

Effect of Protonation, Sodiation, Lithiation, and Potassiation on Chemical Properties of Glucose

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Abstract—Processes in positively charged clusters of biological molecules are studied. Protons, as well as lithium, sodium, and potassium cations, are used as charge sources. It is found that fragments of different structures are formed depending on the positive ion source, which allows sufficiently reliable identification of initial molecules of a studied material.

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Understanding of the processes in biological systems under radiation and ionization is a key problem of both the stability of living organisms to external negative influences and the problem of stability of living systems as a whole. Furthermore, interest in physical and chemical processes in ionized compounds necessitates identification of biomolecules using various mass spectrometry (MS) methods. Currently, an analysis of small or linearly structured molecules is not a difficult problem; however, the determination of the structure of larger branched biomolecules, in particular, complex carbohydrates, still represents a complex technical problem requiring nontrivial experimental approaches and a comprehensive computer analysis.

Amino acids, nucleotides 1, polysaccharides, lipids, and other biomolecules were actively studied both experimentally and theoretically over the last decades, especially, after the invention of laser radiation sources. In contrast to proteins and nucleic acids featuring the linear structure, carbohydrates, glycoproteins, and glycolipids have a complex branched structure with many isomers giving fragments with identical masses, but with completely different structures and biochemical properties. Furthermore, the stability of ionized forms of these compounds and their fragments is very low and leads to a cascade of secondary decomposition reactions, and their affinity to protons is as a rule insufficient for applying such conventional mass spectrometry methods as MALDI and electrospray (ESI).

To solve this problem, it is necessary to find new nondestructive ionization methods yielding stable ions and allowing reliable identification of samples under study. In this case, theoretical (quantum-chemical) calculations of electronic processes in biomolecules are very important. In this study, attention is concentrated on dissociation of glucose molecules incorporated in ionic complexes containing protons, as well as sodium, potassium, and lithium ions (H^+ , Na^+ , K^+ , Li^+).

Recently, photochemical reactions in electron-excited sugars [1, 2] were theoretically studied. Reactions in the simplest ionic carbohydrate complexes containing H^+ , Na^+ , K^+ , Li^+ were also experimentally and theoretically studied [3–12]. In this work, we continue the theoretical study of chemical processes in glucose ion clusters, i.e., the simplest monosaccharide playing the key role in many biochemical processes occurring in living cells.

The geometry of the surface potential energy of ions, glucose molecules, water and formed fragments was optimized by the B3LYP/6-31G* method. The energy at points of minima and maxima were then

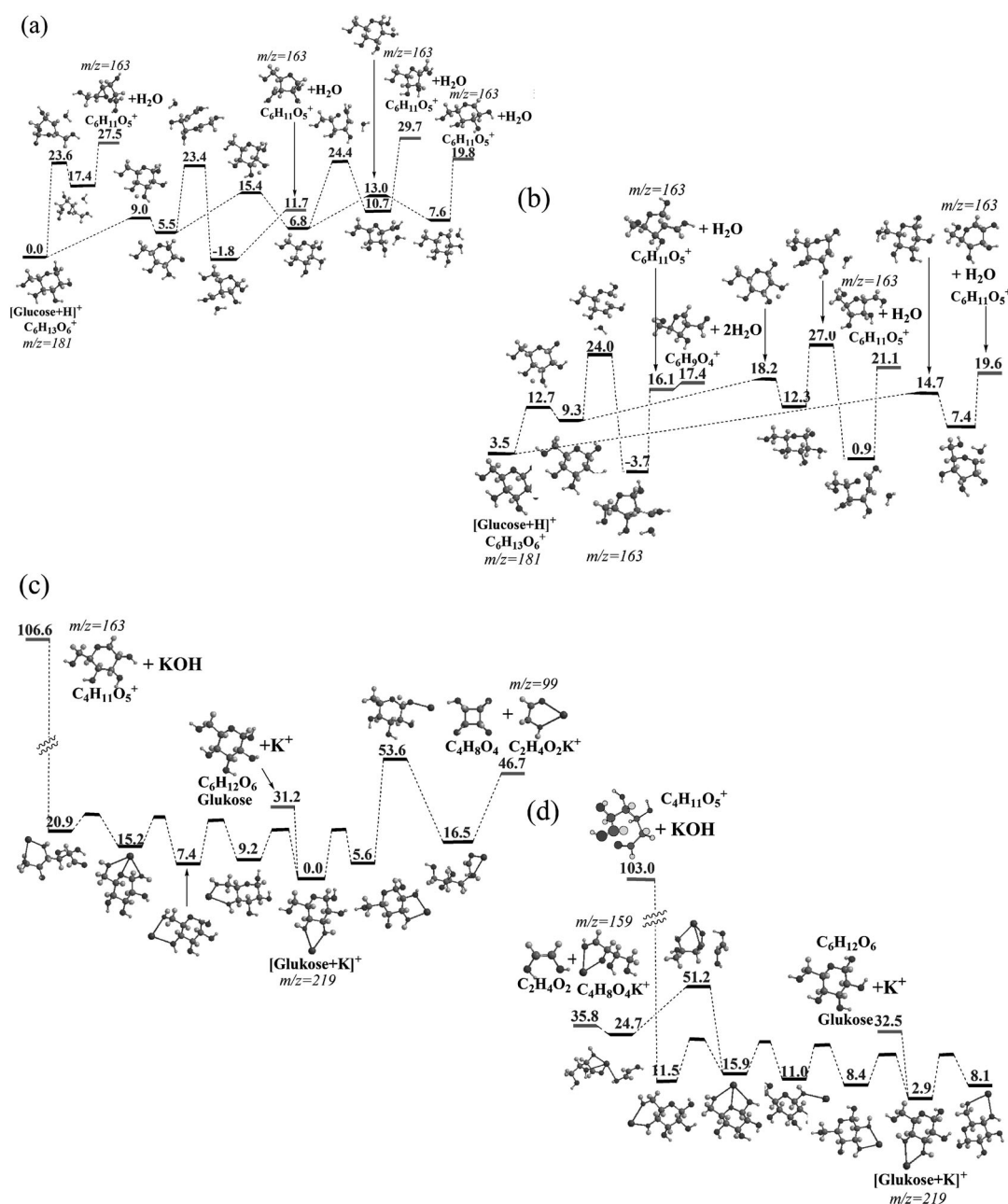


Fig. 1. Decay scheme of α - and β -glucose ion clusters formed using ((a), (b)) protons and ((c), (d)) potassium ions.

recalculated using the G3(MP2,CCSD) method [13, 14]. The energies of zero-point vibrations (ZPE) were used without correcting coefficients. Quantum-chemical calculations were performed using the GAUSSIAN 09 software package [15].

The photo- and thermal stability of heteroatomic molecules containing, in particular, oxygen and nitrogen atoms, is very intensively studied in recent years. The processes in both aromatic [16–21] and saturated [22–28] compounds were actively studied. In particular, it was found that nonradiative transitions from excited to electronic ground states via O – H and N – H bond elongation or molecule deformation are characteristic of unsaturated molecules containing aromatic groups in combination with substituents [16, 17], whereas relaxation into one of local minima of the electronic ground state via ring rupture and deformation is characteristic of saturated compounds and aromatic molecules without substitutional groups [18–21].

Based on the calculated results, protonized α -glucose clusters are energetically more stable than β -glucose clusters. As was already shown in [7, 8, 11], the water molecule abstraction reaction is a main channel of protonized glucose cluster decomposition at low internal energies. The decomposition channels yielding the fragments $\text{C}_2\text{H}_4\text{O}_2 + \text{C}_4\text{H}_9\text{O}_4^+$ ($m/z = 121$) and $\text{C}_4\text{H}_8\text{O}_4 + \text{C}_2\text{H}_5\text{O}_2^+$ ($m/z = 61$) can be detected only at high internal energies of clusters (see Figs. 1(a) and 1(b)). In the case of ionic clusters containing Na^+ cations, according to our calculations, the dominant reaction channel is double ring rupture as was indicated in [8, 9]. In the clusters formed based on K^+ , K^+ abstraction is the main reaction channel. Water molecule abstraction, as well as double ring rupture, is energetically unfavorable, and can be implemented only at high internal molecule energies (Figs. 1(c) and 1(d)). In the case where molecular clusters are formed using lithium ions, the lithium ion channel abstraction competes to the ring rupture and LiOH fragment abstraction channels. However, a specific reaction scheme and an accurate calculation of the potential energy surface calls for an additional analysis.

The result of this study is the fact that the composition of molecular fragments formed during measurements can be significantly changed by varying the composition of the ionic basis of the formed mass spectrum, thus, achieving an accurate identification of a studied material at sufficient preliminary calculations and statistics acquisition.

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