regions. The differences between chain configurations are apparently associated with the character of distribution of the nitrate groups along the chain [8] and with their conformation

states. This is indirectly confirmed by the small difference between the amorphous and crystalline densities of CN [17]: it is one of the smallest values known for different polymer classes. Clearly, the nitration and CN structure formation occur with preservation of the morphological structure of the starting cellulose. Judging by the strong dichroism in the low-frequency region of the IR spectrum of cellulose [18], it also has highly oriented chains, whether they lie in the crystalline or amorphous regions.

EXPERIMENTAL

Nitration of cellulose fiber with a mixture of nitric and sulfuric acids and water to DS 2.54 is described in [19]. For polarization measurements the CN fibers were carefully smoothed out and squeezed between the potassium bromide plates. The difficulty of sample preparation was in making an optimally thin layer of fiber to minimize hollows between the fibers distorting the IR spectrum. Unfortunately, a layer had to be somewhat thicker than desired in order to ensure a good quality of the IR spectrum, so we failed to measure the dichroism of the strongest bands in the spectrum but managed to measure the dichroic ratio of many weak bands.

Polarized IR spectra were recorded on a UR20 spectrophotometer. The band frequencies were refined under optimal recording conditions with subsequent measurement of the IR spectrum of polystyrene used as a graduating substance. To obtain polarized IR radiation, we used the polyethylene and teflon polarizer gratings LOMO (polarization degree above 98.5%), mounted in the plane of the aperture diaphragm of the spectrophotometer.

The ^{15}N CN sample was prepared by nitration of cellulose with a mixture of nitric ^{15}N acid and dichloromethane to DS = 2.35, as described in [20]; concurrently a sample of ordinary, not isotope-substituted CN, was obtained under identical conditions. During the nitration process (with the same nitrating mixture), CN samples with different DS were taken and their IR spectra were also examined.

The IR spectra of CN were recorded on samples in the form of thin films, compacted or molded from solution, or as very dilute solutions of CN in tetrahydrofurane (0.01 M) with compensation of the spectrum of the solvent on a Bruker IFS 113v Fourier spectrometer and a spectrophotometer UR20.

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