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Changes in the structure and spectra of IR absorption and Raman scattering of aqueous solutions of ascorbic acid during their degradation

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The results of molecular modeling of the IR absorption and Raman spectra of aqueous solutions of ascorbic acid and its degradation products: dehydroascorbic acid, diketogulonic acid, and furfural are presented. Changes in the spectra have been discovered, which make it possible to reveal successive changes in the structure of molecules in the process of degradation of ascorbic acid solutions.

The need to develop modern methods for analyzing the quality of medicines is due to the high requirements for their safety, efficacy and quality. Among such methods, the methods of IR absorption spectroscopy and Raman scattering play a special role.

Experimental studies of the stability of aqueous solutions of ascorbic acid with changes in temperature, illumination, and acidity of solutions were carried out at the Department of Laser Physics of the Volgograd State University [1, 2].

Ascorbic acid, or vitamin C ($C_6H_8O_6$) is an organic compound that is a white solid. The structural formula of the molecule is shown in Figure 1.

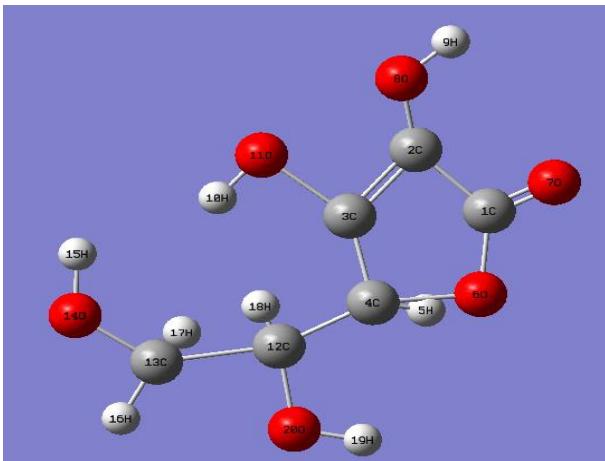
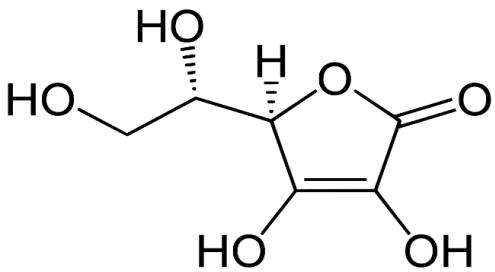


Figure 1. Structural formula of ascorbic acid

One of the structural features of the ascorbic acid molecule is the presence of the C=C group, which determines the ability of vitamin C to be easily oxidized and at the same time reduce other compounds. The degradation of the structure of the ascorbic acid molecule accelerates with increasing temperature and increasing heating time [1].

The chemical processes of oxidation and degradation of ascorbic acid have not yet been sufficiently studied.

It is believed that these processes proceed in several stages. First, ascorbic acid is oxidized to dehydroascorbic acid, donating two hydrogen atoms. This reaction can be reversed: dehydroascorbic acid, having attached two hydrogen atoms back, will easily be reduced to ascorbic acid. Dehydroascorbic acid can receive hydrogen from the reduced form of the dehydrogenase coenzyme. Subsequently, dehydroascorbic acid is converted into 2,3-diketogulonic acid and, finally, in an acidic environment into furfural [3,4,5].

These transformations are accompanied by changes in the IR absorption and Raman spectra.

The results of modeling these spectra are presented in this paper.

Before the calculation of the vibrational spectra, a geometric optimization of the structure of the molecules was performed. The complete optimization of the geometry of the molecule is the search for a deep minimum of the total energy over all geometric parameters (bond lengths, valence and dihedral angles). The initial structure of the molecule of ascorbic acid was constructed from the known data [] on the typical lengths of the bond and the angles between individual bonds.

Optimization of the structure of the molecule of ascorbic acid was carried out by semi-imperical methods AM1, PM3 and PM6, as well as Hartree-Fock and DTF methods with different bases: STO-3G, 3-21G, 6-31G and 6-311G.

The calculation method was chosen in such a way that the obtained value of the total energy of the molecule was minimal.

The minimum value of the total energy of the molecule has been reached as a result of optimization by the method of ***Density Functional Theory (DFT) with the approximation of B3LYP and the basis of 6-311G.***

The values of the total energies of the molecules of ascorbic acid and its decomposition products after optimization by this method are presented in Table 1

Table 1. The values of the total energies of the molecules of ascorbic acid and its decay products

	Ascorbic acid	Dehydroascorbic acid	2,3-diketogulonic acid	Furfural
Total energy of molecules, kcal/mol	-429718	-361354	-181405	-81978

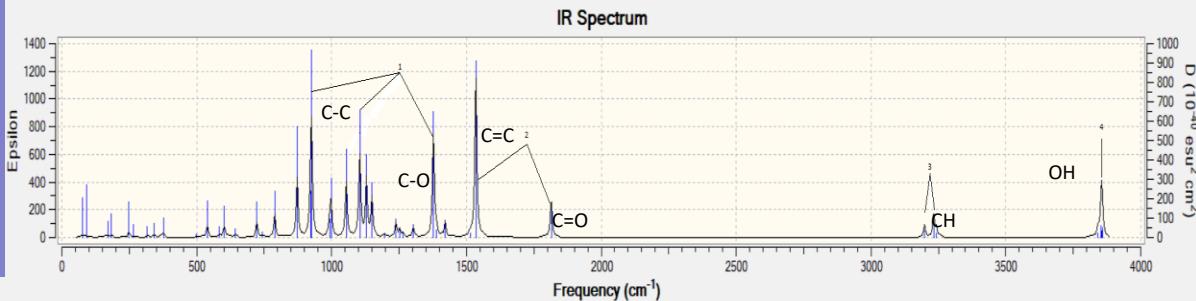
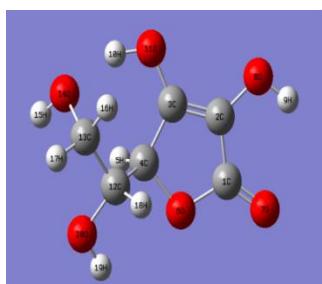
Calculations of IR and Raman spectra of aqueous solutions of ascorbic acid were carried out by the Hartree-Fock and DFT methods with bases 3-21G, 6-31G and 6-311G.

Accounting for the solvation was carried out within the framework of two models: IEFPCM and CPCM, based on the model of the reactive field - Polarized Continuum Model. According to this model, the molecule of the dissolved substance is placed in a cavity whose surface is given by a set of spheres whose centers are located on the atoms of the molecule of the dissolved substance, and the radii are determined by the atomic radii of Van der Waals.

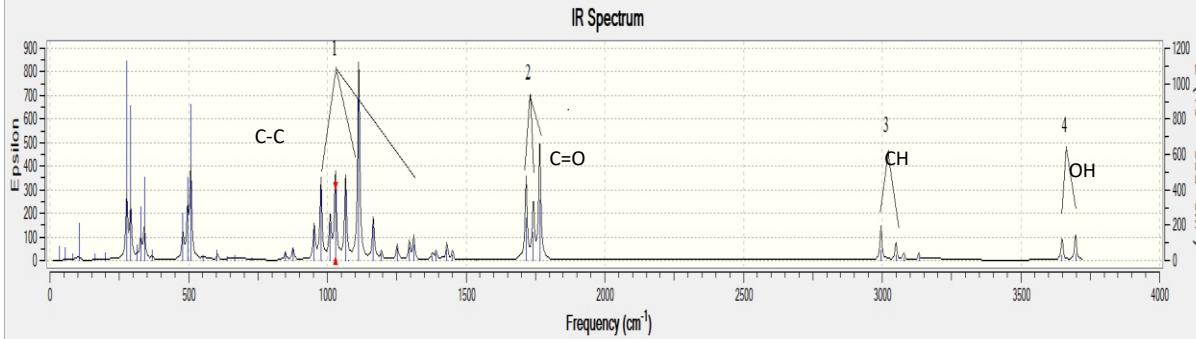
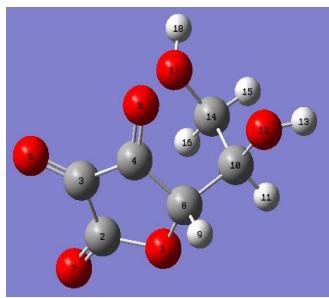
Changes in the molecular structure and IR absorption spectra during the conversion of ascorbic acid into furfural are shown in Figure 2.

The molecular structures constructed after their optimization are shown on the left, and the corresponding IR spectra on the right. The type of bond whose change caused absorption at a given frequency is indicated next to the corresponding band.

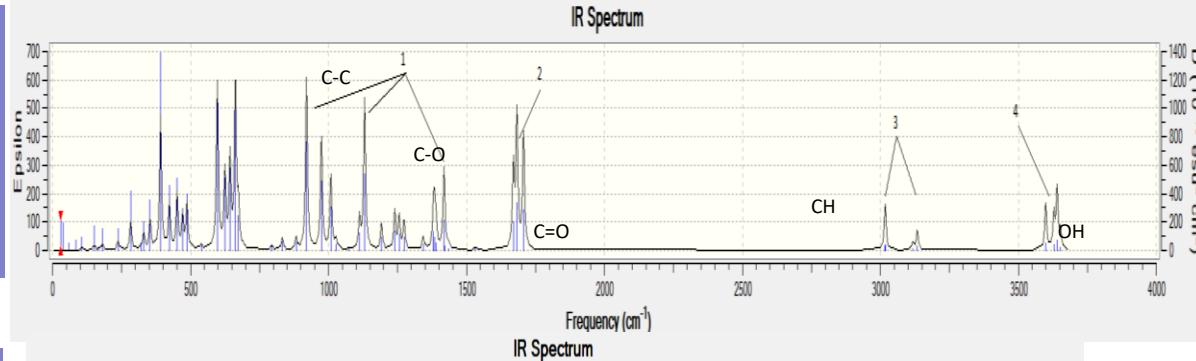
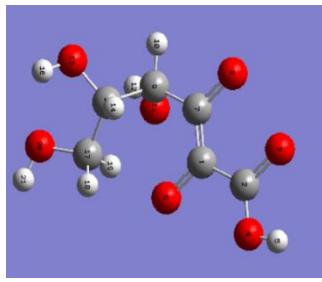
a) ascorbic acid



b) dehydroascorbic acid



c) 2,3diketogulonic acid



d) furfural

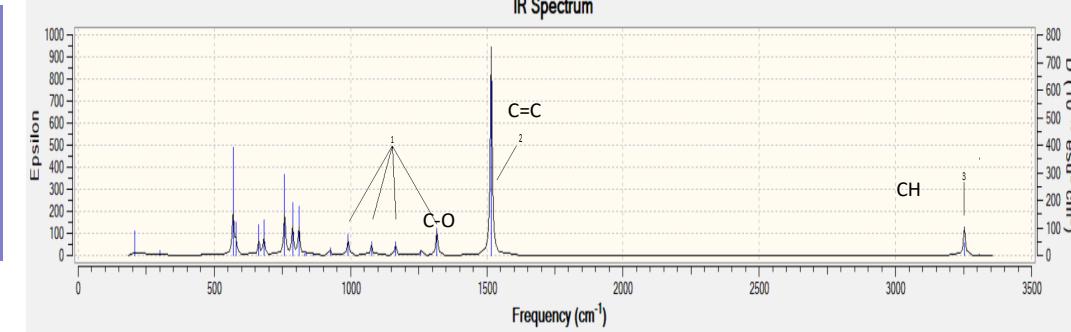
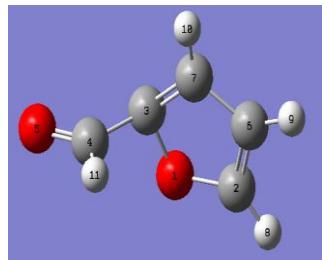


Figure 2. Structural formulas and IR absorption spectra of aqueous solutions of ascorbic acid and its decomposition products

The frequencies of the vibrational bands are correlated with certain types of molecular vibrations. In the IR spectrum of ascorbic acid, absorption bands at frequencies of 925 cm^{-1} , 1104 cm^{-1} and 1377 cm^{-1} correspond to composite symmetric and asymmetric stretching vibrations of the C-C bond of the lactone ring.

Bands at frequencies of 1534 cm^{-1} and 1814 cm^{-1} correspond to stretching vibrations of the C=O double bond in conjugated systems with double C=C and C-O bonds, respectively.

Absorption bands at frequencies 3196 cm^{-1} , 3198 cm^{-1} arise as a result of stretching vibrations of CH bonds.

The bands at 3854 cm^{-1} and 3857 cm^{-1} belong to the characteristic stretching vibrations of the bound OH groups.

The absorption bands of dehydroascorbic acid, corresponding to C-C vibrations at frequencies of 976 cm^{-1} , 1029 cm^{-1} and 1066 cm^{-1} , experienced a bathochromic shift in comparison with the similar bands of ascorbic acid.

New bands appeared at frequencies of 1716 cm^{-1} , 1742 cm^{-1} , 1765 cm^{-1} related to stretching vibrations of C=O double bonds. These bonds were formed as a result of the loss of two hydrogen atoms by the ascorbic acid molecule and the transformation of the conjugated system of C=C bonds into C-C.

During the formation of the diketogulonic acid molecule, the lactone ring was broken, and therefore the intensity of the bands associated with it decreased. At the same time, the number of bands in the region 700 cm^{-1} - 1400 cm^{-1} , associated with C-C vibrations, increased. These bands experienced a bathochromic shift of over 200 cm^{-1} due to lactone ring scission.

The bands corresponding to vibrations of C=O bonds experienced a hypsochromic shift and are recorded at frequencies of 1669 cm^{-1} , 1706 cm^{-1} and 1728 cm^{-1} .

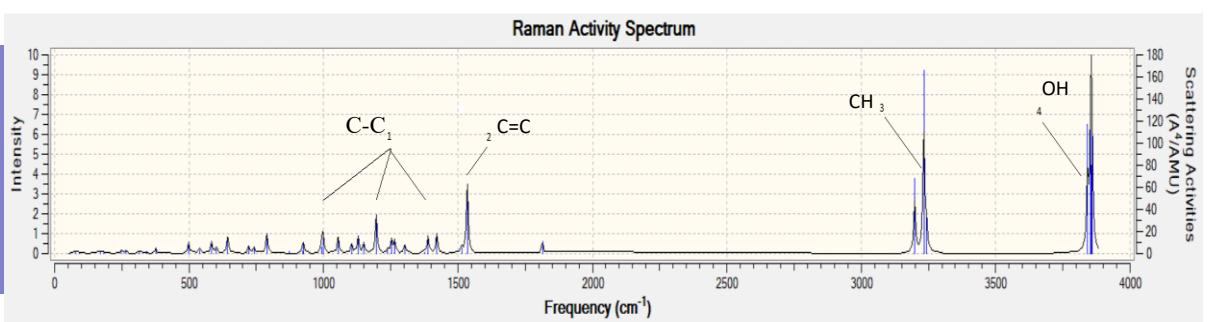
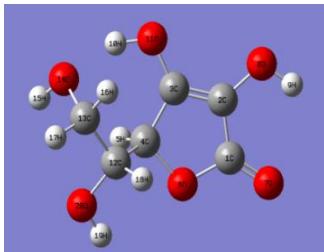
The intensity of the bands corresponding to stretching vibrations of C-H and O-H bonds, which experienced a slight hypsochromic shift, increased.

The furfural molecule has a simple structure containing a lactone ring. In the spectrum of furfural, the most intense band at a frequency of 1512 cm^{-1} corresponds to the C=O bond.

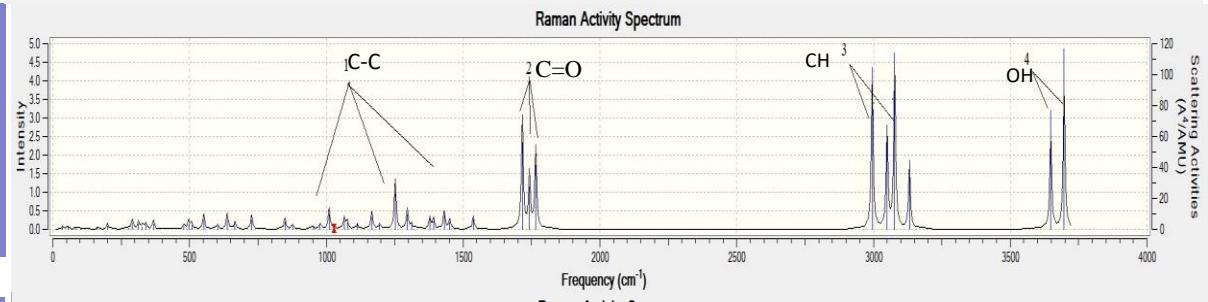
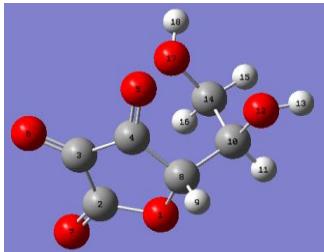
The intensities of the bands at frequencies of 1066 cm^{-1} , 1103 cm^{-1} , 1285 cm^{-1} and 1299 cm^{-1} corresponding to vibrations of C-C and C=C bonds of the lactone ring significantly decreased.

Changes in the structure of molecules and Raman spectra during the conversion of ascorbic acid to furfural are shown in Figure 3.

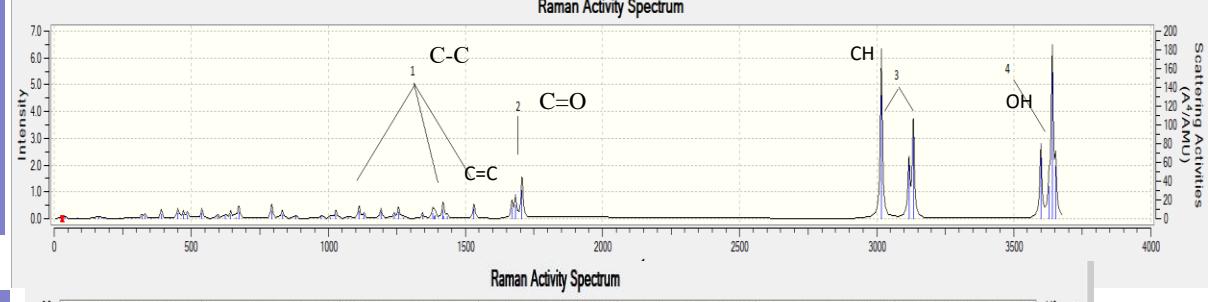
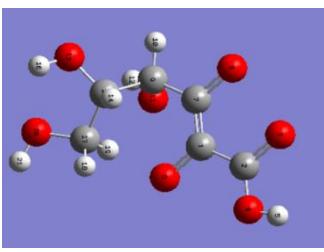
a) ascorbic acid



b) dehydroascorbic acid



c) 2,3diketogulonic acid



d) furfural

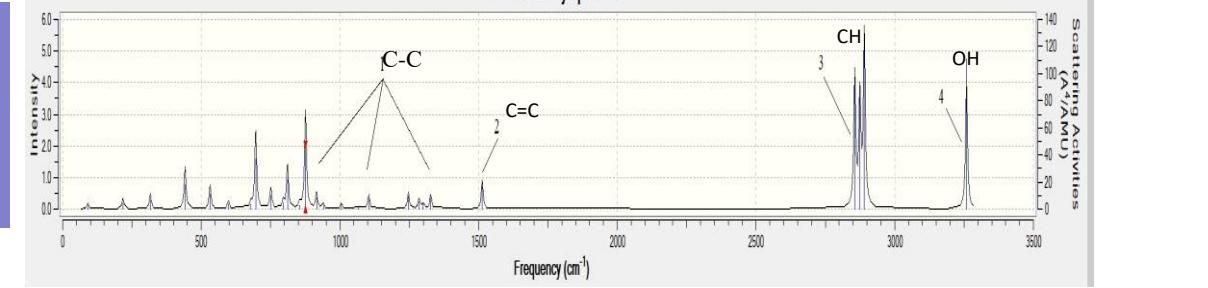
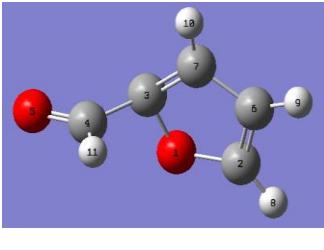


Figure.3. Structural formulas and Raman spectra of aqueous solutions of ascorbic acid and its decomposition products

The bands corresponding to the stretching vibrations of the CH and OH groups are the most intense in the Raman spectra of all the investigated molecules.

When comparing the Raman spectra of ascorbic and dehydroascorbic acids, one can see that the number of bands has increased, and their frequencies have decreased.

The intensity of the band related to stretching vibrations of C=O bonds decreased. The decrease in the intensity of this band continued with the conversion of dehydroascorbic acid to 2,3 diketogulonic acid and then to furfural.

Bands corresponding to stretching vibrations of CH bonds at frequencies of 2855 cm^{-1} - 2890 cm^{-1} appear only in the Raman spectrum. The intensity of all bands corresponding to stretching vibrations of CH, OH, and C=O bonds in the spectrum of furfural is lower than in the spectrum of diketogulonic acid.

Conclusion

Thus, the change in the structure of molecules during the transformation of ascorbic acid into dehydroascorbic, diketogulonic and furfural is manifested in the IR absorption and Raman spectra of their aqueous solutions.

It is preferable to use the IR absorption spectrum to reveal the cleavage of the lactone ring and the formation of new C=O bonds associated with it. In the Raman spectrum, the bands corresponding to changes in the stretching vibrations of the CH and OH groups show up better.

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