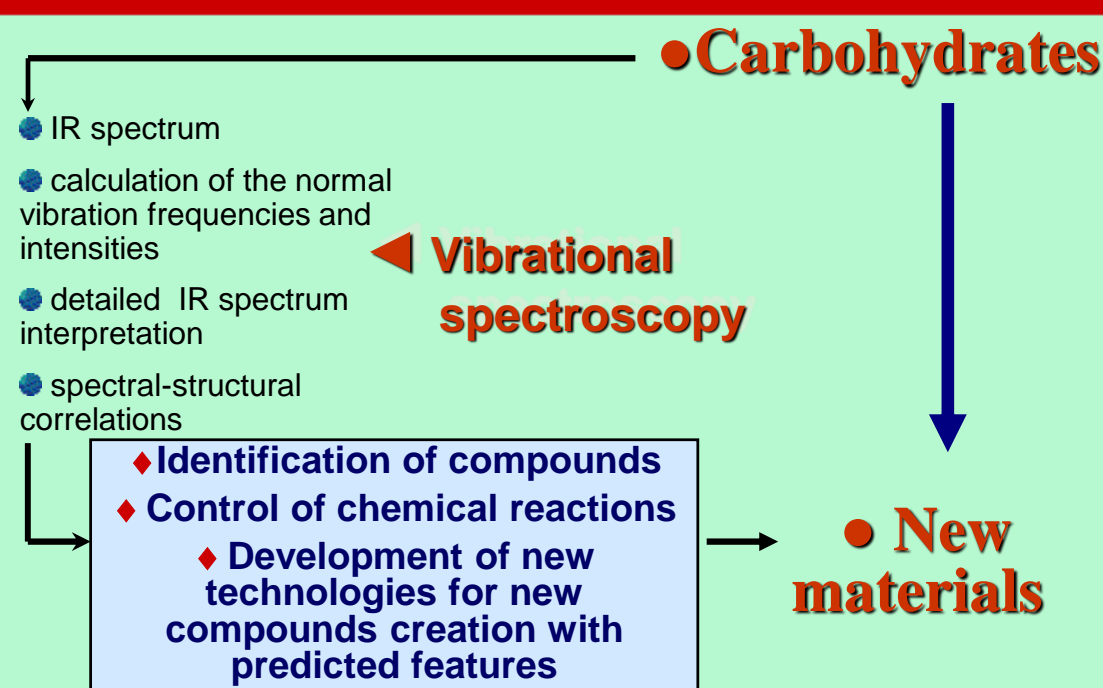


STRUCTURE, INFRARED SPECTRA AND SPECTROSCOPIC PROPERTIES OF DERIVATIVES OF MONOSACCHARIDES: EXPERIMENTAL DATA, THEORETICAL MODELING, RESULTS

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FROM WORLD OF MOLECULES TO NEW TECHNOLOGIES



Vibrational spectroscopy occupies a priority place in the investigation of the structure and properties of carbohydrates. It makes it possible to establish spectral-structural correlations that enable one to solve problems of identification of compounds and to develop methods of monitoring and diagnostics of the state of substances in technological processes and those of evaluation of the quality of finished products.

In this work the effectiveness of coupled using of theoretical vibrational spectroscopy and quantum chemistry is demonstrated when applied for solving the problems of spectral-structural correlations in the studies of methyl- and nitro- derivatives of crystalline glucopyranosides.

We have carried out complete calculations of vibration frequencies and intensities of a set of compounds of selectively substituted nitrates of methylglucopyranosides with a gradually complicated molecular structure (methyl- β -D-glucopyranoside, 4-O-methyl- β -methyl-D-glucopyranoside, 2,3-, 2,6-, and 3,6-di-O-nitro-methyl- β -D-glucopyranoside, 4-O-methyl-2,3-di- and 4-O-methyl-2,3,6-tri-O-nitro-methyl- β -D-glucopyranoside). Our original program technique [1] was used combining the classical calculation of frequencies (ν) and the potential energy distributions (PED) of normal vibrations of complex molecules with the quantum-chemical intensity (A) estimation.

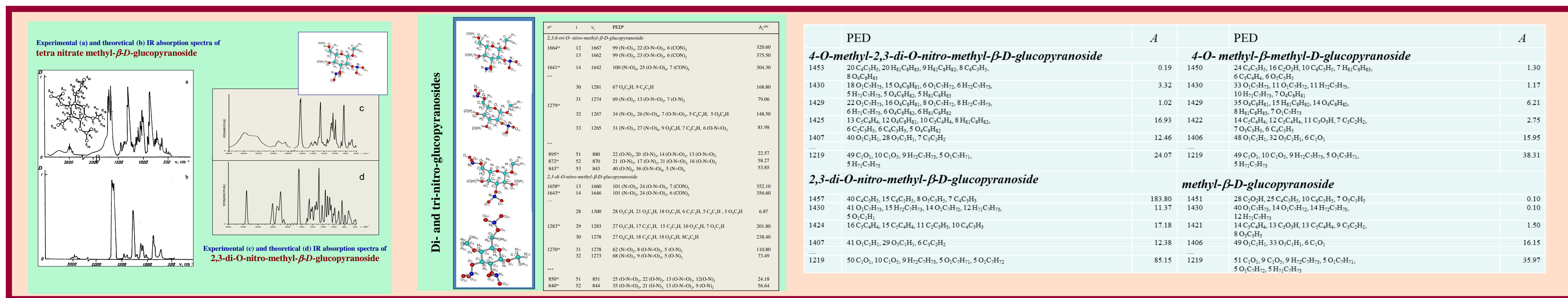
On the basis of a good agreement achieved with experiment (both in frequencies and intensities) a detailed interpretation of the IR spectra of compounds investigated has been performed. The absorption spectra sensitivity to the O-methyl substitution of hydroxyl groups has been discovered in details.

[1] M.V. Korolevich, Analytical Infrared spectra of saccharides, Doctoral dissertation, National Academy of Sciences of Belarus, Minsk, 2009, 333 pp.

Basic Stages of Work Preceding the Results [1]

- We obtained a convenient for computer programming matrix expression for the calculation of intensities with the use of the quantum-chemical technique and suggested an algorithm of coupled analysis of the IR spectra which combines a classical method of calculation of normal vibration with a quantum-chemical evaluation of intensities.
- We created an original highly automated complex of programs for calculating the vibrational spectra of polyatomic molecules both isolated and taking into account their molecular environment. This program complex realized a coupled approach which combines the calculation of normal vibration frequencies within the framework of the classical scheme in a valence force field approximation and the quantum-chemical calculations of vibration intensities by the CNDO/2 method.
- A complete calculation of vibration frequencies and intensities has been carried out for both relatively simple organic compounds (free molecules of methanol and its deutero derivatives, benzene, methyl nitrate, *cis*- and *trans*-isomers of biurete and their deutero analogues, as well as adsorption benzene complexes) and complex molecules of monosaccharides (α -, β - anomers of D-glucose, α -D-galactose) and their derivatives (di-, tri- and tetra-nitrates of methyl- β -D-glucopyranoside).
- Within the cluster approximation, the influence of the intermolecular hydrogen bonds upon the electronic structure and intensities of the absorption bands of crystalline monosaccharides has been studied.

Subjects of Investigation @ Results of Spectra Calculations

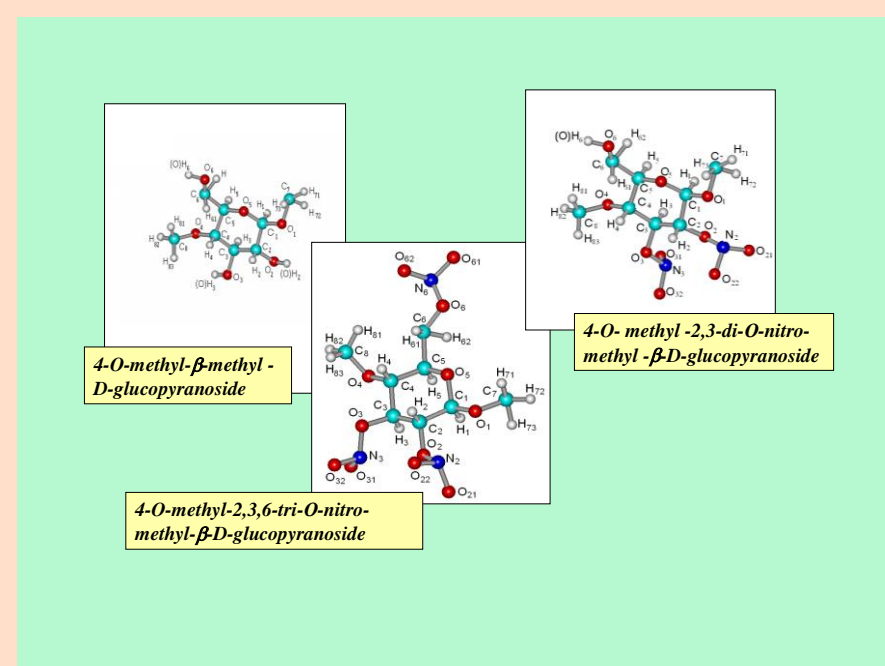


An analysis of the results obtained

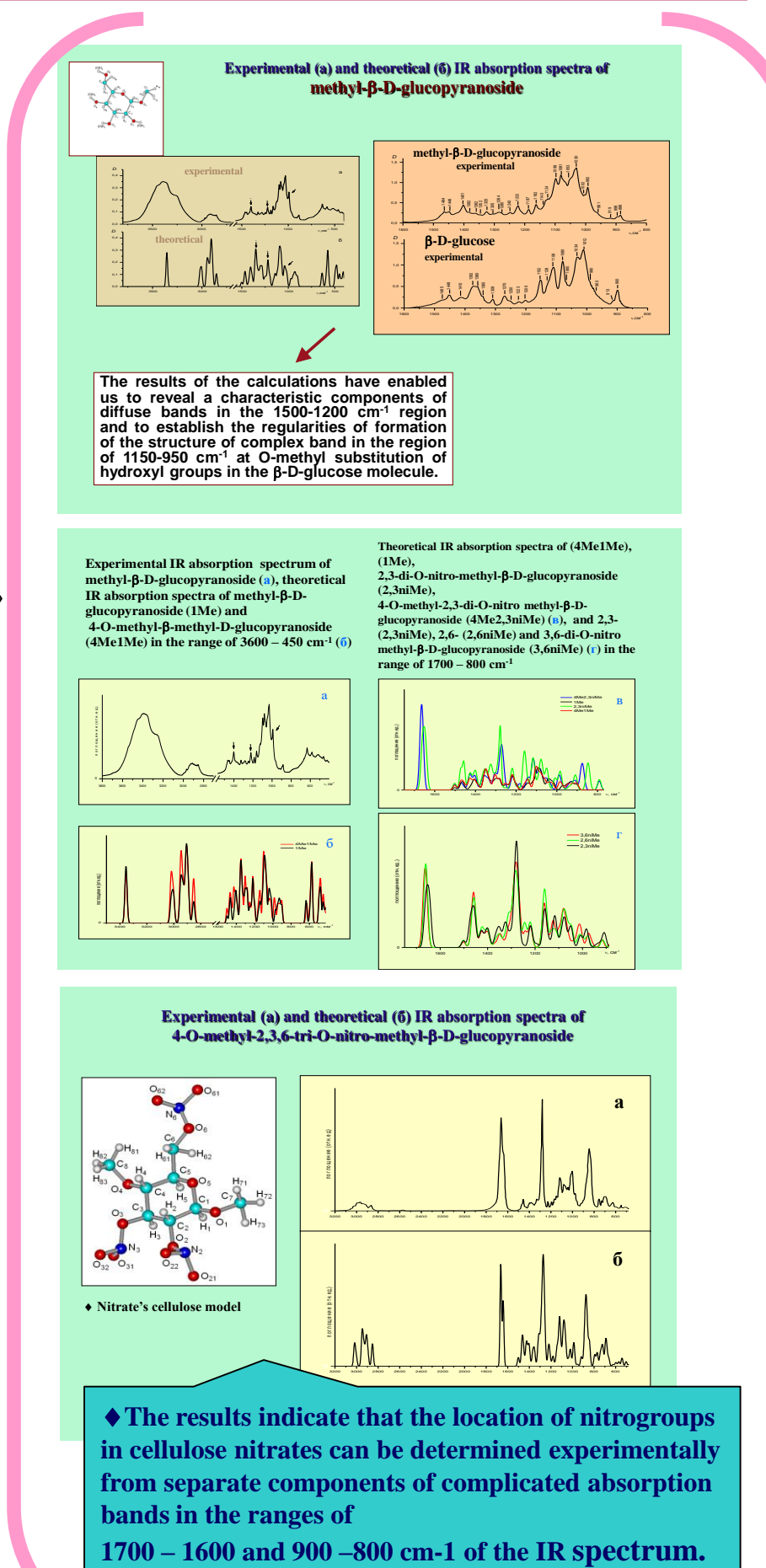
has allowed to establish the regularities of formation of complex absorption bands caused by the vibrations of the nitro groups on selective nitrosubstitution.

It was studied whether the spectral features of the oxymethyl group in methyl- β -D-glucopyranoside (1MeGlu) with additional oxymethyl and nitro substituents are characteristic.

The possibilities of using these features in spectral analysis have been also investigated.



This study was based on the comparison of the results obtained and the theoretical spectral curves of 1MeGlu and 4Me1MeGlu with the corresponding data obtained for 2,3-, 2,6-, and 3,6-di-O-nitro-methyl- β -D-glucopyranoside, and 4-O-methyl-2,3-di- and 4-O-methyl-2,3,6-tri-O-nitro-methyl- β -D-glucopyranoside.



CONCLUSION

- The bands at 1401 и 1222 cm^{-1} may serve as a recognition sign of oxymethyl substitution at the atom C₍₁₎ in β -D-glucose.
- The peak at 992 cm^{-1} is initiated by the presence of the oxymethyl substituent at the atom C₍₁₎ and at the atom C₍₄₎ alike.
- Increase in the intensity of this band compared to the methyl- β -D-glucopyranoside spectrum is related to the additional substitution for the hydroxyl group at the atom C₍₄₎.

The results indicate that the location of nitro groups in cellulose nitrates can be determined experimentally from separate components of complicated absorption bands in the ranges of 1700 – 1600 and 900 – 800 cm^{-1} of the IR spectrum.