CALCULATION AND ANALYSIS OF THE FREQUENCIES OF NORMAL VIBRATIONS OF 2,3-DI-O-NITRO-METHYL-β-D-GLUCOPYRANOSIDE

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A calculation of the frequencies and forms of the normal vibrations of the 31-atom molecule 2,3-di-O-nitro-methyl-β-D-glucopyranoside has been performed. Particular emphasis has been placed on the interpretation of the strongest bands in the spectrum of 2,3-di-O-nitro-methyl-β-D-glucopyranoside, which are due to vibrations of the nitrate groups.

Key words: monosaccharide nitrates, IR spectrum, analysis of normal vibrations, potential-energy distribution.

The present work is a continuation of investigations devoted to theoretical analysis of the vibrational spectra of monosaccharide (MS) nitrates [1, 2]. The vibrational spectra of MS have a complex diffuse form that is a consequence of the superposition of a great number of adjacent absorption bands. The assignment of vibrational frequencies is a problem even when selective deuteration and cooling of the samples to the liquid nitrogen temperature are used. The substitution of hydroxyls for the nitrate groups in the pyranose rings can markedly modify the form of the spectrum. However, in spite of the well-defined changes in the spectrum, arising as a result of the selective nitrosubstitution, the detailed interpretation of the spectra of MS nitrates is a very complicated problem. The nature of the splitting of the absorption bands corresponding to characteristic vibrations of the nitro groups is not clearly understood. Complete and reliable interpretation of the observed spectra of such complex compounds as MS nitrates requires a theoretical analysis, including spectral curves directly comparable with experimental spectra.

For a complete theoretical analysis of the vibrational spectra of MS and their derivatives, a method of complex analysis of the IR spectra of polyatomic molecules was developed and realized via a complex of programs. This method combines calculation of the frequencies and forms of the normal vibrations by the classical semiempirical method within the valence-force field approximation with quantum-chemical (QC) estimation of the intensities of the IR absorption bands by the CNDO/2 method [1]. The direct QC calculation of derivatives (∂μ/∂Q) with regard to the form of the normal vibrations used here makes it possible to control the choice of the appropriate set of force constants in the process of analysis of normal vibrations. Within the limits of the combined approach devised by us, allowance is made for inclusion of the influence of intermolecular interactions on the intensity of the absorption bands in the spectrum of the molecule [1].

This approach has been successfully applied to calculation of the spectra of relatively simple molecules (methanol, benzene, methyl nitrate, biuret, and certain of their deuterium analogs) [4-7] as well as complicated MS molecules [1-3, 8-10]. Coincident with the investigation of free organic molecules, calculations of the adsorption spectra of benzene complexes [7] and the spectrum of α-D-glucose in a cluster [8] have been performed. The

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results obtained for these compounds strongly suggest that the combined approach can be applied to the solution of spectroanalytical problems in the investigation of both free organic molecules and with allowance for the molecular environment. Such an approach can serve as a fully reliable means of choosing an adequate force field of the molecule in the process of analysis of normal vibrations.

The aim of the present work was interpretation of the IR spectrum of 2,3-di-O-nitro-methyl-β-D-glucopyranoside (diNMG) on the basis of calculation of the frequencies of normal vibrations with the use of the valence-force field of methyl-β-D-glucopyranoside tetranitrate (MGTN).

In calculation of the vibrational spectrum of diNMG we used the molecular geometry from [11], which was devoted to x-ray structural analysis of MGTN crystals. The same geometry was used for theoretical analysis of the spectrum of MGTN [2, 3]. A model of the valence-force field of the diNMG molecule was constructed with the use of the force constants obtained for the MGTN molecule, while in the case of hydroxyl groups we used the force constants of the β-D-glucose molecule. It was found that this force field, with no any changes introduced into it, reproduces the observed IR spectrum of diNMG adequately. Recall that in the process of analysis of normal vibrations the choice of an appropriate set of empirical force constants for MGTN was controlled through direct QC calculation of the vibrational intensities. The final results of the complete calculation of the spectrum of MGTN